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PHOTO-INDUCED ELECTRON TRANSFER PROCESSES AND THEIR RÔLE IN OXIDATION REACTIONS

by

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A thesis submitted for the Degree of
DOCTOR OF PHILOSOPHY
in the Chemistry Department of
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DEDICATED

TO

MY PARENTS

ABSTRACT

The processes leading to the formation and decay of excimers and exciplexes are briefly outlined. Excited complexes can be considered as potential sensitisers of singlet oxygen on the basis of their ability to decay to yield localised triplet excited states.

Fluorescence and laser flash photolysis studies have shown that amines and sulphides can quench the excited states of polycyclic aromatic hydrocarbons as well as their chloro- and cyano- derivatives. This quenching is proposed to occur via an electron transfer process. The ability of amines and sulphides to enhance the photo-reductive dehalogenation of halo-aromatics and decyanation of cyano-aromatics can be rationalised on the basis of electron transfer reactions between these compounds.

The photophysical properties of intramolecular exciplex forming systems were found to be sensitive to the isotopic composition of protic, but not aprotic, solvents.

The most commonly encountered photo-oxidation processes are reviewed.

Evidence for the involvement of electron transfer processes in the direct photo-decarboxylation of α-keto-carboxylic acids and esters has been obtained from the observed effects, upon these reactions, of added electron acceptors. α-Keto-carboxylic esters are found to undergo photo-oxidative decarboxylation. The effects of changes in oxygen concentration upon the dye-sensitised decarboxylation of α-keto-carboxylic acids and esters are indicative of a mechanism involving electron transfer processes rather than a singlet oxygen mediated reaction.

The observed effects of the nature and concentration of the sensitising dye upon the magnitude of kinetic solvent isotope effects upon the photo-oxidation of alkenes are attributed to quenching of singlet oxygen by the dyes.

An example of how the sensitivity of photophysical parameters to the isotopic composition of the solvent can result in kinetic solvent isotope effects being almost impossible to interpret is provided by the direct photo-oxidation of 1,3-diphenyl-2-pyrazoline.

Kinetic solvent isotope effects, despite their drawbacks, have proved useful in determining the rôle of singlet excited states in the production of singlet oxygen by anthracene compounds.

Both intramolecular and intermolecular excited complex forming systems are found to sensitise the photo-oxidation of alkenes and sulphides. On the basis of kinetic solvent isotope effects it is proposed that these reactions occur, at least in part, via a singlet oxygen mediated process.

Titanium dioxide, a well-known semiconductor, has been shown to sensitise the photo-oxidation of sulphides via an electron transfer mechanism. As a consequence of the ability of the intermediate radical ions to undergo a variety of reactions the yields of oxidation products were often low.

PUBLICATIONS

Some of the work contained in this thesis has been published or submitted for publication as outlined below:-

1. Some charge transfer reactions of excited aromatic compounds with sulphides.

   R.S. Davidson, J.W. Goodin and J.E. Pratt, Tetrahedron Letter, 23, 2225-2228 (1982).

2. Dyes as quenchers of singlet oxygen.

   R.S. Davidson and J.E. Pratt, Tetrahedron Letters, 23, 3729-3732 (1982).

3. Photo-induced electron transfer reactions - pitfalls and opportunities.

   R.A. Beecroft, R.S. Davidson, D. Goodwin and J.E. Pratt, Pure and Applied Chemistry, 54, 1605-21 (1982).

4. A solvent isotope effect upon exciplex photochemistry.

   R.A. Beecroft, R.S. Davidson, D. Goodwin, J.E. Pratt, L.A. Chewter and D.A. Phillips, Chemical Physics Letters, 93, 468-474 (1982).

5. The mechanism of the direct photo-oxidative decarboxylation of α-oxo-carboxylic esters.

   R.S. Davidson, D. Goodwin and J.E. Pratt, Tetrahedron, 39, 1069-74 (1983).

6. Factors affecting dye sensitised photo-oxidation reactions: the effect of oxygen concentration and its use to probe the mechanism of the decarboxylation of α-oxo-carboxylic acids and esters.

   R.S. Davidson, D. Goodwin and J.E. Pratt, Tetrahedron, 2373-2379 (1983).

7. The rôle of electron transfer processes in the photo-induced decarboxylation of alkyl pyruvates.

   R.S. Davidson, D. Goodwin and J.E. Pratt, J.C.S. Perkin Trans. II, in the press (1983).

8. The titanium dioxide sensitised photo-oxidation of sulphides.

   R.S. Davidson and J.E. Pratt (submitted for publication).

9. The use of solvent isotope effects to determine the rôle of excited singlet states in the direct photo-oxidation of anthracene compounds.

   R.S. Davidson, D. Goodwin and J.E. Pratt (submitted for publication).

10. An example of how photophysical properties can influence the magnitude of kinetic solvent isotope effects upon photo-oxidation reactions.

    R.S. Davidson and J.E. Pratt (submitted for publication).

11. Excimers and exciplexes as sensitisers for photo-oxidation reactions.

    R.S. Davidson and J.E. Pratt (submitted for publication).

The following work has been presented at conferences:-

1. Photo-induced electron transfer reactions - pitfalls and opportunities.

   Ninth IUPAC Symposium on Photochemistry, Pau, France, July 1982.

2. Some limitations and applications of the solvent isotope effect upon photo-oxidation reactions.

   Post-graduate Seminar on Organic Photochemistry, The City University, London, April 1983.

3. a) Generation of singlet oxygen from excited singlet states

   b) The mechanism of the direct photo-oxidative decarboxylation of α-oxo-carboxylic esters.

   Third International Conference on Oxygen Radicals in Chemistry and Biology, Munich, Germany, July 1983.

CHAPTER 1

INTRODUCTION TO PHOTOCHEMISTRY

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1.1 Preface

Photochemistry is the study of chemical changes brought about by the action of UV or visible light, and chemical reactions which lead to the generation of light. The variety of compounds which plants can synthesise using solar energy gives an insight into the potential utility of photochemical reactions. Although photochemical reactions have been studied for many decades it is only with the development of sophisticated instrumentation that detailed mechanistic investigations of fast photochemical processes has become possible. As there are many text books[1-4] which provide excellent reviews of photochemistry this chapter merely provides a basic introduction to the creation, general properties and decay pathways open to excited states.

1.2 Electronic excitation of organic molecules

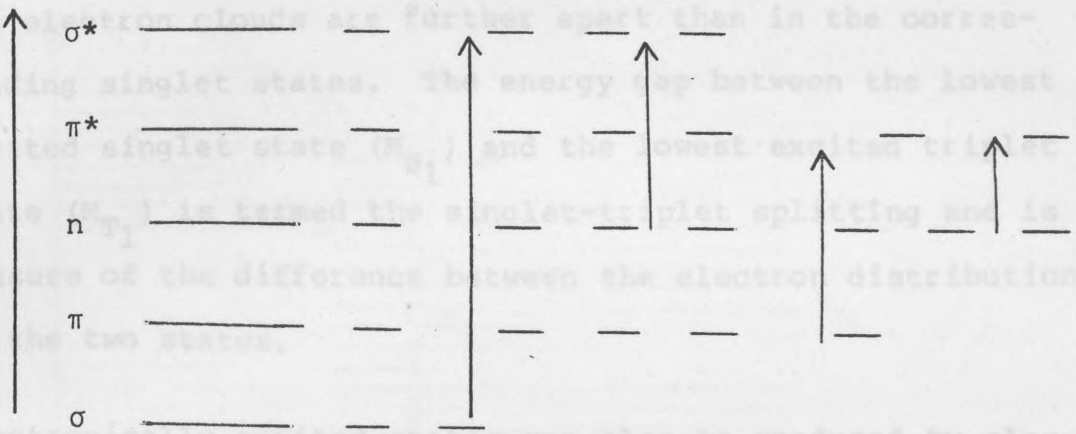
Light can be thought of as a quantised source of energy which is absorbed, transmitted and emitted in discrete units known as photons. The energy of photons is related to the frequency (ν) of the radiation by Equation 1.1.

$$E = h\nu = hc/\lambda \qquad (1.1)$$

(where h = Planck's constant, c = velocity of light, ν = frequency and λ = wavelength of the radiation)

Absorption of a photon by a molecule may cause the promotion of an electron from the ground state to an upper excited state. As the energy of the photon often exceeds the energy gap between the lowest vibrational levels of the ground and excited state the latter will usually be produced in an upper vibrational/rotational state. The types of electronic transitions associated with organic molecules are illustrated in Figure 1.1 $n \rightarrow \sigma^*$ transitions are partially forbidden, giving rise to weak absorptions in a range of molecules, e.g. R-X, R-OH, R-SH and R-NH_2. The promotion of a non-bonding electron into an antibonding orbital results in efficient dissociation of these molecules upon irradiation in the near UV . As the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions often require the least energy they are involved in many photo-chemical reactions of organic molecules. $\pi \rightarrow \pi^*$ transitions are allowed and give rise to intense absorptions by compounds such as alkenes. $n \rightarrow \pi^*$ transitions are characteristic of molecules possessing multiply bonded heteroatoms, e.g. C=O, C=N, C=S and N=O. These $n \rightarrow \pi^*$ transitions are symmetry and/or overlap forbidden giving rise to a weak absorption, usually at the longest wavelength.

As all the electrons in the ground states of organic molecules are usually spin-paired, the outer electrons will have anti-parallel spins in the initially created excited state because no change of electron spin can take place during the time interval required for an electronic transition. Similarly, as stated in the Franck-Condon principle, no change in nuclear position or nuclear kinetic energy occurs during an electronic transition. Electronic states in which the two outer electrons have anti-parallel spins are designated as singlet states (^1M or M_{S_n} where n = zero or a positive integer), whereas



Transition	σ→σ*	n→σ*	π→π*	n→π*
Excited state formed	σ,σ*	n,σ*	π,π*	n,π*

Figure 1.1 Electronic Excitation Processes in Organic Molecules
(where n = non-bonding orbital;
σ and π = bonding orbitals;
σ* and π* = antibonding orbitals.)

those in which the electron spins are parallel are designated as triplet states (^3M or M_{T_n}). Triplet states will always be more stable because their wavefunctions are antisymmetric so the electron clouds are further apart than in the corresponding singlet states. The energy gap between the lowest excited singlet state (M_{S_1}) and the lowest excited triplet state (M_{T_1}) is termed the singlet-triplet splitting and is a measure of the difference between the electron distributions in the two states.

Electronically excited states can also be produced by electrical discharge, ionizing radiation (e.g. α, β or γ rays), extreme temperatures, chemical activation (e.g. chemiluminescence[5,6]), electron transfer reactions and the decomposition of peroxide compounds.

1.3 Photophysical processes of excited states

The modified Jablonski diagram[7] outlined in Figure 1.2 provides a simple representation of the photophysical processes involved in the interconversion and deactivation of excited states. The energy level to which an electron is initially promoted will depend upon the energy of the photon absorbed. Vibrational cascade to the lowest vibrational energy level of the electronic energy level is rapidly achieved in solution by intermolecular collisions. The electron may then undergo internal conversion from the lowest vibrational level of an upper electronic state to a higher vibrational level of a lower excited state. Once the electron has reached the lowest vibrational level of the lowest excited (S_1) state the molecule

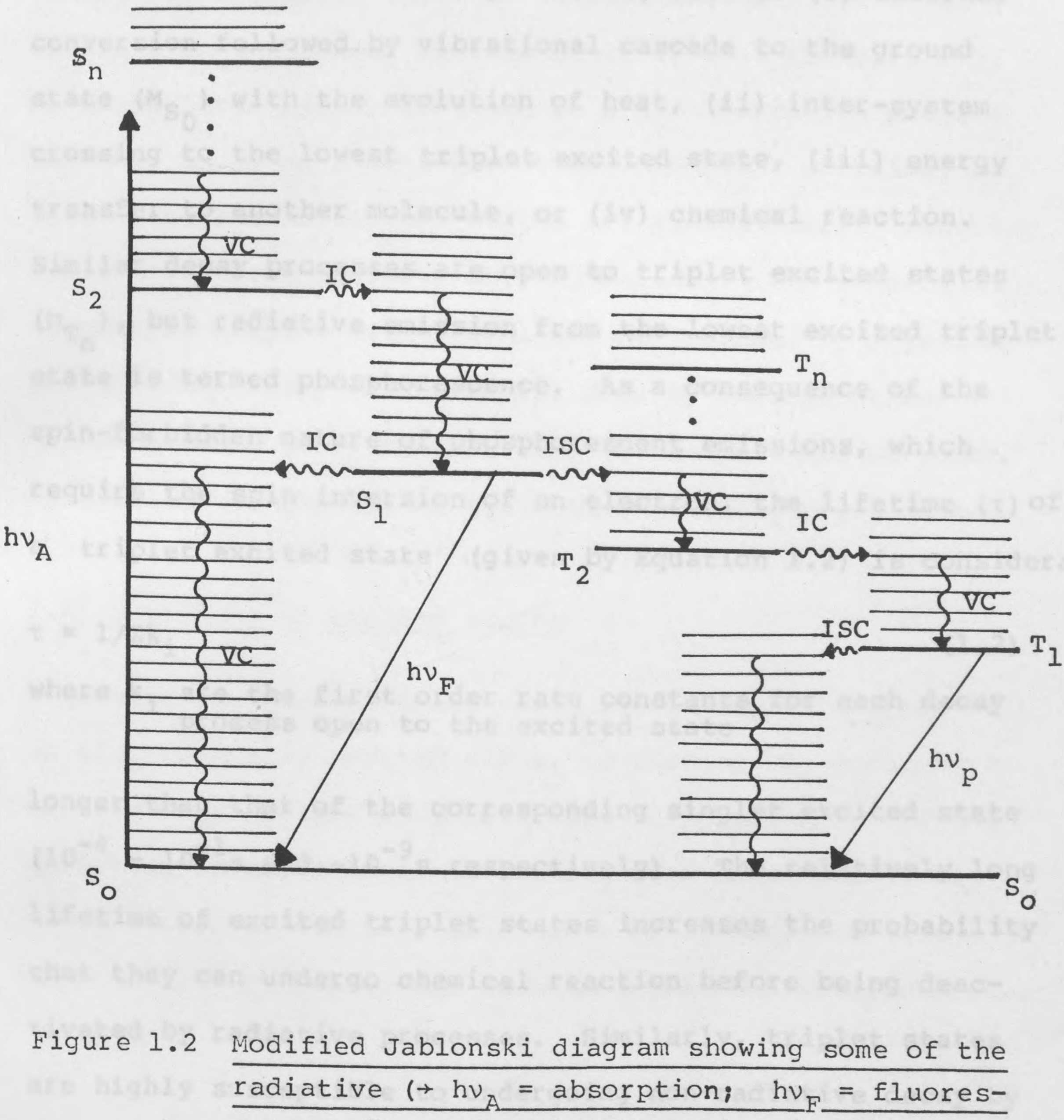


Figure 1.2 Modified Jablonski diagram showing some of the radiative ($\rightarrow$ $h\nu_A$ = absorption; $h\nu_F$ = fluorescence; $h\nu_P$ = phosphorescence) and non-radiative ($\rightsquigarrow$ VC = vibrational cascade; IC = internal conversion and ISC = intersystem crossing) processes available to molecules.

may lose its excitation energy by radiative (fluorescent emission) or non-radiative processes, such as (i) internal conversion followed by vibrational cascade to the ground state (M_{S_0}) with the evolution of heat, (ii) inter-system crossing to the lowest triplet excited state, (iii) energy transfer to another molecule, or (iv) chemical reaction. Similar decay processes are open to triplet excited states (M_{T_n}), but radiative emission from the lowest excited triplet state is termed phosphorescence. As a consequence of the spin-forbidden nature of phosphorescent emissions, which require the spin inversion of an electron, the lifetime (τ) of a triplet excited state (given by Equation 1.2) is considerably

$$\tau = 1/\Sigma k_i \qquad (1.2)$$

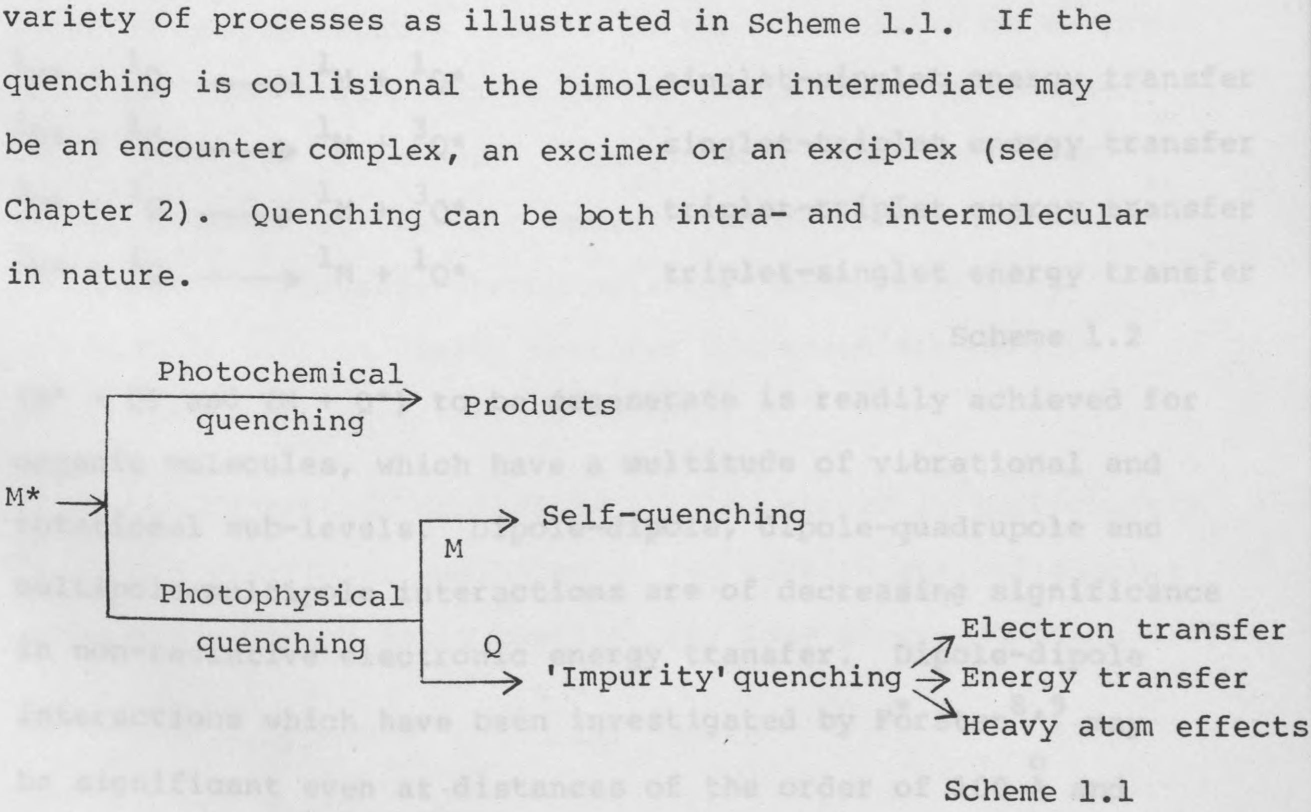
where k_i are the first order rate constants for each decay process open to the excited state

longer than that of the corresponding singlet excited state (10^{-4} - 10^{-1}s and ~10^{-9}s respectively). The relatively long lifetime of excited triplet states increases the probability that they can undergo chemical reaction before being deactivated by radiative processes. Similarly, triplet states are highly susceptible to undergoing non-radiative decay by intermolecular collisions, so phosphorescent emissions are not usually observed in solution.

Internal conversion and inter-system crossing occur between degenerate vibrational and rotational levels of different electronic states, of the same molecule, of the same and different multiplicity respectively. The rates of these processes decrease as the energy gap between the electronic levels, in their lowest vibrational states, of the two electronic states increases. As upper excited states rapidly undergo spin-allowed internal conversion, emission usually occurs from the lowest excited state of each multiplicity. Although inter-system crossing is a spin forbidden process it takes place as a consequence of spin-orbit coupling, by which singlet and triplet states are mixed, thereby reducing the restrictions on their interconversion. The probability of singlet-triplet transitions can be enhanced by internal and external heavy atom effects, e.g. by incorporation of an iodine atom into the molecule, by the presence of xenon in solution or the use of solvents containing heavy atoms.

1.4 Quenching of excited states

A quencher is any substance which accelerates the decay of an electronically excited state. Quenching may occur by a variety of processes as illustrated in Scheme 1.1. If the quenching is collisional the bimolecular intermediate may be an encounter complex, an excimer or an exciplex (see Chapter 2). Quenching can be both intra- and intermolecular in nature.



Scheme 1.1

1.4.1 Energy transfer quenching

The radiative transfer of energy from an electronically excited state to a ground state molecule, of the same or a different compound will only take place if the emission spectrum of the excited state overlaps effectively with the absorption spectrum of the ground state molecule.

Non-radiative electronic energy transfer requires a physical interaction between the excited donor and the acceptor molecules and as such are subject to the Wigner spin conservation rules[7]. These state that during transfer of electronic energy between an excited atom or molecule and a molecule in its ground or excited states the overall spin angular momentum of the system should not change. The most commonly encountered energy transfer processes in organic photochemistry are outlined in Scheme 1.2. The requirement for (M* + Q) and (M + Q*) to be degenerate is readily achieved for organic molecules, which have a multitude of vibrational and rotational sub-levels. Dipole-dipole, dipole-quadrupole and multipole-multipole interactions are of decreasing significance in non-radiative electronic energy transfer. Dipole-dipole interactions which have been investigated by Förster[8,9] may be significant even at distances of the order of 100 Å and are independent of solvent viscosity, except in very dilute

$^1M^* + {}^1Q \longrightarrow {}^1M + {}^1Q^*$ singlet-singlet energy transfer

$^1M^* + {}^1Q \longrightarrow {}^1M + {}^3Q^*$ singlet-triplet energy transfer

$^3M^* + {}^1Q \longrightarrow {}^1M + {}^3Q^*$ triplet-triplet energy transfer

$^3M^* + {}^1Q \longrightarrow {}^1M + {}^1Q^*$ triplet-singlet energy transfer

Scheme 1.2

solutions (< 10^{-4}M). Only processes which do not involve a change in spin of either component are allowed as a result of coulombic interactions. Multipole-multipole interactions, which have been analysed by Dexter[10], are only important at distances well below 40 Å and in cases where dipole-dipole energy transfer is inhibited. Electron exchange interaction[10] may also be responsible for energy transfer, but is a short range phenomenon which requires overlap of the donor and acceptor orbitals in an intermediate collision complex.

Triplet-triplet energy transfer takes place over shorter distances, (~ 10-15 Å which are comparable with collisional diameters) than singlet-singlet energy transfer. Since close approach of the partners is essential steric effects are significant, and if the energies of M* and Q* are comparable the quenching will be reversible. The relatively long lifetimes of triplet states results in the probability of energy transfer being high relative to the probability of deactivation by other processes. Consequently, triplet-triplet energy transfer is the most common type of energy transfer encountered in organic photochemistry. Singlet-triplet and triplet-singlet energy transfer processes are rarely encountered, but nevertheless do occur.

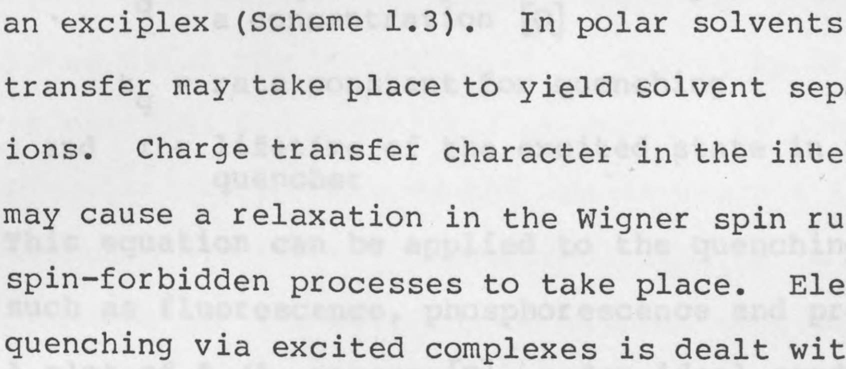
If the concentration of excited triplet states is sufficiently high, triplet-triplet annihilation (to give an excited singlet state and a ground state species) may take place (Equation 1.3).

$$^3M^* + {}^3M^* \longrightarrow {}^1M + {}^1M^* \longrightarrow {}^1M + h\nu \qquad (1.3)$$

Radiative decay of the excited singlet state gives rise to delayed fluorescence.

1.4.2 Electron transfer quenching

Electron transfer quenching of the excited states of organic molecules can occur directly in an encounter complex or via an exciplex (Scheme 1.3). In polar solvents complete electron transfer may take place to yield solvent separated radical ions. Charge transfer character in the intermediate complexes may cause a relaxation in the Wigner spin rules[7] and enable spin-forbidden processes to take place. Electron transfer quenching via excited complexes is dealt with more comprehensively in Chapter 2. If electron transfer is the rate limiting step for quenching, e.g. the quenching of naphthalene fluorescence by alkenes, the rate of quenching will be related to the ionization potential of the quencher.



where * represents a singlet or triplet excited state

Scheme 1.3

1.4.3 Utility of quenching studies to investigate photochemical reactions

Photosensitisation and quenching are important photochemical techniques which can be used to identify the multiplicity of the excited state, or states, from which a given photochemical reaction occurs. The kinetics of photochemical quenching are described by the Stern-Volmer[11] equation:-

$$\frac{\Phi_o}{\Phi_q} = 1 + k_q.\tau.[Q] \qquad (1.4)$$

where Φ_o = the quantum yield in the absence of quencher

Φ_q = the quantum yield in the presence of quencher at a concentration $[Q]$

k_q = rate constant for quenching

and τ = lifetime of the excited state in the absence of quencher

This equation can be applied to the quenching of phenomena such as fluorescence, phosphorescence and product formation. A plot of Φ_o/Φ_q versus $[Q]$, under ideal conditions, will result in a straight line with an intercept at 1 and a gradient equal to $k_q.\tau$. If either k_q or τ is known the other can be calculated from a Stern-Volmer plot. Curvature of the plots will result if excited states of more than one multiplicity are being quenched. The greater the difference between the triplet energies of the sensitiser and quencher molecules the more efficient will be the quenching process. By using quenchers with a range of triplet energies estimates for the value of the triplet energy of a sensitiser molecule, for which such data is not available, can be determined. The incident radiation should selectively excite the sensitiser molecule. If reaction rates are being studied, kinetic analysis should be confined to the first 10% of reaction in order to minimise any interference with the quenching process by the reaction products. If a substance quenches both the fluorescence and a photochemical reaction of a substrate it can be concluded that the reaction occurs, at least in part, via the excited singlet state. Some compounds, such as oxygen and naphthalene, are efficient quenchers of triplet states so if the presence of either oxygen or naphthalene retards the rate of a photo-oxidation reaction the mechanism of that reaction must involve the excited triplet state.

Photosensitisation has proved useful for creating excited states which may be difficult to obtain by direct irradiation. For example, dye-sensitised production of singlet excited molecular oxygen enables the use of visible light rather than microwave discharges. Photosensitisation is also a convenient technique for the creation of triplet excited states of highly fluorescent compounds which have low quantum yields of triplet production.

1.5 Summary

Irradiation with UV or visible radiation is a convenient method for generating electronically excited states. These species can decay via a variety of radiative and non-radiative processes. As electronically excited states often have considerably more internal energy than the corresponding ground state, there is a greater choice of reaction pathways open to excited states on thermodynamic grounds. Sensitising processes can lead to the production of excited states which may otherwise be difficult to obtain whilst the concomitant quenching process results in the deactivation of excited states. The application of sensitising and quenching processes can give a useful insight as to which excited states are responsible for a particular photochemical reaction.

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CHAPTER 2

INTRODUCTION TO EXCIMERS AND EXCIPLEXES AND THEIR POTENTIAL RÔLE AS INTERMEDIATES IN PHOTO-OXIDATION REACTIONS

CHAPTER 2

INTRODUCTION TO EXCIMERS AND EXCIPLEXES AND THEIR POTENTIAL RÔLE AS INTERMEDIATES IN PHOTO-OXIDATION REACTIONS

2.1 Definitions

Exciplex - an electronically excited molecular complex, formed between two different species, which has a definite stoichiometry but is unstable in its ground state.

Excimer - an electronically excited complex, formed between identical molecules or atoms, which has a definite stoichiometry but is unstable in its ground state.

Excited charge-transfer complex (electron-donor-acceptor complex) - a complex generated by direct excitation of a ground state molecular complex only differing from an exciplex because it has a degree of ground state stability

All these excited complexes occupy energy minima on the excited state potential surface.

2.2 Introduction

The first excimer was identified by Förster and Kaspar in 1954[1] when the fluorescence quantum yield of pyrene in non-polar solvents was found to decrease as the concentration was raised, while a new red-shifted fluorescence band, lacking any vibrational structure, increased in intensity. It was not until 1963 that the first exciplex was identified by Leonhardt and Weller[2]. The exciplex was formed as a result of the quenching of perylene fluorescence by N,N-dimethylaniline in non-polar solvents.

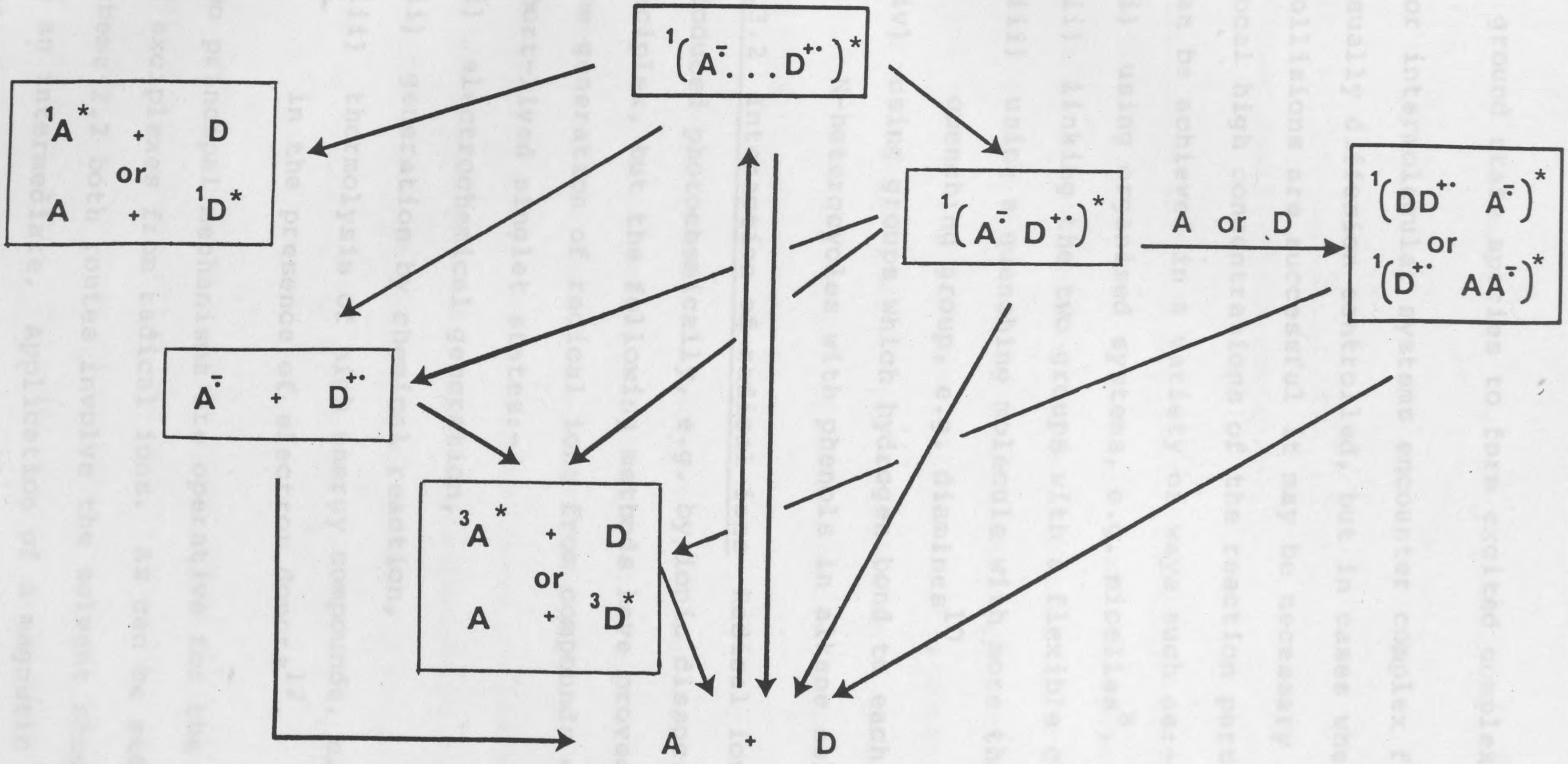
Excimers and exciplexes have since been proposed as intermediates in a wide variety of photochemical processes such as photo-dimerisation, chemiluminescence and photo-oxidation. This is a consequence of the ability of these excited complexes to decay to reactive species such as triplet states and radical ions (Scheme 2.1). However, in many cases excimer and exciplex formation merely leads to energy wastage.

Since there are several excellent reviews on the chemistry of excited complexes[3-7], the aim of this chapter is to provide an outline of the major routes available for the formation and decay of excited complexes.

2.3 Generation of Excited Complexes

Excited complexes are usually generated by photochemical means but can also be produced by chemical or electrochemical processes which give rise to radical ions as outlined below.

2.3.1 Molecular collisions A collision between a ground state species and a molecule in its singlet excited state may result in the formation of an encounter complex (D*....A), the components of which are randomly orientated (separation ~7 Å or more). This encounter complex may subsequently relax to form an excimer or exciplex. In some cases, e.g. the photoreduction of aromatic carbonyl compounds by amines[4], triplet rather than singlet excited states can interact with



SCHEME 2.1 DECAY PROCESSES OPEN TO NON-RELAXED AND EQUILIBRIUM EXCIPLEXES. THE BOXES INDICATE SPECIES WHICH MAY LEAD TO CHEMICAL REACTION

a ground state species to form excited complexes.

For intermolecular systems encounter complex formation is usually diffusion controlled, but in cases where few collisions are successful it may be necessary to create local high concentrations of the reaction partners. This can be achieved in a variety of ways such as:-

(i) using organised systems, e.g. micelles[8],
(ii) linking the two groups with a flexible chain[9],
(iii) using a quenching molecule with more than one quenching group, e.g. diamines[10],
(iv) using groups which hydrogen bond to each other, e.g. N-heterocycles with phenols in alkane solvents[11].

<u>2.3.2 Interaction of radical ions</u> Radical ions may be produced photochemically, e.g. by ionic dissociation of an exciplex, but the following methods have proved useful for the generation of radical ions from compounds with very short-lived singlet states:-

(i) electrochemical generation,
(ii) generation by chemical reaction,
(iii) thermolysis of high energy compounds, e.g. dioxetanes, in the presence of electron donors[12].

Two principal mechanisms are operative for the production of exciplexes from radical ions. As can be seen from Scheme 2.2 both routes involve the solvent shared ion-pair as an intermediate. Application of a magnetic field or addition of triplet quenchers enable the two mechanisms to be differentiated because they will only affect the triplet-

$$\begin{tikzcd} A^{\bar{\cdot}} + D^{+\cdot} \arrow[rr] & & (A^{\bar{\cdot}} \cdots D^{+\cdot})^* \arrow[rr, "a"] \arrow[dl] \arrow[dr] & & {}^1(A^{\bar{\cdot}}\, D^{+\cdot})^* \\ & {}^3A^* + D & & A + {}^3D^* & \end{tikzcd}$$

$${}^3A^* + {}^3D^* \xrightarrow{b} {}^1(A^{\bar{\cdot}}\, D^{+\cdot})^*$$

Scheme 2.2

triplet annihilation route (b).

2.3.3 Excitation of ground state molecular aggregates

Excitation of ground state molecular aggregates is the process by which excimer and exciplex formation occurs in rigid matrices at 77K where no diffusional encounters can take place within the lifetime of the excited monomer, e.g. anthracene exhibits excimer emission in a cyclohexane matrix[13] because competing dimerisation (which prevents emission in solution) is avoided.

Electron-donor-acceptor complexes, which were first observed by Evans[14] when iodine was dissolved in saturated hydrocarbons, differ from exciplexes because they have some stability (but no definite structures) in the ground state. The spectroscopic transition approximates to electron transfer from the donor to the acceptor (Scheme 2.3).

$$D + A \longrightarrow (D\,A) \xrightarrow{h\nu} {}^1(D^{+\cdot}\, A^{\bar{\cdot}})^*$$

Scheme 2.3

2.4 Decay pathways open to non-relaxed excited complexes

Excited complexes which are not relaxed with respect to intrinsic and solvent parameters can relax to form equilibrium excited complexes. This relaxation is in competition with the other forms of radiative and non-radiative decay open to the non-relaxed excited complex.

2.4.1 Radiative decay Non-relaxed excited complexes which have sufficient binding energy for solvent reorganisation to take place during their lifetime may exhibit fluorescence spectra, e.g. pyrene - tri-n-butylamine systems^{15}. The time dependence of the fluorescence spectrum of non-relaxed excited complexes in highly viscous solvents provides evidence that solvent reorganisation is a process which stabilises exciplexes.

2.4.2 The production of species capable of giving rise to chemical reactions If fluorescence quenching is related to the redox properties of the quencher but there is no evidence for the formation of fluorescent complexes or radical ions any observed reaction may have proceeded via a non-relaxed excited complex.

(i) Formation of triplet states The decay of excited complexes to yield triplet excited states (aided by the presence of any heavy atoms) competes with equilibrium exciplex formation from non-relaxed complexes of low binding energy, e.g. the β-naphthyl-alkyl halide (Figure 2.1) below, does not exhibit exciplex fluorescence, but quenching of the naphthalene fluorescence by the halogen group enhances

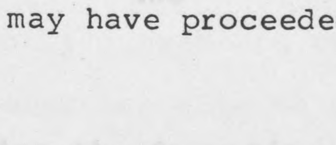
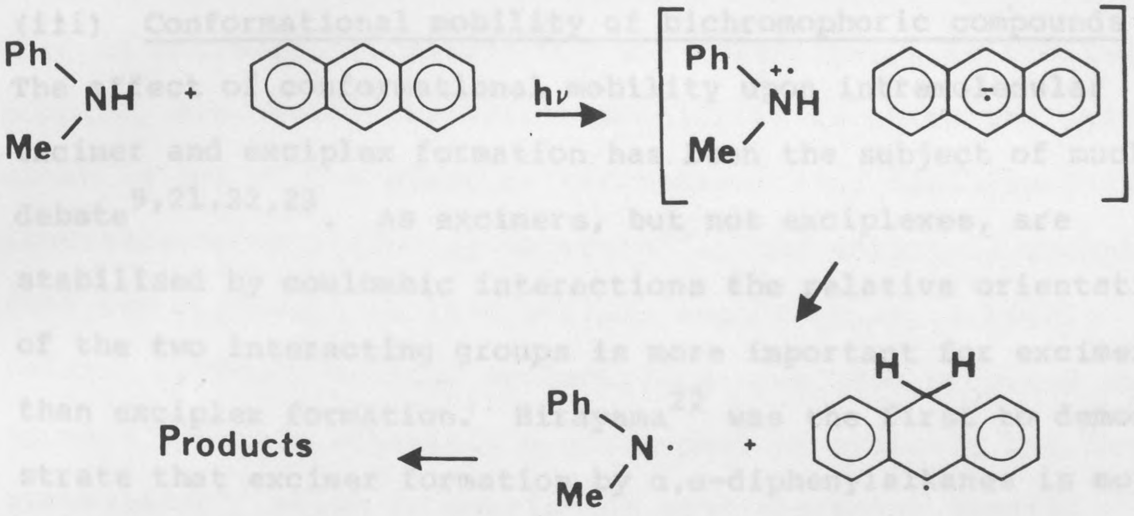


Figure 2.1

triplet formation^{16}. The decay of radical ions can also lead to the production of triplet states.

(ii) Electron transfer The formation of radical ions can prevent fluorescent exciplex formation, e.g. a mixture of

N-methylaniline and anthracene does not exhibit fluorescent exciplex formation[17]. In this case the initial electron transfer is followed by rapid proton transfer yielding neutral radicals which give rise to the observed products (Scheme 2.4).



Scheme 2.4

2.4.3 Factors affecting the formation of equilibrium excimers and exciplexes

(i) Solvent effects Reorganisation of the solvent is required for maximum stabilisation of the initially created excited complex because electron distributions will have altered during excitation. The polarity of the solvent affects the relative contributions of polar and non-polar states to the wave function of the excited complex so will have a marked affect upon the probability of exciplex formation relative to other decay routes of the non-relaxed exciplex, but little affect upon excimer formation (see Section 2.5.1).

(ii) Steric effects Steric interactions affect the entropy of formation of excimers[18] and exciplexes[19]. If rehybridisation is required, in order to minimise steric interactions, it must take place within the lifetime of the excited complex if the relaxed exciplex is to be produced. For this reason exciplex formation by 2-methylnaphthalene is less efficient with N-methylpiperidine than with triethylamine[20].

(iii) Conformational mobility of bichromophoric compounds

The affect of conformational mobility upon intramolecular excimer and exciplex formation has been the subject of much debate[9,21,22,23]. As excimers, but not exciplexes, are stabilised by coulombic interactions the relative orientation of the two interacting groups is more important for excimer than exciplex formation. Hirayama[22] was the first to demonstrate that excimer formation by α,ω-diphenylalkanes is most efficient when the phenyl groups are separated by a trimethylene chain. The phenyl groups are able to adopt a sandwich configuration in which there are no eclipsing interactions in the linking trimethylene chain. Unfavourable eclipsing interactions in polymethylene chains may be alleviated by placing an oxygen atom between methylene groups. The more polar the solvent the less strict the requirement for the adoption of a sandwich configuration because coulombic interactions increase the encounter distance required for complex formation[23]. By using strong electron acceptor and donor groups intramolecular exciplex emission has been observed with linking chains containing up to ten groups[24].

For ω-(N,N-diethyl)aminoalkylnaphthalenes the conformational requirements for fluorescence quenching and fluorescent exciplex formation are different[25]. The latter, but not the former, is dependent upon chain length because quenching can occur over greater distances than exciplex formation so for these compounds fluorescence quenching does not give rise to fluorescent exciplex formation.

Coplanarity of a donor and acceptor group linked by a sigma bond is not a pre-requisite for the formation of an excited complex, e.g. 4-dimethylaminobenzonitrile in which the amino group is out of the plane of the benzene ring exhibits dual fluorescence in non-polar solvents[26]. The emissions emanate from two different excited states, one of which is highly polar. Although several explanations have been proposed to account for this behaviour a great deal of evidence has been accumulated[27] which is consistent with the polar excited state corresponding to full electron transfer between the donor and acceptor groups mutually twisted by 90°. These twisted intramolecular charge transfer (TICT) excited states may be treated as intramolecular exciplexes with a definite structure. A structural requirement for all TICT states is minimum overlap between the molecular orbitals which are involved in the electron transfer from the donor to the acceptor group. This is in marked contrast to the generally accepted maximum overlap rules derived by Mulliken[28a,b] for weakly polar ground state charge-transfer complexes.

2.5 Properties of Excimers and Exciplexes

<u>2.5.1 Electronic and geometrical structures</u> Excited complexes formed between two chromophores can be described by the following wave-function[5]:-

$$\psi \approx c_1\phi(M_1^* M_2) + c_2\phi(M_1 M_2^*) + c_3\phi(M_1^- M_2^+) + c_4\phi(M_1^+ M_2^-) + c_5\phi(M_1 M_2) \qquad (2.1)$$

The c_5 term will only be significant if the complex is stable in its ground state. Quantum mechanical treatments[29,30] reveal that both exciton resonance and charge-transfer interactions are needed to account for the stability of excited complexes. The weighting of (c_1 and c_2) relative to (c_3 and c_4) determines the relative contributions of exciton resonance and charge transfer to stabilisation of the excited complex.

Solvent polarity has a pronounced affect upon the energetics of excited complex formation in solution. Rehm and Weller's equation[31] applies for cases where charge-transfer is important (Equation 2.2).

$$\Delta G^0 = E_{ox} - E_{red} - \frac{e^2}{\varepsilon\, a} - \Delta E_{00} \qquad (2.2)$$

where E_{ox} = the oxidation potential of the donor,

E_{red} = the reduction potential of the acceptor,

e = the coulombic interaction between two radical ions at the encounter distance a apart in a solvent of dielectric constant ε,

ΔE_{00} = the electronic excitation energy of fluorescence.

It can be seen from Equation 2.2 that both the bulk dielectric constant and the encounter distance play an important part in determining the probability of excited complex formation.

<u>2.5.2 Photophysical properties</u> Lifetimes of excited complexes are determined by the rates of emission, dissociation and other non-radiative processes. These are in turn determined by the binding energy of the exciplex and the nature of its

environment, e.g. temperature and solvent. If the binding energy is less than kT the excited complex will be very short-lived and non-luminescent.

The absorption spectra of excited complexes give an insight into the variation in their electronic structure with changes in solvent polarity. Since excimers have zero dipole moments their absorption spectra are relatively independent of the solvent polarity. However, the absorption spectra of exciplexes vary from being identical to those of the radical ions, in highly polar solvents, to resembling the spectra of the radical ions modified by the strong field of the counter ion in non-polar solvents.

2.6 Decay Pathways open to Equilibrium Excited Complexes

Excited complexes can decay by either radiative or non-radiative decay pathways. Since the latter can be extremely important, especially in polar solvents where the formation of radical ions can be an efficient process, the absence of emission does not necessarily indicate that excited complexes are not being formed.

2.6.1 Radiative decay The fluorescent emission from excimers and exciplexes occurs to a dissociative ground state complex so the emission is always a broad, structureless band bathochromically shifted from the fluorescence of the monomer. The extent to which solvent polarity affects the fluorescence reflects the dipole moment of the excited complex and indicates that most exciplexes have dipole moments corresponding to complete electron transfer[32,33].

Weller and co-workers[34] have established that for intermolecular exciplex formation between aromatic hydrocarbons and tertiary amines an increase in solvent polarity causes:-

a) exciplex fluorescence to shift to the red,

b) the quantum yield of exciplex fluorescence to decrease,

c) the lifetime of the exciplex to decrease.

These effects are attributed to the greater tendency for dissociation of exciplexes into radical ions as solvent polarity increases.

The contrasting effects of solvent polarity upon excimer formation compared to exciplex formation are illustrated by the compound in Figure 2.2 which can form both an intramolecular excimer and an intramolecular exciplex. In non-polar solvents emission from both the excimer and the exciplex are observed but in polar solvents the energy of the exciplex is lowered below that of the excimer so only exciplex emission is observed in polar solvents[35]. Twisted intramolecular charge transfer excited singlet states are unlikely to fluoresce strongly because radiative transitions to the lowest singlet state will be forbidden as a consequence of the minimum overlap between the molecular orbitals of the donor and acceptor groups in the excited state[27].

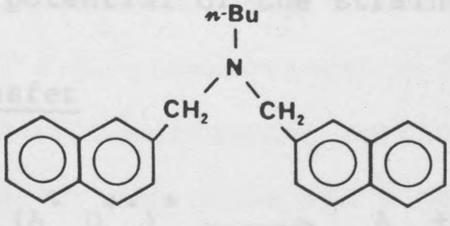


Figure 2.2

2.6.2 Non-radiative decay Excited complexes have been implicated in photodimerisation reactions, many quenching processes and in the production of species which can give rise to chemical reaction such as triplet excited states and radical ions (Scheme 2.1).

(i) Energy wastage Excited complex formation often leads, in part or totally, to energy wastage, e.g. the physical quenching of singlet oxygen by sulphides[36].

(ii) Valence-bond tautomerism Many strained hydrocarbons quench the fluorescence of polycyclic aromatic hydrocarbons and undergo valence-bond tautomerism in the process, e.g. quadricyclene is converted to norbornadiene by this method[37]. Evidence for the intermediacy of exciplexes is found in the correlation between the efficiency of valence-bond tautomerism and the oxidation potential of the strained hydrocarbon.

(iii) Energy transfer

$$A^{*} + D \longrightarrow (A^{\bar{\cdot}} D^{+\cdot})^{*} \longrightarrow A + D^{*} \qquad (2.3)$$

where * denotes a singlet or triplet excited state.

The importance of energy transfer (Equation 2.3) depends upon the relative energies of A*, B* and the exciplex which are in turn affected by the nature of the solvent. As the entropy requirements are less for intramolecular than intermolecular exciplex formation it is possible for an intramolecular system to exhibit exciplex fluorescence, whereas in the corresponding intermolecular case the exciplex is of higher energy than the excited singlet state of the quenching moiety so exciplex fluorescence is not observed, e.g. benzene and N-methylpyrollidine compared with the amine in Figure 2.3.

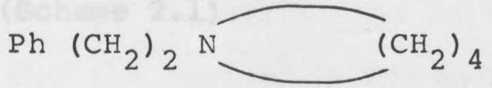


Figure 2.3

In solvents of medium polarity exciplex formation can lead to the production of triplet states (Scheme 2.1), e.g. the quenching of aromatic hydrocarbon fluorescence by amines leads to the formation of the triplet aromatic hydrocarbon[2]. Triplet formation can be enhanced both intra- and intermolecularly by the heavy atom effect.

Triplet formation via excimers has received less attention. Pyrene excimer formation leads to a decrease in the quantum yield of triplet production, whereas benzene excimer formation leads to an increase in the quantum yield of triplets[7].

There is little evidence for triplet exciplexes, whereas there is evidence, e.g. phosphorescence, for the existence of triplet excited charge transfer complexes[38]. Inter-system crossing in the latter can occur via a mechanism involving spin-orbit interactions which compete with other decay pathways of the excited complex. (Scheme 2.8)

(iv) <u>Electron transfer</u> In highly polar solvents direct electron transfer to produce a solvent shared ion-pair effectively competes with fluorescent exciplex generation.

(a) <u>Back electron transfer to give A + D</u> As a consequence of its exothermic nature (the extent of which depends on the solvent) back electron transfer to give A + D is often more favourable than dissociation into radical ions. Excess energy may be released as heat or in the generation of an excited singlet or triplet state of one of the partners (Scheme 2.1).

(b) Dissociation into radical ions Due to their polar nature exciplexes and excited charge-transfer complexes often dissociate into radical ions in polar solvents, e.g. the photoreduction of aromatic hydrocarbons by primary and secondary amines (Scheme 2.4). Coulombic attractive forces have to be overcome in order to separate geminate radical ions so dissociation will be most important in highly polar solvents. Weller and co-workers[32] attributed the polarity dependence of the fluorescence lifetime and quantum yield of exciplexes to ionic dissociation by two competitive routes (Scheme 2.5). The quenching of anthracene fluorescence by 9,10-dimethylanthracene, in pyridine, leads to the production of radical ions by path a with only a small fraction being formed via path b. Excited charge-transfer complexes can give rise to ion pairs via either their singlet or triplet excited states (Scheme 2.6).

$$\begin{tikzcd}
{}^{1}A^{*} + D & & (A^{\overline{\cdot}} \ldots D^{+\cdot}) \arrow[r] & A^{\overline{\cdot}} + D^{+\cdot} \\
\text{or} \arrow[urr, "a"] \arrow[drr, "b"'] & & & \\
A + {}^{1}D & & {}^{1}(A^{\overline{\cdot}}\ D^{+\cdot})^{*} \arrow[uu] &
\end{tikzcd}$$

Scheme 2.5

$$\begin{tikzcd}
(A\ D) \arrow[r, "h\nu"] & {}^{1}(A^{\overline{\cdot}}\ D^{+\cdot})^{*} \arrow[d, "\text{ISC}"'] \arrow[dr] & \\
 & & A^{\overline{\cdot}} + D^{+\cdot} \\
 & {}^{3}(A^{\overline{\cdot}}\ D^{+\cdot})^{*} \arrow[ur] &
\end{tikzcd}$$

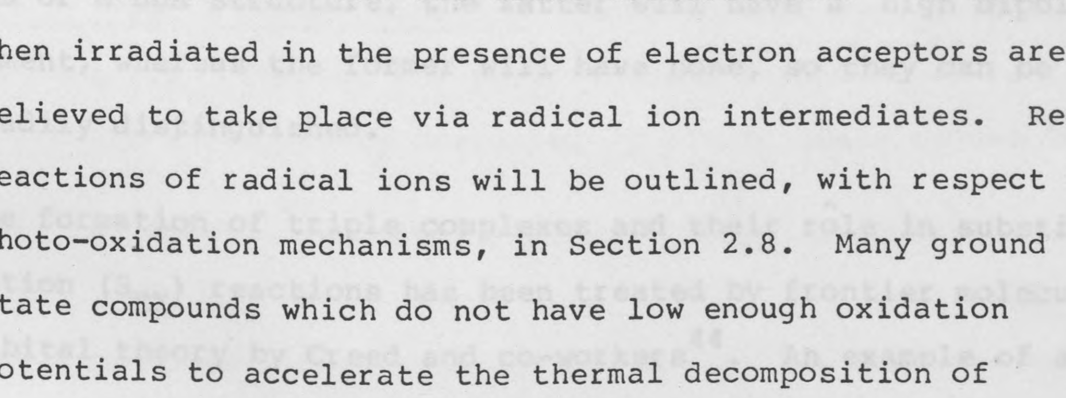
Scheme 2.6

Evidence for the presence of radical ions can be obtained from absorption spectra, conductivity measurements, esr spectra or by trapping of radical cations with nucleophiles and of radical anions by electrophiles. In the presence of D_2O any radical anions should be deuterated to yield neutral radicals and ultimately products containing deuterium[39] (Equation 2.4). It must be established that deuterium

$$D_2O + (C_6H_5Cl)^{\overset{-}{\bullet}} \longrightarrow DO^- + (C_6H_5DCl)^{\bullet} \rightleftharpoons HOD + (C_6H_4DCl)^{\overset{-}{\bullet}} \quad (2.4)$$

incorporation into the products was not due to reaction of the product after its formation.

Once radical ions have been produced they can be trapped, as above, by nucleophiles or electrophiles, undergo proton transfer, fragment, combine, undergo redox reactions, etc. The dimerisation[40] and cis-trans isomerisation[41] of alkenes when irradiated in the presence of electron acceptors are believed to take place via radical ion intermediates. Redox reactions of radical ions will be outlined, with respect to photo-oxidation mechanisms, in Section 2.8. Many ground state compounds which do not have low enough oxidation potentials to accelerate the thermal decomposition of peroxides have more than sufficient energy in their excited singlet states, e.g. singlet excited pyrene (P_y) sensitises the decomposition of phthaloyl peroxide[42] (Scheme 2.7).



Scheme 2.7

2.7 Triple Complexes

There is an optimum concentration of tertiary amines for fluorescent exciplex formation as the result of the quenching of aromatic hydrocarbon fluorescence by these amines. At higher amine concentrations the intensity of the exciplex fluorescence decreases and an emission band further to the red, due to a termolecular complex, appears (Equation 2.5).

$$(D^{+\bullet}\ A^{\overline{\bullet}})^{*} + D \rightleftharpoons (DD^{+\bullet}\ A^{\overline{\bullet}})^{*} \qquad (2.5)$$

In the quenching of naphthalene fluorescence by 1,4-dicyanobenzene, in toluene, the resultant exciplex fluorescence is quenched by naphthalene to produce an emissive triple complex[43]. Triple complexes may have either a symmetrical DAD or a DDA structure, the latter will have a high dipole moment, whereas the former will have none, so they can be readily distinguished.

The formation of triple complexes and their rôle in substitution (S_{EX}) reactions has been treated by frontier molecular-orbital theory by Creed and co-workers[44]. An example of an S_{EX} reaction is the displacement of trans-anethole by N,N-diethylaniline from an anethole-3,10-dicyanophenanthrene exciplex.

Quenching of exciplex fluorescence by oxygen, which has been proposed[45] to occur via a triple complex of the type $(A\text{-}D\text{-}O_2)^{*}$, can lead to diffusion controlled generation of triplet excited states in non-polar solvents.

$$\begin{tikzcd}
(\mathrm{D\ A}) \arrow[r, "h\nu"] & {}^{1}(\mathrm{A}^{\overline{\cdot}}\ \mathrm{D}^{+\cdot})^{*} \arrow[r, "\mathrm{ISC}"] \arrow[dr] & {}^{3}(\mathrm{A}^{\overline{\cdot}}\ \mathrm{D}^{+\cdot})^{*} \arrow[d] \\
 & & {}^{3}\mathrm{A}^{*} + \mathrm{D} \text{ or } \mathrm{A} + {}^{3}\mathrm{D}^{*}
\end{tikzcd}$$

Scheme 2.8

2.8 The potential rôle of excited complexes as intermediates in photo-oxidation reactions

Photo-oxidation reactions mainly occur via Type I, Type II or electron transfer processes, all of which are treated in depth in Chapter 5. The potential rôle of excited complexes in these reactions relies upon their ability to decay to yield reactive species such as triplet excited states and radical ions which can take part in chemical reactions.

2.8.1 Type I photo-oxidation

Photochemical Type I reactions (Scheme 2.9) involve the photo-induced formation of radicals which are subsequently scavenged by ground state oxygen to

$$\mathrm{Sens} + \mathrm{Subs} \xrightarrow{h\nu} \mathrm{Sens}\cdot + \mathrm{Subs}\cdot \xrightarrow{O_2} \mathrm{Products}$$

Scheme 2.9

yield products. Both exciplexes and electron-donor-acceptor complexes can act as sources of radical ions which in turn can undergo reactions such as protonation and dissociation to yield neutral radicals. Excited complexes can therefore play a part in the initiation of Type I photo-oxidation reactions.

2.8.2 Electron transfer photo-oxidation

Excited complexes can participate in electron transfer photo-oxidation reactions as a consequence of their ability, especially in polar solvents, to decay to radical ions (Scheme 2.1). An excited complex may be formed between the excited sensitiser and the substrate and decay to yield the sensitiser radical anion and the substrate radical cation. Electron transfer from the radical anion (provided it has a suitable redox potential) to ground state oxygen can then lead to the generation of the superoxide anion which can subsequently interact with the substrate radical cation to yield oxidation products (Scheme 2.10), e.g. the 9,10-dicyanoanthracene sensitised photo-oxidation of trans-stilbene[46]. Alternatively, the intermediate excited complex may be the result of interaction

$$\begin{tikzcd}
\mathrm{DCA} \arrow[r, "h\nu"] & {}^{1}\mathrm{DCA}^{*} \arrow[r, "\mathrm{D}"] & (\mathrm{D}^{+\cdot} + \mathrm{DCA}^{\bar{\cdot}})^{*} \arrow[d, "{}^{3}\mathrm{O}_2"] \\
 & \mathrm{DO}_2 & \mathrm{D}^{+\cdot} + \mathrm{O}_2^{\bar{\cdot}} + \mathrm{DCA} \arrow[l]
\end{tikzcd}$$

Scheme 2.10

between the excited substrate and ground state oxygen or between an electron rich substrate, e.g. a sulphide[47] in its ground state and molecular oxygen in its lowest excited singlet state (singlet oxygen). Such a complex can undergo radiative decay to yield the substrate radical cation and superoxide anion directly (Scheme 2.11). A third possibility

$$\mathrm{D} + {}^{1}\mathrm{O}_2 \longrightarrow (\mathrm{D}^{+\cdot}\ \mathrm{O}_2^{\bar{\cdot}})^{*} \longrightarrow \mathrm{D}^{+\cdot} + \mathrm{O}_2^{\bar{\cdot}}$$

Scheme 2.11

involves the excitation of a ground state charge transfer complex between the sensitiser, or ground state oxygen, and the substrate to yield an excited complex which can decay to yield radical ions. The utility of excited complexes as initiators of electron transfer photo-oxidation reactions is dependent upon the extent to which they decay to yield radical ions rather than undergoing other forms of non-radiative and radiative decay.

Interaction between the superoxide anion and a substrate radical cation may involve initial reversible excited complex formation whatever the method of generation of the radical ions. The excited complex must be capable of decaying to products, or rearranging to form the required transition state for product formation, if it is to play an active rôle in the photo-oxidation reaction rather than representing an intermediate whose formation merely leads to energy wastage.

<u>2.8.3 Type II photo-oxidation</u> Type II photo-oxidation reactions are those in which singlet oxygen is the reactive species responsible for oxidation. The singlet oxygen is often generated as a result of oxygen quenching of the triplet excited state of a sensitiser (Scheme 2.12). As

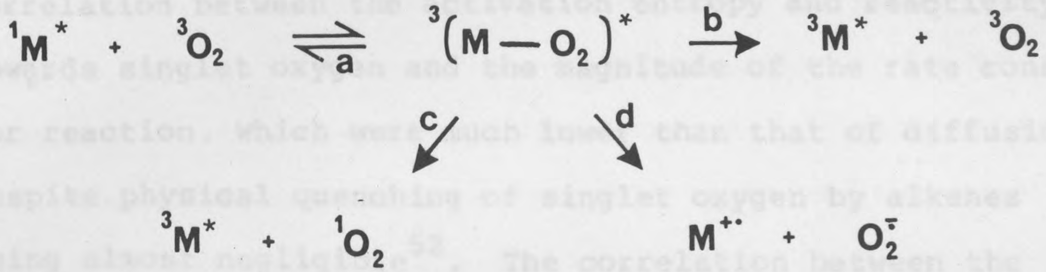
$$^3\text{Sens.}^* \; + \; ^3O_2 \longrightarrow \text{Sens.} \; + \; ^1O_2$$

$$\text{Subs.} \; + \; ^1O_2 \longrightarrow \text{products}$$

Scheme 2.12

many excited complexes are capable of decaying by a pathway which leads to the generation of triplet excited states the possibility exists that they could be utilised as sensitisers for Type II photo-oxidation reactions. For example pyrene excimer has been used to sensitise the photo-oxidation of 9,10-dimethylanthracene, a reactive singlet oxygen acceptor[48].

The quenching of both singlet and triplet excited states by ground state molecular oxygen has been proposed to occur via excited complexes[49] (see Chapter 5, Scheme 5.14 and 5.15) as illustrated for triplet states in Scheme 2.13. In the



Scheme 2.13

case of oxygen quenching of singlet excited states, generation of singlet oxygen can only take place if the singlet-triplet splitting of the sensitiser exceeds the excitation energy of singlet oxygen (94.5 kJ mol^{-1}). The extent to which decay of these complexes gives rise to the generation of singlet oxygen is dependent upon the degree of charge transfer character of the complex. The greater the charge-transfer component in the complex the greater the probability that spin-forbidden processes[50] and radical ion formation[51] will effectively compete with singlet oxygen production which is spin allowed.

Once formed the singlet oxygen may be physically quenched to ground state oxygen or chemically quenched to yield oxidation products. Recently, rapid reversible exciplex formation has been proposed[52,53] as the first step in the "ene" type and dioxetane forming reactions between singlet oxygen and alkenes. The rate determining step is believed to involve entropy-controlled rearrangement, of the initially created excited complex, to the transition state required for the generation of oxidation products. Evidence for exciplex intermediates was obtained from the low enthalpies of activation, the correlation between the activation entropy and reactivity towards singlet oxygen and the magnitude of the rate constants for reaction, which were much lower than that of diffusion despite physical quenching of singlet oxygen by alkenes being almost negligible[52]. The correlation between the ionization potential of cis-alkenes and their reactivity towards singlet oxygen and the similar correlation for trans-alkenes indicates that donor-acceptor interactions play some rôle in the transition state for the "ene" type reactions[52]. As many singlet oxygen mediated oxidation processes exhibit activation enthalpies close to zero, highly negative activation entropies and rate constants well below that for diffusion[54] exciplexes may well be involved in many Type II photo-oxidation reactions.

2.9 Conclusions

Excited complex formation is a widespread phenomenon in photochemical processes. Although they have been postulated as intermediates in processes as diverse as dimerisation and valence-bond tautomerism their rôle in photo-oxidation reactions is only starting to be appreciated. The ability of excited complexes to dissipate excitation energy or decay to yield reactive species such as excited singlet and triplet states and radical ions enables them to be considered as potential intermediates in practically all photochemical processes. However, evidence for their intermediacy is not always easy to obtain because only exciplexes which decay radiatively can be directly identified. As radiative decay is in competition with non-radiative decay to yield reactive species evidence for exciplexes as intermediates in photochemical reactions must often be obtained by indirect means. Once excited complexes have been identified as intermediates in a photochemical process the conditions can be adjusted to favour the desired decay route of the complex, e.g. decay to yield reactive species such as radical ions. Consequently, an understanding of the processes involved in the formation and decay of excited complexes is of fundamental importance.

2.10 References*

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* JACS = J. Amer. Chem. Soc.

Tet. Letts. = Tetrahedron Letters

CHAPTER 3

THE PHOTOLYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE PRESENCE OF AMINES AND SULPHIDES

CHAPTER 3

THE PHOTOLYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE PRESCENCE OF AMINES AND SULPHIDES

3.1 Quenching of the excited states of aromatic hydrocarbons by sulphides

3.1.1 Introduction

It is well known that amines quench the fluorescence of aromatic hydrocarbons by an electron transfer process[1a-e]. Although the ionisation potentials of sulphides are higher than those of amines the possibility arises that sulphides could behave similarly. Cyano-aromatic hydrocarbons have been found to sensitise the photo-oxygenation of sulphides in polar solvents[2a,b] and the proposed mechanism involves electron transfer from the sulphide to the singlet excited sensitiser (Scheme 3.1). The involvement of radical ions

$$^{1}\mathrm{ArCN}^{*} + \mathrm{R_2S} \longrightarrow \mathrm{ArCN}^{\overset{-}{\cdot}} + \mathrm{R_2S}^{+\cdot}$$

$$\mathrm{ArCN}^{\overset{-}{\cdot}} + {}^{3}\mathrm{O_2} \longrightarrow \mathrm{ArCN} + \mathrm{O_2}^{\overset{-}{\cdot}}$$

$$\mathrm{R_2S}^{+\cdot} + \mathrm{O_2}^{\overset{-}{\cdot}} \longrightarrow \text{oxidation products}$$

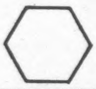
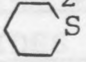
Scheme 3.1

has been demonstrated using the technique of esr spectroscopy[2b]. Laser flash photolysis studies have demonstrated the ability of dialkyl and aryl alkyl sulphides to quench triplet excited benzophenone with the concomitant generation of radical ions[3]. Experiments were therefore performed in order to evaluate the ability of a range of sulphides to quench the singlet and triplet excited states of a variety of aromatic hydrocarbons.

3.1.2 Results and discussion

The results in Table 3.1 reveal that both cyclic and acyclic sulphides quench the fluorescence of a range of aromatic hydrocarbons and their cyano-derivatives. The finding that the fluorescence quenching is more efficient in acetonitrile than in the non-polar solvents suggests that the quenching process involves an electron transfer mechanism. A weak fluorescence emission, red-shifted from the monomer emission, which may have emanated from an exciplex intermediate, was observed when di-(n-butyl)sulphide was used to quench the fluorescence of 1-cyanonaphthalene in cyclohexane. Exciplex formation as a result of the quenching of aromatic hydrocarbons by amines has been well documented[1a-e]. Steric effects upon the quenching are illustrated by the efficiency with which di-butyl sulphides quench the fluorescence of a range of aromatic hydrocarbons, i.e. n-Bu_2S > s-Bu_2S > t-Bu_2S. It is clear from the results in Table 3.1 that these steric effects are most marked in the non-polar solvents (Figure 3.1). This observation provides further evidence for an electron-transfer quenching process because the more polar the solvent the greater the distance over which electron-transfer can occur, and consequently steric interactions will be less important in the more polar solvent.

The results in Tables 3.2 to 3.5, obtained using the technique of nanosecond laser flash photolysis, show that the sulphides also quenched the triplet states of a range of

AROMATIC HYDROCARBON	SULPHIDE	$K_{SV}(M^{-1})$	
		MeCN	
Biphenyl	Et_2S	65	16.7
"	$n\text{-}Bu_2S$	101.7	21.9
"	$s\text{-}Bu_2S$	21.2	2.8
"	$t\text{-}Bu_2S$	15.7	1.6
"	$MeS(CH_2)_2SMe$	121.9	39.5
Naphthalene	Et_2S	1.9	*a*
9-Cyanoanthracene	Et_2S	4.8	*a*
"	Ph_2S	26	*a*
"	Me S Ph	15.5	*a*
9,10-Dicyanoanthracene	Et_2S	243	*a*
"	Me S Ph	26.7	*a*
4-Cyanobiphenyl	Et_2S	37	*a*
1-Cyanonaphthalene	Me_2S	131	120^b
"	Et_2S	125	87^b
"	$n\text{-}Bu_2S$	143	85^b
"	$s\text{-}Bu_2S$	115	30^b
"	$t\text{-}Bu_2S$	80	3.9^b
"	$MeS(CH_2)_2SMe$	137	78^b
"	$MeS(CH_2)_3SMe$	166	95^b
"		145	95.6^b
"	1,3-dithiane	122^b	112^b
"	1,4-dithiane	104^b	58.8^b

a - not determined; *b* - reference 4

TABLE 3.1 STERN-VOLMER CONSTANTS (K_{SV}) FOR QUENCHING OF THE FLUORESCENCE OF A RANGE OF AROMATIC HYDROCARBONS BY SULPHIDES IN BOTH POLAR AND NON-POLAR SOLVENTS, UNDER DEGASSED CONDITIONS

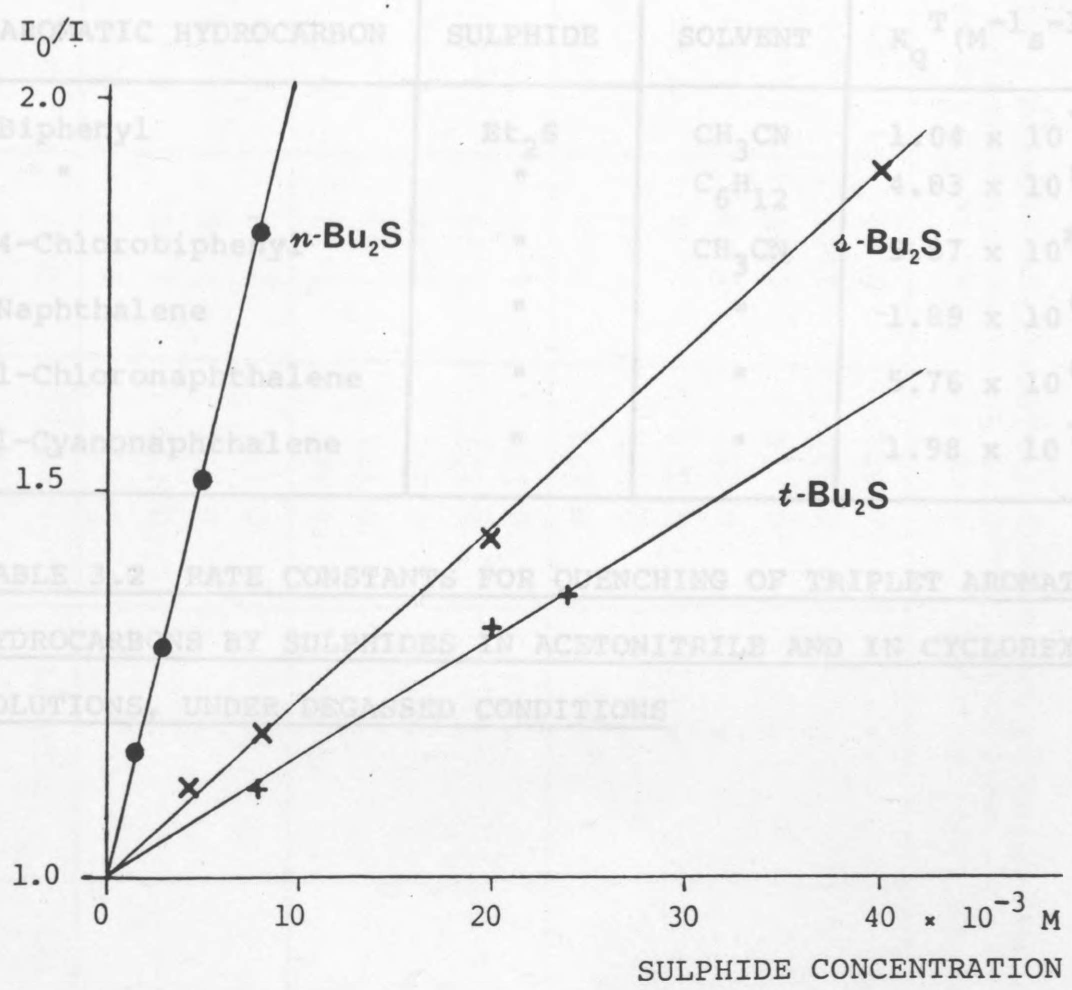
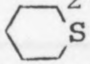
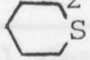


FIGURE 3.1 STERN-VOLMER PLOT FOR THE QUENCHING OF BIPHENYL FLUORESCENCE BY DIBUTYL SULPHIDES IN ACETONITRILE SOLUTION

AROMATIC HYDROCARBON	SULPHIDE	SOLVENT	K_q^T $(M^{-1}s^{-1})$
Biphenyl	Et_2S	CH_3CN	1.04×10^7
"	"	C_6H_{12}	4.83×10^6
4-Chlorobiphenyl	"	CH_3CN	5.87×10^7
Naphthalene	"	"	1.89×10^6
1-Chloronaphthalene	"	"	5.76×10^6
1-Cyanonaphthalene	"	"	1.98×10^7

TABLE 3.2 RATE CONSTANTS FOR QUENCHING OF TRIPLET AROMATIC HYDROCARBONS BY SULPHIDES IN ACETONITRILE AND IN CYCLOHEXANE SOLUTIONS, UNDER DEGASSED CONDITIONS

SULPHIDE[a]	SULPHIDE CONCENTRATION (M)	SOLVENT	OD[b] (414nm)	τ_1 (μs)	τ_2 (μs)
None	0	CH_3CN	0.099	4.63	9.76
n-Bu$_2$S[c]	2.33×10^{-3}	"	0.155	2.88	6.41
s-Bu$_2$S[c]	2.9×10^{-3}	"	0.153	3.08	7.22
t-Bu$_2$S[c]	4.16×10^{-3}	"	0.158	2.67	6.89
None	0	CH_3CN	0.168	3.03	5.13
MeS(CH$_2$)$_2$SMe[d]	7.3×10^{-3}	"	0.171	1.67	11.54
MeS(CH$_2$)$_3$SMe[d]	6.02×10^{-3}	"	0.132	1.48	7.52
 [d]	6.89×10^{-3}	"	0.177	1.94	5.01
1,4-dithiane [d]	9.6×10^{-3}	"	0.128	1.92	7.91
None	0	C_6H_{12}	0.173	5.53	8.76
Et$_2$S[d]	1.15×10^{-2}	"	0.277	2.44	6.24
n-Bu$_2$S[d]	1.17×10^{-2}	"	0.370	2.54	7.07
s-Bu$_2$S[d]	3.33×10^{-2}	"	0.252	2.08	6.09
MeS(CH$_2$)$_2$Sme[d]	1.28×10^{-2}	"	0.228	1.59	3.05
MeS(CH$_2$)$_3$SMe[d]	1.05×10^{-2}	"	0.222	1.05	2.24
 [d]	1.05×10^{-2}	"	0.273	2.87	6.88

a - in some cases the sulphides acted as light filters; *b* - optical density at the wavelength of maximum triplet-triplet absorption; *c* - sufficient sulphide to cause 25% quenching of 1-cyanonaphthalene fluorescence
d - sufficient sulphide to cause 50% quenching of 1-cyanonaphthalene fluorescence

TABLE 3.3 EFFECTS OF ADDED SULPHIDES UPON THE YIELD OF TRIPLETS, AND THEIR LIFETIMES, FROM 1-CYANONAPHTHALENE IN ACETONITRILE AND IN CYCLOHEXANE SOLUTIONS, UNDER DEGASSED CONDITIONS

AROMATIC HYDROCARBON	SULPHIDE	SULPHIDE CONCENTRATION (M)	SOLVENT	OD^{a}	τ_1 (μs)	τ_2 (μs)
Biphenyl	None	0	CH_3CN	0.473^{d}	5.84	7.54
"	n-Bu_2S^{b}	3.28×10^{-3}	"	0.515^{d}	2.53	7.67
"	s-Bu_2S^{b}	1.57×10^{-2}	"	0.477^{d}	3.01	7.19
"	t-Bu_2S^{b}	6.37×10^{-2}	"	0.507^{d}	3.55	6.74
Biphenyl	None	0	CH_3CN	0.580^{d}	5.10	7.44
"	Et_2S^{c}	1.54×10^{-2}	"	0.612^{d}	2.36	4.10
"	$MeS(CH_2)_2SMe^{c}$	8.2×10^{-3}	"	0.559^{d}	1.69	3.27
Biphenyl	None	0	C_6H_{12}	0.581^{d}	11.41	-
"	Et_2S^{c}	5.98×10^{-2}	"	0.622^{d}	2.53	4.49
"	$MeS(CH_2)_2SMe^{c}$	2.53×10^{-2}	"	0.612^{d}	2.20	3.96
4-Chlorobiphenyl	None	0	CH_3CN	0.638^{e}	4.44	6.79
"	Et_2S	1×10^{-2}	"	0.592^{e}	2.76	4.42
4-Chlorobiphenyl	None	0	C_6H_{12}	0.597^{e}	7.74	11.62
"	Et_2S	1×10^{-2}	"	0.569^{e}	5.41	8.33

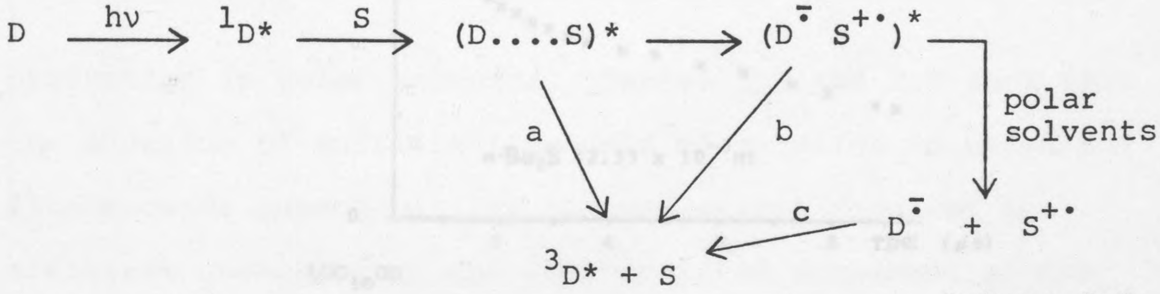
a - optical density of triplet-triplet absorption spectrum at its maximum intensity; *b* - sufficient sulphide to quench 25% of the biphenyl fluorescence; *c* - sufficient sulphide to quench 50% of the biphenyl fluorescence; *d* - λ = 358nm; *e* - λ = 372nm.

TABLE 3.4 EFFECTS OF ADDED SULPHIDE UPON THE TRIPLET YIELD AND TRIPLET LIFETIMES FOR A RANGE OF AROMATIC HYDROCARBONS IN ACETONITRILE AND IN CYCLOHEXANE SOLUTIONS UNDER DEGASSED CONDITIONS

AROMATIC HYDROCARBON	SULPHIDE CONCENTRATION (M)	SOLVENT	OD^{a}	τ_1 (μs)	τ_2 (μs)
Biphenyl	0	CH_3CN	0.566^{b}	4.81	10.30
"	5×10^{-3}	"	0.559^{b}	3.34	5.16
"	1×10^{-2}	"	0.577^{b}	3.13	5.45
"	2×10^{-2}	"	0.556^{b}	2.34	5.61
Biphenyl	0	C_6H_{12}	0.584^{b}	8.37	15.60
"	2×10^{-2}	"	0.567^{b}	4.84	7.90
"	4×10^{-2}	"	0.582^{b}	3.21	8.07
"	8×10^{-2}	"	0.514^{b}	2.72	9.88
4-Chlorobiphenyl	0	CH_3CN	0.554^{c}	6.15	-
"	1×10^{-2}	"	0.586^{c}	2.79	3.87
"	4×10^{-2}	"	0.529^{c}	2.08	4.35
"	8×10^{-2}	"	0.478^{c}	1.46	2.97
Naphthalene	0	CH_3CN	0.344^{d}	3.67	6.71
"	3×10^{-3}	"	0.361^{d}	2.88	6.16
"	5.3×10^{-3}	"	0.349^{d}	2.70	6.36
"	7×10^{-3}	"	0.328^{d}	2.44	3.80
1-Chloronaphthalene	0	CH_3CN	0.422^{e}	2.50	3.62
"	1×10^{-2}	"	0.429^{e}	2.02	3.01
"	2.5×10^{-2}	"	0.410^{e}	1.64	2.61
"	5×10^{-2}	"	0.340^{e}	1.48	2.94
"	8×10^{-2}	"	0.291^{e}	1.12	2.76
1-Cyanonaphthalene	0	CH_3CN	0.145^{f}	3.58	7.60
"	4×10^{-3}	"	0.150^{f}	2.57	5.01
"	1×10^{-2}	"	0.168^{f}	2.62	6.80
"	8×10^{-3}	"	0.204^{f}	2.20	8.26

a - optical density of triplet-triplet absorption spectra at their maximum intensity;
b - λ = 358nm; *c* - λ = 372nm; *d* - λ = 412nm; *e* - λ = 418nm; *f* - λ = 414nm.

TABLE 3.5 EFFECT OF ADDED DIETHYL SULPHIDE UPON TRIPLET YIELDS, AND TRIPLET LIFETIMES, FOR A RANGE OF AROMATIC HYDROCARBONS IN ACETONITRILE AND IN CYCLOHEXANE SOLUTIONS, UNDER DEGASSED CONDITIONS aromatic hydrocarbons. In some cases the yield of triplets, as determined from the optical density of the triplet-triplet absorption at the wavelength of maximum absorption, was found to increase in the presence of sulphides. Figure 3.2 illustrates the effect of butyl sulphides on the yield and lifetime of 1-cyanonaphthalene triplet. The enhanced quantum yields of triplet production provide evidence for intermediate exciplex formation between the sulphide and the singlet excited aromatic hydrocarbon. Scheme 3.2 outlines



Scheme 3.2

a possible mechanism for the observed enhancement of inter-system crossing in the presence of sulphides. Decay of the initial encounter complex, the equilibrium exciplex or re-combination of solvent separated radical ions can all lead to triplet production[5]. The importance of paths a, b and c (Scheme 3.2) will be dependent upon the extent to which each of the intermediate species are generated and undergo these and other decay processes (see Chapter 2). In some cases the triplet yield is lower in the presence of a sulphide (Tables 3.3-3.5) and is attributed to the sulphides behaving as light filters. Consequently, the absolute extents to which the sulphides enhance inter-system crossing is not known.

From Table 3.2 it can be seen that the quenching of triplet

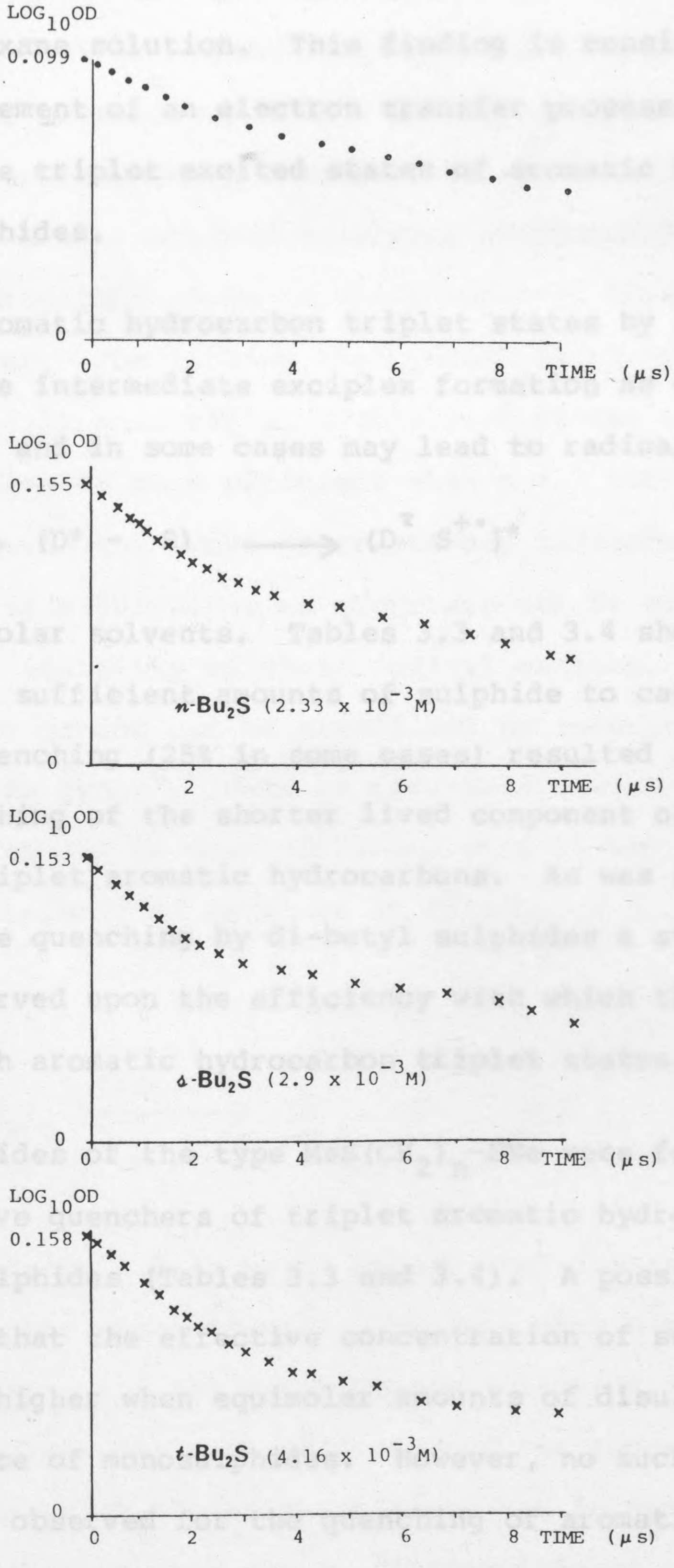


FIGURE 3.2 DECAY OF THE TRIPLET-TRIPLET ABSORPTION OF 1-CYANONAPHTHALENE IN THE ABSENCE AND PRESENCE OF DIBUTYL SULPHIDES (ENOUGH TO CAUSE 25% QUENCHING OF 1-CYANONAPHTHALENE FLUORESCENCE) IN DEGASSED ACETONITRILE SOLUTION

biphenyl by diethyl sulphide is more efficient in acetonitrile than in cyclohexane solution. This finding is consistent with the involvement of an electron transfer process in the quenching of the triplet excited states of aromatic hydrocarbons by sulphides.

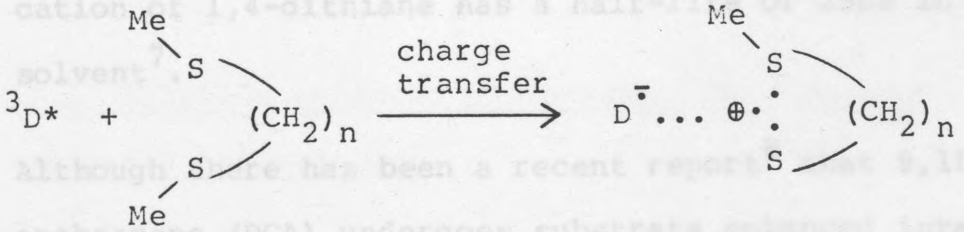
Quenching of aromatic hydrocarbon triplet states by sulphides may also involve intermediate exciplex formation as outlined in Equation 3.1 and in some cases may lead to radical ion

$$^{3}D^{*} + S \longrightarrow (D^{*} - S) \longrightarrow (D^{\overline{\cdot}}\ S^{+\cdot})^{*} \qquad (3.1)$$

production in polar solvents. Tables 3.3 and 3.4 show that the addition of sufficient amounts of sulphide to cause 50% fluorescence quenching (25% in some cases) resulted in efficient quenching of the shorter lived component of the decay of the triplet aromatic hydrocarbons. As was found for fluorescence quenching by di-butyl sulphides a steric effect was observed upon the efficiency with which these compounds quench aromatic hydrocarbon triplet states.

Acyclic disulphides of the type $MeS(CH_2)_n$-SMe were found to be more effective quenchers of triplet aromatic hydrocarbons than the monosulphides (Tables 3.3 and 3.4). A possible explanation is that the effective concentration of sulphide groups will be higher when equimolar amounts of disulphides are used in place of monosulphides. However, no such clear distinction was observed for the quenching of aromatic hydrocarbon fluorescence by these compounds. Fluorescence quenching of biphenyl, which was considerably less efficient in non-polar solvents, was increased when $MeS(CH_2)_2SMe$ was used as the quencher rather than monosulphides (Table 3.1).

In contrast the quenching of 1-cyanonaphthalene fluorescence by sulphides was not so markedly affected by a decrease in solvent polarity or a change from a mono to a disulphide as the quenching species. This behaviour can be rationalised if electron transfer reactions involving 1-cyanonaphthalene occur more readily than those in which biphenyl acts as the electron acceptor. The finding that quenching of both the singlet (Table 3.1) and triplet (Table 3.3) states of 1-cyanonaphthalene is more efficient when n = 3 than when n = 2, coupled with the above observations, indicates that the efficiency of disulphides as quenchers can be attributed to the relative stability of their radical cations. A sulphide radical cation can be stabilised by interaction with a second sulphide group[6]. Such an interaction will facilitate electron transfer and be most efficient when it can take place intramolecularly as outlined in Equation 3.2. From



(3.2)

the results in Table 3.3 it would appear that interaction between the sulphur atoms is more efficient when n = 3 than when n = 2. When n = 3 the unfavourable eclipsing interactions in the polymethylene chain which disfavour the adoption of conformations in which the sulphide atoms can interact must be less important than when n = 2. Intramolecular exciplex formation between groups separated by polymethylene chains is often most efficient[5] when n = 3 (see Chapter 2).

The cyclic pentamethylene sulphide and dithianes were no more effective than acyclic sulphides and disulphides, respectively, at quenching the singlet and triplet excited states of 1-cyanonaphthalene. This is despite through bond interactions between sulphur atoms in the dithianes. Intramolecular sulphur-sulphur interactions in these compounds will be maximal when they adopt the configurations illustrated in Figure 3.3. In non-polar solvents 1,3-dithiane is a much more effective quencher of 1-cyanonaphthalene fluorescence (Table 3.1) than 1,4-dithiane. This may reflect the greater stability of the radical cation of 1,3-dithiane which has a half-life of 300μs in aqueous solution, whereas the radical cation of 1,4-dithiane has a half-life of 25μs in the same solvent[7].

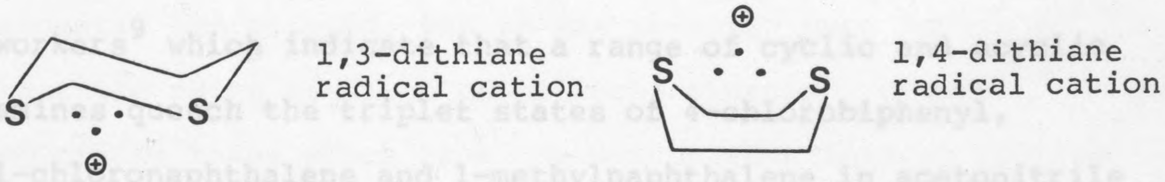


Figure 3.3

Although there has been a recent report[8] that 9,10-dicyanoanthracene (DCA) undergoes substrate enhanced intersystem crossing in the presence of thioanisole no quantitative data was provided in support of this claim. Laser flash photolysis experiments revealed that addition of thioanisole, diphenyl sulphide or diethyl sulphide to a solution of 9,10-dicyanoanthracene, at concentrations sufficient to cause either 50% or total fluorescence quenching, did not result in any significant enhancement of the triplet yield. Any enhancement was within the bounds of experimental error (which was accentuated due to the low intensity of the triplet-triplet absorption spectrum of DCA obtained under our experimental conditions).

3.1.3 Conclusions

A range of sulphides are capable of quenching the singlet and triplet excited states of aromatic hydrocarbons and their chloro- and cyano-derivatives. The finding that sulphides quench the triplet states of aromatic hydrocarbons is consistent with recent results obtained by Davidson and co-workers[9] which indicate that a range of cyclic and acyclic amines quench the triplet states of 4-chlorobiphenyl, 1-chloronaphthalene and 1-methylnaphthalene in acetonitrile solution. The sulphides also enhance inter-system crossing from the aromatic hydrocarbon singlet states. All the results are consistent with the involvement of intermediate charge transfer complex formation in the quenching of both the singlet and triplet excited states of the hydrocarbons.

3.2 Sulphide enhanced photo-reductive dehalogenation of aromatic hydrocarbons

3.2.1 Introduction

There are many reports pertaining to the ability of amines[10a-g] and dienes[10c,11], which are known to behave as electron donors, to assist the photo-induced dehalogenation of aryl halides. The mechanisms of these reactions are believed to involve initial electron transfer between the hydrocarbon and the electron donor as illustrated, for the methylamine assisted dechlorination of chloro-aromatic compounds, in Equation 3.3. Evidence for the intermediacy of radical ions

$$Et_3N + ArCl^* \longrightarrow Et_3N^{+\cdot} + (ArCl)^{\dot{-}} \longrightarrow \dot{Ar} + Cl^- \qquad (3.3)$$

has been obtained from (i) the finding that the effect of added electron donors is greater in acetonitrile than in methanol or cyclohexane[10c,d] and (ii) observed deuterium incorporation into the substrate and the dehalogenated aromatic hydrocarbons when the reactions are carried out in a CH_3CN/D_2O solvent mixture[10d,e,11]. The reactions were believed[10a] to occur via the singlet excited state of the aromatic hydrocarbon, but it has recently been suggested[10e] that the amine assisted photo-dechlorination of aryl chlorides takes place from the hydrocarbon triplet excited state. The original proposal[10a] was based on the observation that electron donors quench the fluorescence of aryl halides and the inability of 1,3-pentadiene (a triplet quencher) to inhibit photo-reduction in acetonitrile. However, it has since been found[10e] that 1,3-pentadiene can actually enhance the photodegradation of 4-chlorobiphenyl. This reaction can also be sensitised, in non-polar solvents, by triethylamine, even when the amine is present at a sufficiently high concentration to quench almost all the singlet excited 4-chlorobiphenyl molecules.[10e] These and other kinetic results are consistent with a mechanism involving triplet excited states although singlet excited states may also play a part in the dehalogenation reactions. Unassisted photo-dehalogenation of chlorobenzene has been proposed[12] to occur from the triplet state with the formation of a singlet excimer being an unproductive side reaction. After electron transfer to the aryl halide three modes of reaction are open to the radical anion (i) loss of halogen ion followed by hydrogen abstraction,

(ii) protonation by an external proton donor and (iii) protonation within the exciplex or ion pair. Triethylamine only markedly enhances the rate of dehalogenation of aryl halides which do not readily undergo dehalogenation upon photolysis in the absence of electron donors[10d,g].

As the results reported in Section 3.1.2 indicate that sulphides can quench the singlet and triplet excited states of a range of aromatic hydrocarbons including 1-chloronaphthalene and 4-chlorobiphenyl, via an electron transfer process, the possibility arises that sulphides, like amines, may enhance the photo-induced dehalogenation of aromatic halides.

3.2.2 Results and discussion

The addition of diethyl sulphide was found to accelerate the rate of dehalogenation of a range of halo-aromatic compounds (Table 3.6). The reactions were notably faster in polar than non-polar aprotic solvents as would be expected for an electron transfer process. Yields of the photo-produced parent aromatic hydrocarbons were usually considerably less than would be expected from the loss of substrate, e.g. in acetonitrile solution 40% of the 1-chloronaphthalene consumed gave rise to the production of naphthalene, whereas in methanol and in cyclohexane solutions the values were 16.7% and 6.5% respectively. Identification of the other products awaits a complete product study. Some dimerisation of the 9-chloro- and 9-bromo-anthracenes took place and accounts for some of the discrepancy in the product yields. The precipitated crystals of the dimers were compared with authentic

SUBSTRATE	REACTION TIME (HRS)	SUBSTRATE CONSUMED (%)	YIELD OF DEHALOGENATED HYDROCARBON (%)[a]	COMPARATIVE RATE OF PRODUCT FORMATION		
				CH_3CN	CH_3OH	C_6H_{12}
4-Chlorobenzonitrile	2	44	34	5.48	1.09	1
4-Chlorobiphenyl	4	100	26	15[b]	13[b]	1
1-Chloronaphthalene	4	20	11	5.71	1.66	1
1-Bromonaphthalene	4	53	28	4.1	3.4	1
9-Chloroanthracene[c]	4	69	18	3.18	2.99	1
9-Bromoanthracene[c]	2	58	22	1.3[b]	1.8	1

a - based on the amount of substrate initially present; *b* - control experiments confirmed that no reaction took place in the absence of diethyl sulphide; *c* - some dimerisation took place.

TABLE 3.6 EFFECT OF SOLVENT UPON THE PHOTO-INDUCED DEHALOGENATION OF HALO-AROMATIC COMPOUNDS (0.04g/12mls) IN THE PRESENCE OF DIETHYL SULPHIDE (0.8mls/12mls), UNDER DEGASSED CONDITIONS, IN ACETONITRILE, METHANOL AND CYCLOHEXANE SOLUTIONS samples using i.r. spectroscopy. As reported[10d] for the amine assisted dehalogenation of aryl halides the accelerating effect of the diethyl sulphide (Table 3.6) was found to be more marked for chloro-compounds than for bromo-compounds. As dehalogenation of bromo-compounds is less energy demanding[13] than that of chloro-compounds, homolysis of the carbon-bromine bond will compete effectively with electron transfer from the electron donor (Scheme 3.3).

$$\mathrm{ArBr} \xrightarrow{h\nu,\ k_1} \mathrm{Ar}\cdot + \mathrm{Br}\cdot$$

$$\mathrm{ArBr} + \mathrm{D} \xrightarrow{h\nu,\ k_2} (\mathrm{ArBr})^{\overline{\cdot}} + \mathrm{D}^{+\cdot}$$

where $k_1 [\mathrm{ArBr}^*] > k_2 [\mathrm{ArBr}^*] [\mathrm{D}]$

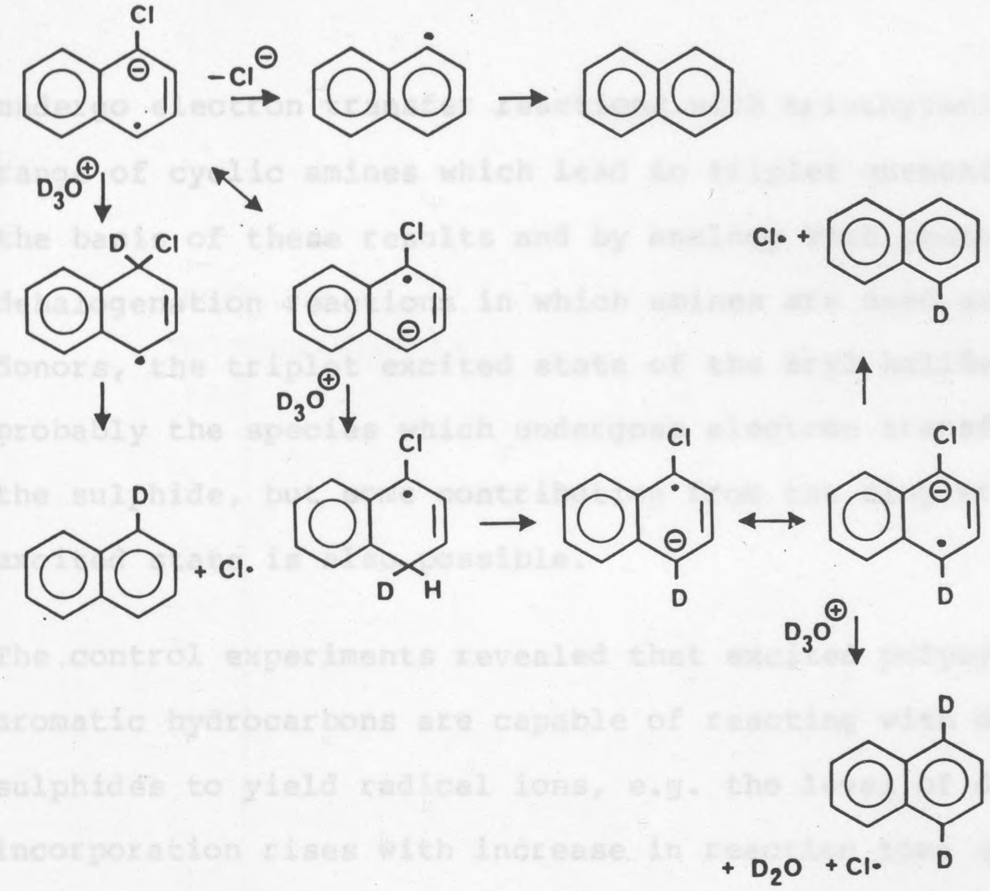
Scheme 3.3

Reaction with the electron donor will be more important for chloro-compounds because homolytic cleavage of chloro-compounds is energetically less favourable. Due to the heavy atom effect the lifetimes of the excited states of bromo-aromatics are shorter than those of their chloro-analogues. Consequently, bromo-aromatics are less likely than their chloro counterparts to undergo bimolecular reactions from their excited states.

In order to ascertain whether radical ions were involved the reactions were carried out in an acetonitrile-deuterium oxide (5:1 v/v) solvent mixture. The extent of deuterium incorporation into reactants and products was determined by mass spectrometry, taking into account the natural abundance of ^{13}C. It was necessary to ensure that deuterium incorporation into the aromatic hydrocarbon was due to the sulphides reacting with the aryl halide, rather than as a consequence of the excited photo-produced aromatic hydrocarbon undergoing further reaction with the sulphide[14]. Therefore, solutions of the aryl halide and diethyl sulphide were irradiated under standard conditions with the addition of a "marker" aromatic hydrocarbon. The concentration of the latter was equal to the expected yield of dehalogenated aromatic hydrocarbon. The extent of deuterium incorporation into the hydrocarbon, substrate and marker are summarised in Table 3.7. Little or no incorporation into the aryl halides was observed indicating that their radical ions cannot be reverting, to any significant extent, to starting aryl halides. This probably reflects the ease with which the radical ions of the aryl halides break up to give halide ions[15]. In contrast, the photo-produced aromatic hydrocarbons showed substantial deuterium incorporation, significantly greater than in the marker compounds, incorporation into which was negligible. Such a large difference in levels of incorporation is unlikely to be entirely due to the lower reactivity of the marker compounds. Therefore, deuterium incorporation into the dehalogenated aromatic hydrocarbon can be rationalised on the basis of aryl halide radical anions being intermediates in these reactions. A possible route[10d] to deuterium incorporation into naphthalene, produced upon photolysis of 1-chloronaphthalene in the presence of diethyl sulphide and deuterium oxide is outlined in Scheme 3.4. On the basis of the results presented in Chapter 4 deuteration of the intermediate exciplex rather than the solvent separated radical anion cannot be ruled out. However, if this was the case the lack of deuterium incorporation into the aryl halide can only be explained if equilibrium exciplex

SUBSTRATE	MARKER	(%) INCORPORATION OF ONE DEUTERIUM HYDROCARBON	SUBSTRATE	MARKER
4-Chlorobenzonitrile	4-cyanotoluene	28	0	0
4-Chlorobiphenyl	3-phenyltoluene	44	0	0
1-Chloronaphthalene	2-methylnaphthalene	74	0	0
1-Bromonaphthalene	2-methylnaphthalene	65	1	0
9-Bromoanthracene	2-methylanthracene	36	0	0

TABLE 3.7 DEUTERIUM INCORPORATION INTO THE SUBSTRATE AND PRODUCTS RESULTING FROM 2hrs IRRADIATION OF HALO-AROMATICS (0.1g/30mls) IN THE PRESENCE OF DIETHYL SULPHIDE (2mls/30mls) IN CH_3CN/D_2O (5:1 v/v), UNDER DEGASSED CONDITIONS



Scheme 3.4

formation is largely irreversible.

On the basis of the above results the following mechanism is proposed for the dehalogenation of aryl halides in the presence of sulphides:-

$$\mathrm{ArHal}^{*} + \mathrm{R_2S} \longrightarrow \mathrm{ArHal}^{\overline{\cdot}} + \mathrm{R_2S}^{+\cdot}$$

$$\mathrm{ArHal}^{\overline{\cdot}} \longrightarrow \mathrm{Ar}^{\cdot} + \mathrm{Hal}^{-}$$

$$\mathrm{Ar}^{\cdot} + \mathrm{R_2S}\ (\text{or solvent}) \longrightarrow \mathrm{ArH}$$

$$\mathrm{ArHal}^{\overline{\cdot}} + \mathrm{D_2O} \longrightarrow \dot{\mathrm{A}}\mathrm{rHalD} + \mathrm{DO}^{-}$$

$$\dot{\mathrm{A}}\mathrm{rHalD} \longrightarrow \mathrm{ArD} + \mathrm{Hal}^{\cdot}$$

Scheme 3.5

It can be seen from Table 3.2 that diethyl sulphide quenches the triplet states of both 4-chlorobiphenyl and 1-chloronaphthalene in acetonitrile solution. The excited triplet states of these aryl halides have recently[9] been shown to undergo electron transfer reactions with triethylamine and a range of cyclic amines which lead to triplet quenching. On the basis of these results and by analogy with photo-reductive dehalogenation reactions in which amines are used as electron donors, the triplet excited state of the aryl halide is probably the species which undergoes electron transfer with the sulphide, but some contribution from the singlet excited state is also possible.

The control experiments revealed that excited polycyclic aromatic hydrocarbons are capable of reacting with dialkyl sulphides to yield radical ions, e.g. the level of deuterium incorporation rises with increase in reaction time (Figure 3.4). Therefore, a variety of aromatic hydrocarbons were irradiated in the presence of a variety of sulphides (Table 3.8). Incorporation of deuterium into the aromatic hydrocarbons when a CH_3CN/D_2O solvent mixture was used can be rationalised by the mechanism outlined in Scheme 3.6.

$$ArH^* + R_2S \longrightarrow ArH^{\overset{-}{\cdot}} + R_2S^{+\cdot}$$

$$ArH^{\overset{-}{\cdot}} + D_2O \longrightarrow \dot{A}rHD + DO^-$$

$$\dot{A}rHD \longrightarrow ArD^{\overset{-}{\cdot}} + H^+$$

$$ArD^{\overset{-}{\cdot}} + R_2S^{+\cdot} \longrightarrow ArD + R_2S$$

Scheme 3.6

At the concentrations employed the sulphides quench the hydrocarbon fluorescence and reduce the lifetime of the excited triplets (Section 3.1), so both the excited singlet and triplet states may be responsible for reaction. The low value for deuterium incorporation into anthracene, in the presence of diethyl sulphide, may be partly due to the

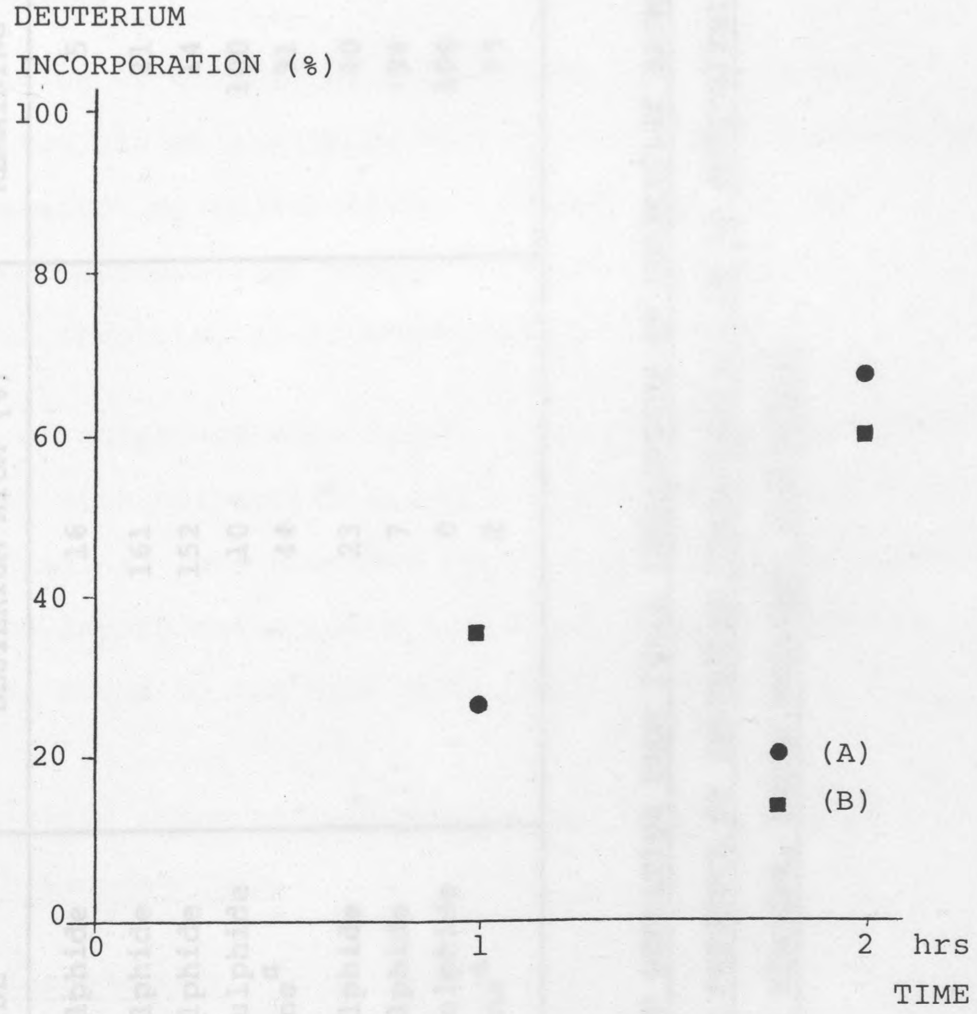


FIGURE 3.4 DEUTERIUM INCORPORATION INTO NAPHTHALENE WHICH IS PRODUCED AS A RESULT OF THE PHOTOLYSIS OF (A),1-CHLORONAPHTHALENE AND (B),1-BROMONAPHTHALENE IN THE PRESENCE OF DIETHYL SULPHIDE IN AN MeCN/D_2O SOLVENT MIXTURE

HYDROCARBON	SULPHIDE	INCORPORATION OF ONE DEUTERIUM ATOM (%)	HYDROCARBON REMAINING (%)
Anthracene	diethyl sulphide	16	5
Biphenyl	diethyl sulphide	161	21
"	dibutyl sulphide	152	14
"	diphenyl sulphide	10	100
"	1,4-dithiane^{a}	44	91
Naphthalene	diethyl sulphide	23	40
"	dibutyl sulphide	7	94
"	diphenyl sulphide	0	100
"	1,4-dithiane^{a}	2	95

a - 1g/30mls

TABLE 3.8 DEUTERIUM INCORPORATION RESULTING FROM 20hrs IRRADIATION OF POLYCYCLIC AROMATIC HYDROCARBONS (0.01g/30mls) IN THE PRESENCE OF SULPHIDES (2mls/30mls), IN AN ACETONITRILE-DEUTERIUM OXIDE (5:1 v/v) SOLVENT MIXTURE, UNDER DEGASSED CONDITIONS extremely inefficient quenching of anthracene fluorescence by the sulphide.

3.2.3 Conclusions

The addition of diethyl sulphide as an electron donor accelerates, in an analagous manner to tertiary amines, the dehalogenation of aryl halides. Solvent effects and deuterium incorporation studies are consistent with a mechanism involving an electron transfer process.

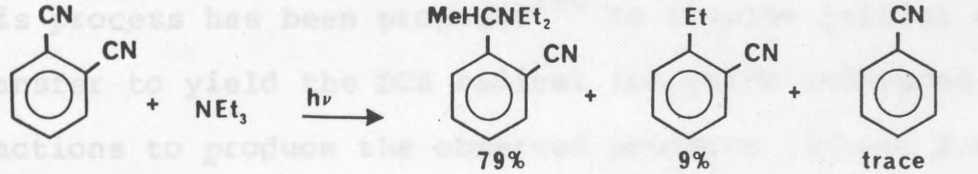
A range of sulphides were found to undergo electron transfer reactions with polycyclic aromatic hydrocarbons. The involvement of radical ions provided an explanation for the observed deuterium incorporation into the aromatic hydrocarbons, which was found to increase with reaction time.

3.3 Sulphide enhanced photo-reductive decyanation of aromatic hydrocarbons

3.3.1 Introduction

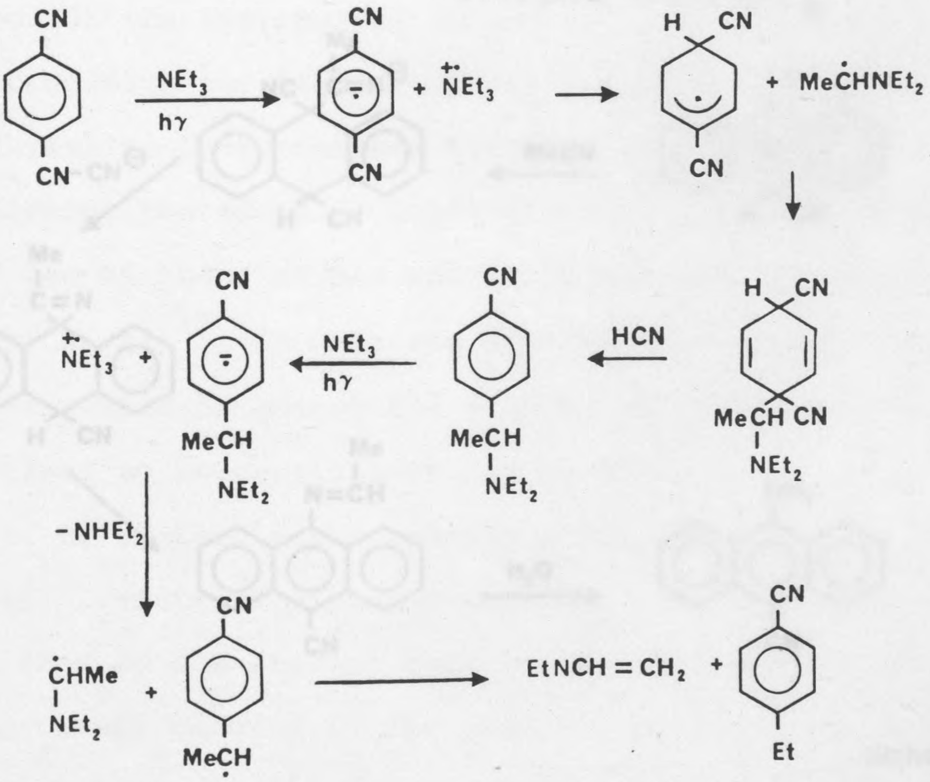
As cyano-aromatic hydrocarbons, e.g. 9,10-dicyanoanthracene are known to undergo electron transfer reactions with organic sulphides[2,3] the possibility arises that decyanations of these compounds could take place in the presence of sulphides. Amines, which tend to be more efficient electron donors than their sulphide counterparts are even more likely to be capable of causing decyanation reactions.

There have been several reports of electron transfer reactions between amines and cyano-aromatic hydrocarbons[16a-c]. 1,2 and 1,4-dicyanobenzenes were found to react with primary, secondary and tertiary aliphatic amines to give substitution products in which one of the cyano groups is replaced by the amine at the α-CH position or by an alkyl group of the amine and a trace of benzonitrile[16a,c] (Equation 3.4). These reactions



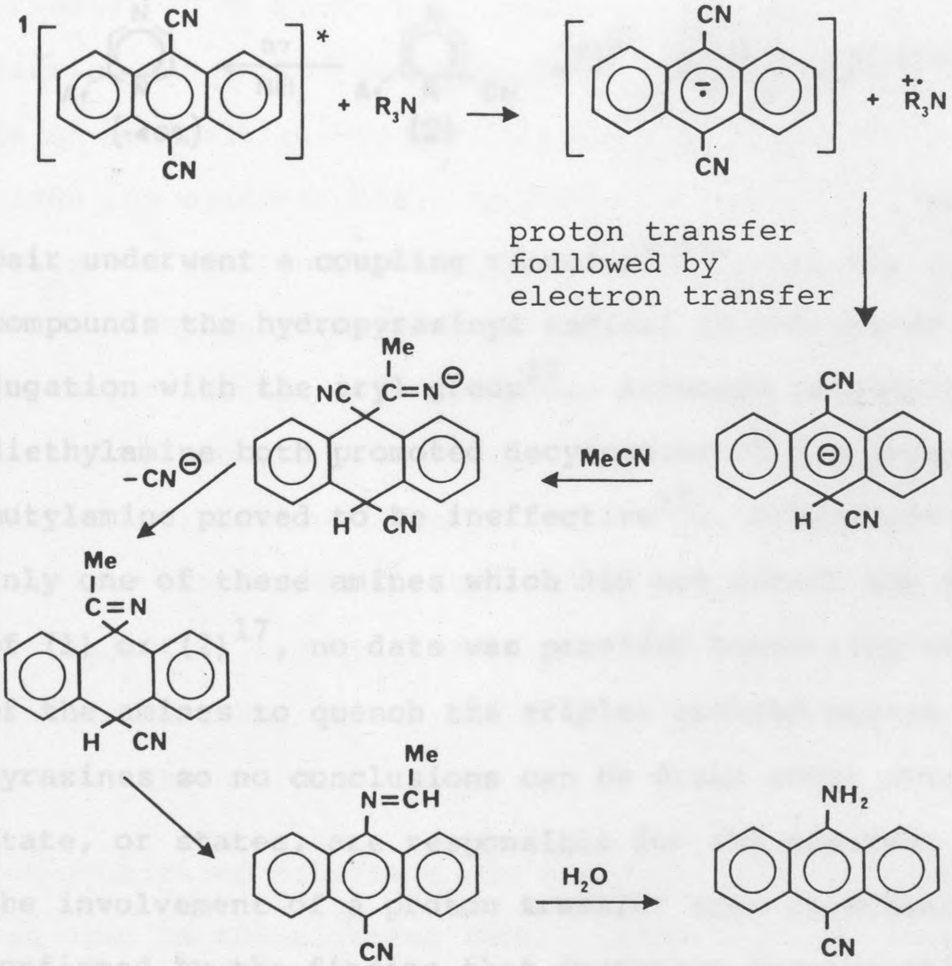
(3.4)

are believed to involve initial exciplex formation followed by proton transfer to yield radicals which can then undergo further reactions as illustrated for ρ-dicyanobenzene in Scheme 3.7. In deuterated methanol (MeOD) deuterium incor-



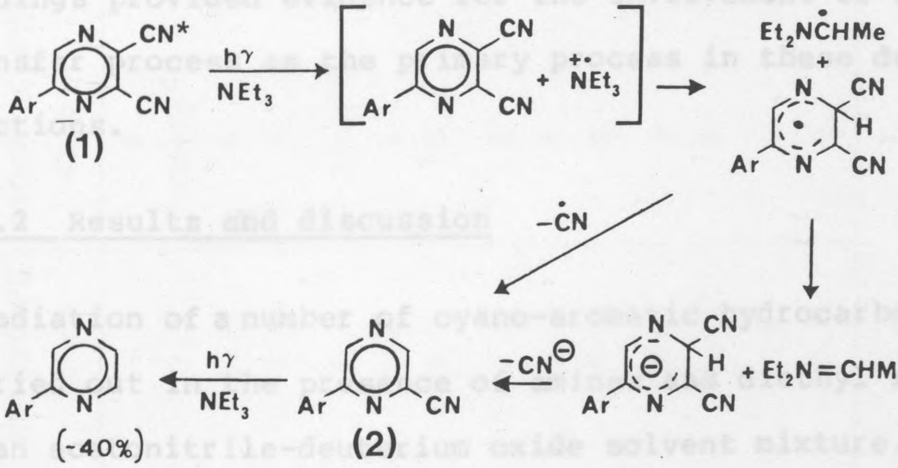
Scheme 3.7

poration into the products was reported to take place[16c]. When acetonitrile was used as solvent the photolysis of 9,10-dicyanoanthracene (DCA) in the presence of aliphatic amines led to the production of 9-amino,10-cyanoanthracene[16b]. This process has been proposed[16b] to involve initial electron transfer to yield the DCA radical ion which undergoes further reactions to produce the observed products (Scheme 3.8).



Scheme 3.8

More recently the reductive decyanation of 4'-(5,6-dicyano-2-pyrazinyl)benzo-15-crown-5 and 5,6-dicyano-2-(3,4-dimethoxyphenyl)-pyrazines has been reported[17] to take place upon irradiation of these compounds in the presence of secondary or tertiary amines. The following electron-transfer mechanism was proposed^{17} to account for the observed product formation (Scheme 3.9). In the case of dicyanobenzenes the radical pair underwent a coupling reaction^{16a-c}, but for the pyrazine compounds the hydropyrazinyl radical is stabilised by conjugation with the aryl group^{17}. Although triethylamine and diethylamine both promoted decyanation of the pyrazines butylamine proved to be ineffective^{17}. Butylamine was the only one of these amines which did not quench the fluorescence of (1) or (2)^{17}, no data was provided concerning the ability of the amines to quench the triplet excited states of the pyrazines so no conclusions can be drawn about which excited state, or states, are responsible for the observed reactions.



Scheme 3.9

The involvement of a proton transfer step in Scheme 3.8 was confirmed by the finding that deuterium incorporation into the products occured in the presence of deuterium oxide, but not when acetonitrile-d_3 was used as the solvent^{17}. In the absence of a protic solvent the proton must have been derived from the α-hydrogen of the amine while in the presence of a protic solvent, the proton was proposed^{17} to come from either the solvent or the amine. The variation in the quantum yields of photo-product and of fluorescence quenching were found to parallel changes in the reduction potential and energy of the singlet state of the pyrazine derivatives. These findings provided evidence for the involvement of an electron transfer process as the primary process in these decyanation reactions.

3.3.2 Results and discussion

Irradiation of a number of cyano-aromatic hydrocarbons was carried out in the presence of amines and diethyl sulphide in an acetonitrile-deuterium oxide solvent mixture. In all cases the cyano-aromatic hydrocarbons were consumed and deuterium incorporation into the substrate and photo-produced aromatic hydrocarbon was sometimes observed (Table 3.9). Deuterium incorporation provides evidence for the intermediacy of radical ions in these reactions. In contrast to the analagous reactions of aryl halides deuterium incorporation into the cyano-aromatic hydrocarbons was observed (Table 3.9). Consequently, radical ion formation must be a reversible process for many of the electron donor/cyano-aromatic hydrocarbon interactions.

Consumption of substrate was most marked when triethylamine was used as the electron donor. However, the yields of aromatic hydrocarbons in the presence of triethylamine were quite low. This may be a consequence of proton transfer from the amine radical cation to the radical anion of the cyano-aromatic hydrocarbon as illustrated for cyano-pyrazines in Scheme 3.8. The photolysis of 1-cyanonaphthalene was therefore carried out in the presence of DABCO which does not have

SUBSTRATE	ELECTRON DONOR	SUBSTRATE CONSUMED (%) 20hrs	YIELD[a] OF AROMATIC HYDROCARBON (%) 20hrs	(%) ONE DEUTERIUM INCORPORATION SUBSTRATE 20hrs	AROMATIC HYDROCARBON 4hrs	20hrs
1-Cyanonaphthalene	Et_2S	46.6	<4	0	*b*	*b*
"	NEt_3	>95	<4	43.5	(M+2)[c]	(M+3)[c]
"	DMP	14.3	<4	1.7	*b*	*b*
"	DABCO[d]	19.4	<4	0	*b*	*b*
4-Cyanobiphenyl	Et_2S	25.5	21.8	0	25.3	40.1
"	NEt_3	>95	14.2	(M+4)	*b*	51.8
"	DMP	12.1	4.7	0	0	1.7
9-Cyanoanthracene	Et_2S	70.1	<4	2	*b*	*b*
"	NEt_3	>95	<4	71	*b*	(M+4)[c]
"	DMP	89.2	10.3	0	*b*	84.6
9-Cyanophenanthrene	Et_2S	45.1	7.5	(M+4)[c]	*b*	16.4
"	NEt_3	>95	<4	(M+4)[c,e]	*b*	*b*
4-Cyanopyridine	Et_2S	38.8	<4	0.7	*b*	8.1
"	NEt_3	>95	<4	25.6	*b*	*b*

where DMP = N,N-dimethylpiperazine; DABCO = 1,4-diazobicyclo[2.2.2.]octane; *a* - based on amount of substrate present prior to irradiation; *b* - insufficient hydrocarbon to be detected; *c* - most intense peak; *d* - 0.28g/15mls and *e* - 4hrs irradiation.

TABLE 3.9 EXTENT OF CONSUMPTION OF SUBSTRATE AND DEUTERIUM INCORPORATION INTO THE SUBSTRATE AND PRODUCT AROMATIC HYDROCARBON UPON IRRADIATION OF CYANO-AROMATIC HYDROCARBONS (0.05g/15mls) IN THE PRESENCE OF ELECTRON DONORS (1ml/15mls) IN A CH_3CN/D_2O (5:1 v/v) SOLVENT MIXTURE any abstractable α-hydrogen atoms and the extent of consumption of the cyano-aromatic hydrocarbon was found to be considerably lower than when triethylamine was used as the electron donor. Consequently, it would appear that the 1-cyano-naphthalene radical anion abstracts a proton from triethylamine more readily than it abstracts a deuteron from the solvent. An additional pathway for the consumption of 9-cyanoanthracene is its dimerisation reaction which resulted in the precipitation of crystals (identified as 9-cyanoanthracene dimers by comparison with an authentic sample).

Although diethyl sulphide quenches both the singlet and triplet excited states of 1-cyanonaphthalene (Tables 3.1 and 3.2) no naphthalene product was detected and there was no deuterium incorporation into the 1-cyanonaphthalene (Table 3.3). As 1-cyanonaphthalene was consumed in this process back electron transfer of any radical ions must have been inefficient.

In some cases extensive deuteration of the substrate and product aromatic hydrocarbon was observed (Table 3.9). The mass spectral data in Table 3.10 illustrates the extent of deuterium incorporation for cases where more than one deuterium atom had been substituted for hydrogen atoms. Deuterium incorporation into the product aromatic hydrocarbons could either occur via the intermediate radical ions or by further reaction of the products with the electron donors. To determine whether the latter process was feasible anthracene was irradiated in the presence of triethylamine and N,N-dimethylpiperazine (DMP). The results obtained are shown in Table 3.11 and reveal that considerable incorporation of deuterium atoms into the anthracene molecule took place.

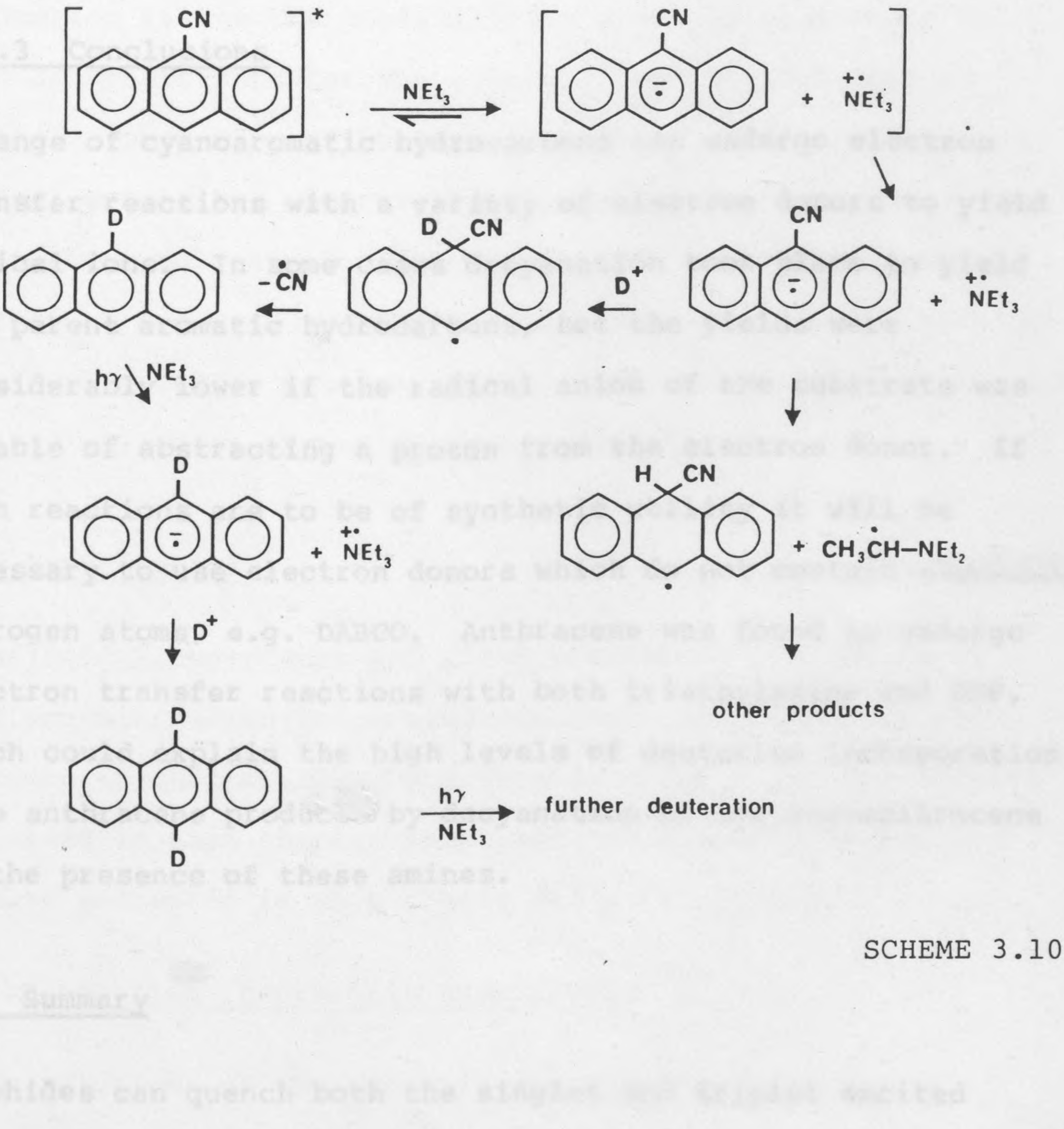
COMPOUND	MASS ION	M+1	M+2	M+3	M+4	M+5	M+6	M+7	M+8
	RELATIVE PEAK INTENSITY (%)								
4-Cyanobiphenyl	11.27	8.82	13.7	67.7	100	60.1	41	40.9	19.4
Biphenyl[a]	100	65	15.5	2.1	-	-	-	-	-
9-Cyanoanthracene	100	87.5	15.6	-	-	-	-	-	-
Anthracene[a]	18.7	33.6	53.1	83.5	100	60.4	30.8	7.1	-
1-Cyanonaphthalene	100	55.6	-	-	-	-	-	-	-
Naphthalene[a]	5.2	34.7	72.8	100	48.6	49.1	12.1	13.9	18.5
9-Cyanophenanthrene[b]	16.4	27.1	30	56.1	100	37.9	8.2	-	-

a - product aromatic hydrocarbon; *b* - 4hrs irradiation.

TABLE 3.10 DEUTERIUM INCORPORATION INTO THE SUBSTRATE AND HYDROCARBON PRODUCTS AS A RESULT OF THE PHOTOLYSIS OF CYANO-AROMATIC HYDROCARBONS (0.05g/15mls) IN THE PRESENCE OF TRIETHYLAMINE (1ml/15mls) IN A CH_3CN/D_2O (5:1 v/v) SOLVENT MIXTURE FOR 20hrs

ELECTRON DONOR	MASS ION	RELATIVE PEAK INTENSITY (%) M+1	M+2	M+3	M+4	M+5	M+6	M+7	M+8
NEt_3	14.3	34	63.3	85.2	100	90.1	44.8	14.2	3.1
DMP	11.7	21.5	49	100	81	63.4	24.5	8.2	1.8

TABLE 3.11 DEUTERIUM INCORPORATION INTO ANTHRACENE (0.01g/15mls) AS A RESULT OF PHOTOLYSIS IN THE PRESENCE OF TRIETHYLAMINE AND N,N-DIMETHYLPIPERAZINE (DMP) (both 1ml/15mls) IN A CH_3CN/D_2O (5:1 v/v) SOLVENT MIXTURE FOR 20hrs



SCHEME 3.10

Therefore, anthracene must be capable of undergoing electron transfer reactions with both triethylamine and DMP to yield anthracene radical cations.

Mechanisms, of the type outlined for 1-cyanonaphthane and triethylamine in Scheme 3.10, are consistent with the above results (Tables 3.9 to 3.11). Although amines[9] and sulphides have been shown to quench the singlet and triplet states of aromatic hydrocarbons and their chloro-derivatives and diethyl sulphide quenches the excited states of 1-cyanonaphthalene (Tables 3.1 to 3.5) no evidence has been obtained which enables the reactive state, or states, to be identified.

3.3.3 Conclusions

A range of cyanoaromatic hydrocarbons can undergo electron transfer reactions with a variety of electron donors to yield radical ions. In some cases decyanation took place to yield the parent aromatic hydrocarbons, but the yields were considerably lower if the radical anion of the substrate was capable of abstracting a proton from the electron donor. If such reactions are to be of synthetic utility it will be necessary to use electron donors which do not contain abstractable hydrogen atoms, e.g. DABCO. Anthracene was found to undergo electron transfer reactions with both triethylamine and DMP, which could explain the high levels of deuterium incorporation into anthracene produced by decyanation of 9-cyano-anthracene in the presence of these amines.

3.4 Summary

Sulphides can quench both the singlet and triplet excited states of aromatic hydrocarbons, their chloro- and their cyano-derivatives. The quenching is proposed to involve an electron transfer process. The use of sulphides to generate aromatic hydrocarbon radical cations from their excited states has been utilised in order to carry out reductive dehalogenation of aryl halides. The corresponding reactions of cyano-aromatic hydrocarbons in the presence of amines or diethyl sulphide led, in some cases, to novel decyanation reactions.

The finding that electron transfer reactions between aromatic hydrocarbons and sulphides can lead to enhanced triplet production raises the possibility that exciplexes could be used as sensitisers for the generation of singlet excited molecular oxygen in oxygenated solutions. As deuteration of radical anions was observed to take place it is necessary to use aprotic solvents for photo-oxidation reactions in which exciplexes are used as sensitisers, in order to minimise side reactions which do not lead to the production of either singlet excited molecular oxygen or superoxide anions.

3.5 Experimental

Details of fluorescence and flash photolysis procedures as well as information concerning equipment and chemicals are included in Chapter 11. Experimental details for the results contained in this chapter which are not common to other results presented in this thesis are outlined below.

(i) Laser flash photolysis experiments

Stock solutions of the aromatic hydrocarbon and their derivatives were made up to an optical density of 1.0, at the excitation wavelength (254 or 353nm) in acetonitrile or cyclohexane, and the appropriate amount of sulphide added. The solutions were then degassed by several freeze-pump-thaw-shake cycles. Details of the experimental procedure to determine triplet yields and lifetimes using these solutions are contained in Chapter 11.

(ii) Photolysis reactions

Solutions of the aromatic hydrocarbons in the appropriate solvents, in pyrex photolysis tubes, containing the appropriate electron donor, were flushed with argon (dry and carbon-dioxide-free) for 30 minutes and stoppered. The solutions were then irradiated within a circular array of twelve Sylvania G15T8 fluorescent lamps having a maximal output at 254nm. Samples were taken at t=0,4 and 20 hours and the loss of substrate determined by glc analysis using a 10% SE 30 column. When an acetonitrile-deuterium oxide solvent mixture was used the samples were also subjected to a GC/mass spectral analysis. Products were identified, using glc analysis, by comparison with authentic aromatic hydrocarbons, as well as by GC/mass spectral analysis. Any crystals deposited on the sides of the photolysis tubes were filtered, rinsed with the appropriate solvent and compared with identical samples of all possible dimers, which could be formed during the photolysis reaction, using IR spectroscopy.

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CHAPTER 4

SOLVENT ISOTOPE EFFECTS UPON INTRAMOLECULAR AND INTERMOLECULAR ELECTRON TRANSFER REACTIONS

CHAPTER 4

SOLVENT ISOTOPE EFFECTS UPON INTRAMOLECULAR AND INTERMOLECULAR ELECTRON TRANSFER REACTIONS

4.1 Solvent isotope effects upon the formation and decay of intramolecular α-naphthylalkylamine exciplexes

Compounds containing a naphthalene group and an aromatic or aliphatic amine moiety, as illustrated in Figure 4.1, are known to form intramolecular exciplexes upon irradiation of the naphthalene chromophore[1,2,3]. The abbreviations in Table 4.1 will be used throughout this chapter.

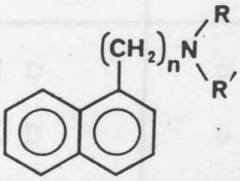


Figure 4.1

4.1.1 Introduction

Photo-induced electron transfer reactions between polycylic aromatic hydrocarbons and amines are known to give rise to fluorescent exciplex formation and triplet production in non-polar solvents[4]. In highly polar solvents the exciplexes can also decay to yield radical ions. Triplet formation can also occur by recombination of radical ions and via the non-relaxed exciplex[5a-d]. Apart from the fact that intramolecular exciplexes formed by α-naphthylalkylamines undergo radiative decay in both highly polar and non-polar solvents these exciplexes behave in a similar way to their intermolecular counterparts.

n	R = R′ = Et	R = Me, R′ = Ph
1	α 1 E	α 1 N
2	α 2 E	α 2 N
3	α 3 E	α 3 N
4	α 4 E	α 4 N

TABLE 4.1 ABBREVIATIONS USED TO DESCRIBE α-NAPHTHYLALKYLAMINES

Exciplex	Dipole Moment	Exciplex	Dipole Moment
α 2 E	16.8 D	α 2 N	14.6 D
α 3 E	15.1 D	α 3 N	17.1 D
α 4 E	15.6 D	α 4 N	15.6 D

TABLE 4.2 REPORTED[3] DIPOLE MOMENTS OF α-NAPHTHYLALKYLAMINE EXCIPLEXES

Chandross and co-workers[6] have established that the geometrical requirements for intramolecular excimer formation by compounds of the type Np-$(CH_2)_n$-Np (n = 1 to 4) are quite strict. The required "sandwich" configuration of the naphthyl groups is accommodated most easily when they are separated by three methylene units. The geometrical requirements for the formation of intramolecular exciplexes by α-naphthylalkylamines are much less demanding since angular interaction of orbitals are sufficient for complexation[1,3,7,8]. The geometrical requirements for fluorescence quenching of aromatic hydrocarbons are far less rigid than for emissive complex formation. The efficiency with which amines quench the fluorescence of aromatic hydrocarbons is strongly dependent upon the ionisation potential of the amine. The dipole moments obtained[3] for a range of α-naphthylalkylamine exciplexes (Table 4.2) reveal that the degree of charge-transfer character is considerable (the calculated dipole moment for complete electron transfer is 16.8 Debye units).

α-Naphthylalkylamines with short linking chains between the interacting groups are constrained from adopting a configuration in which the degree of overlap is sufficient for fluorescent exciplex formation. Consequently, when n = 1 other processes for the deactivation of the encounter complex effectively compete with equilibrium exciplex formation. As the naphthalene and amine groups cannot be separated by as much as 5Å when n = 1 the molecule is considered to exist totally in a charge-transfer state when excited. However, when n is small the proportion of the total number of conformations where the two groups are in an interacting position is significant, in contrast to the situation where n is large. Due to the poor overlap between the nitrogen lone pair and the naphthalene π cloud the exciplex fluorescence from diethyl and N-methylanilino α-naphthylalkylamines is very weak and the maximum wavelength of fluorescence emission is close to that of naphthalene (294nm) when n = 1. However, this is not always the case, e.g. ω-(1-naphthyl)-N-methyl pyrrole (in which n = 1) exhibits exciplex fluorescence which has a maximum emission at 490nm and 398nm in acetonitrile and cyclohexane respectively[9]. Formation of emissive exciplexes by α-naphthylalkylamines is most efficient when n = 2 for $R = R' = Et$ or $R = Me$, $R' = Ph$ and n = 3 for $R = R' = Me$[1]. Fluorescence quenching is less efficient when n = 3 compared to cases where n = 1 or 2. For α-naphthylalkylamines, where n = 2 or 3, N-methylanilino groups are more efficient quenchers of naphthalene fluorescence than diethylamine groups in cyclohexane, whereas in polar solvents there is a dramatic reduction in fluorescence quenching by the aliphatic relative to the aromatic amino groups. When n = 4 fluorescence quenching increases but complex formation is less efficient. The number of degrees of freedom and consequently the ease of attainment of quenching configurations increases, but the effective concentration of the quencher decreases, as n increases. The substantial decrease in the efficiency of complex formation when n = 4 may be attributed to eclipsing interactions, in the linking polymethylene chain, which disfavour the adoption of configurations suitable for complex formation. Yields of equilibrium exciplex formation are higher for aromatic amines in both polar and non-polar solvents, when n = 4, and the wavelength of maximum fluorescence emission is at higher energy than for aliphatic amines[3]. For α-naphthylalkylamines significant interactions between the amine group and the 'peri' hydrogen at C_8 restricts rotation about the naphthalene-carbon bond. The most likely configuration for exciplex formation involves overlap between the nitrogen lone pair and the naphthalene π orbitals as illustrated in Figure 4.2 for $\alpha 2N^3$.

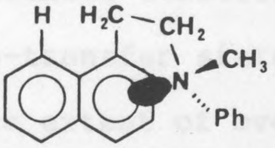


Figure 4.2

Although the quantum yield of fluorescence from α-naphthylalkylamine exciplexes decreases as the solvent polarity increases the effect is much less marked for these systems than for their intermolecular counterparts. This may be because the linking chain restricts the ability of the radical ions to diffuse apart so back electron-transfer is more efficient; in which case these compounds should exhibit delayed fluorescence. Although delayed fluorescence from α-naphthylalkylamines has not been detected, short-lived delayed fluorescence would be difficult to observe, so solvent effects upon back electron-transfer cannot be ruled out as a possible explanation for the decrease in exciplex fluorescence with increasing solvent polarity. Lifetimes of some intramolecular exciplexes increase in polar media as a consequence of decay from the encounter complex being much more important than radical ion formation from the relaxed exciplex[10]. It is therefore possible that in polar solvents decay from the encounter complex, formed between the donor and acceptor groups of α-naphthylalkylamines, reduces the quantum yield of relaxed exciplex formation and consequently the quantum yield of exciplex fluorescence, below that observed in non-polar solvents.

The stability of these intramolecular exciplexes is a function of the ionisation potential of the donor, the electron affinity of the acceptor, coulombic stabilisation, the heat of solvation of the charge-transfer state and the molecular geometry (which determines the extent of overlap). Quenching of aromatic hydrocarbon fluorescence by planar sp^2 hybridised amines, e.g. aromatic amines, is more efficient than quenching by sp^3 hybridised amines, e.g. saturated aliphatic amines. This is because energy must be expended in order for aliphatic amines to rehybridise to the sp^2 configuration required for intramolecular exciplex formation[5a]. Although the yields of exciplex emission from a range of α-naphthylalkylamines give an indication of the probability of exciplex formation by each compound they provide little information about the relative energies of the exciplexes. Wavelengths of maximum fluorescence emission do not correspond exactly to the difference between the ground and excited states (because they have different geometries and bond lengths) so fail to provide much useful information.

As the exciplexes formed by α-naphthylalkylamines have very high dipole moments the possibility arises that in protic solvents the exciplexes may undergo non-radiative decay by protonation. In order to evaluate this possibility the photophysical properties of a number of α-naphthylalkylamine exciplexes were determined in CH_3OH and CH_3OD. These solvents were chosen because the energetics of protonation and deuteration are different, whereas most other properties of the two solvents should be very similar.

4.1.2 Results and discussion

As intermolecular hydrocarbon-amine exciplexes do not fluoresce in polar solvents[4a] the broad emission bands observed upon irradiation of α-naphthylalkylamines in methanol solution must emanate from intramolecular exciplexes. The results in Table 4.3 reveal that a change from CH_3OH to CH_3OD as solvent causes an increase in the quantum yield and lifetime of exciplex fluorescence, a decrease in the quantum yield of naphthalene monomer fluorescence and an increase in the quantum yield of triplet production. The solvent isotope effects upon the photophysical properties of α3E and α4N in CD_3CN/CH_3CN were found to be negligible (Table 4.4). Consequently, the effects, on their photophysical properties, of a change from CH_3OH to CH_3OD as solvent must be due to the acidic proton of the alcohol. These results are illustrated in Figures 4.3A to 4.3D.

Protic solvents can affect exciplex formation by hydrogen bonding to the amine, thereby increasing the ionisation potential of the amine and causing an increase in the free energy of activation for the electron transfer process leading to exciplex formation[12]. As the energetics of deuterium bonding to amines will differ from hydrogen bonding a change of solvent from CH_3OH to CH_3OD should affect the efficiency of this intramolecular quenching process. The intramolecular fluorescence quenching is efficient enough to result in very

	$Np(CH_2)_nNEt_2$		$Np(CH_2)_nNMePh$		
	n=2	n=3	n=2	n=3	n=4
$\phi_{Np}^{CH_3OH}$	0.06	0.009	<0.001	0.007	0.006
$\phi_{Ex}^{CH_3OH}$	0.019	0.001	0.043	0.023	0.004
$\tau_{Ex}^{CH_3OH}$ (ns)	5.6	3.4	23.8	11.6	11.6
$\phi_T^{CH_3OH}$	0.13	0.07	0.11	0.11	0.12
$\phi_{Np}^{CH_3OD}$	0.029	0.003	<0.001	0.006	0.005
$\phi_{Ex}^{CH_3OD}$	0.025	0.003	0.056	0.039	0.006
$\tau_{Ex}^{CH_3OD}$ (ns)	8.3	4.6	32.1	22.8	19.5
$\phi_T^{CH_3OD}$	0.17	0.09	0.14	0.19	0.23
$\phi_{Np}^{CH_3OH}/\phi_{Np}^{CH_3OD}$	2.07	3.0	1	1.17	1.2
$\phi_{Ex}^{CH_3OD}/\phi_{Ex}^{CH_3OH}$	1.31	3.0	1.30	1.69	1.50
$\tau_{Ex}^{CH_3OD}/\tau_{Ex}^{CH_3OH}$	1.48	1.35	1.35	1.96	1.68
$\phi_T^{CH_3OD}/\phi_T^{CH_3OH}$	1.31	1.29	1.27	1.73	1.92

TABLE 4.3 QUANTUM YIELDS OF EXCIPLEX (ϕ_{Ex}) AND UNQUENCHED NAPHTHALENE (ϕ_{Np}) FLUORESCENCE, EXCIPLEX FLUORESCENCE LIFETIMES (τ_{Ex}) AND QUANTUM YIELDS OF TRIPLET FORMATION (ϕ_T) FOR SOME α-NAPHTHYLALKYLAMINES IN DEGASSED CH_3OH AND CH_3OD SOLUTION AT 20°C

	$Np(CH_2)_3NEt_2$	$Np(CH_2)_4$ NMePh
$\phi_{Np}^{CH_3CN}$	0.012	0.012
$\phi_{Ex}^{CH_3CN}$	0.015	0.010
$\tau_{Ex}^{CH_3CN}$ (ns)	13	29
$\phi_{Np}^{CD_3CN}$	0.011	0.011
$\phi_{Ex}^{CD_3CN}$	0.016	0.009
$\tau_{Ex}^{CD_3CN}$ (ns)	14	27
$\phi_{Np}^{CH_3CN}/\phi_{Np}^{CD_3CN}$	1.09	1.09
$\phi_{Ex}^{CD_3CN}/\phi_{Ex}^{CH_3CN}$	1.06	0.90
$\tau_{Ex}^{CD_3CN}/\tau_{Ex}^{CH_3CN}$	1.07	0.93

TABLE 4.4 SOLVENT ISOTOPE EFFECTS UPON THE QUANTUM YIELDS OF EXCIPLEX (ϕ_{Ex}) AND UNQUENCHED NAPHTHALENE (ϕ_{Np}) FLUORESCENCE AND THE EXCIPLEX FLUORESCENCE LIFETIMES, (τ_{Ex}) OF α-NAPHTHYLALKYLAMINES IN CH_3CN AND CD_3CN

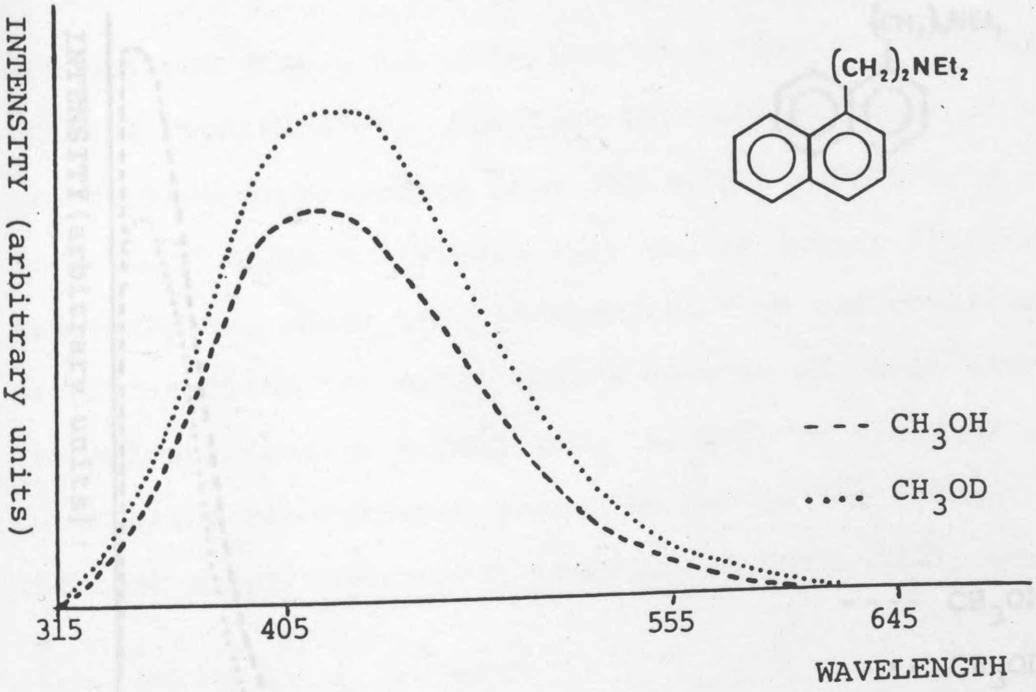


FIGURE 4.3(A) FLUORESCENCE SPECTRA OF α2E IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

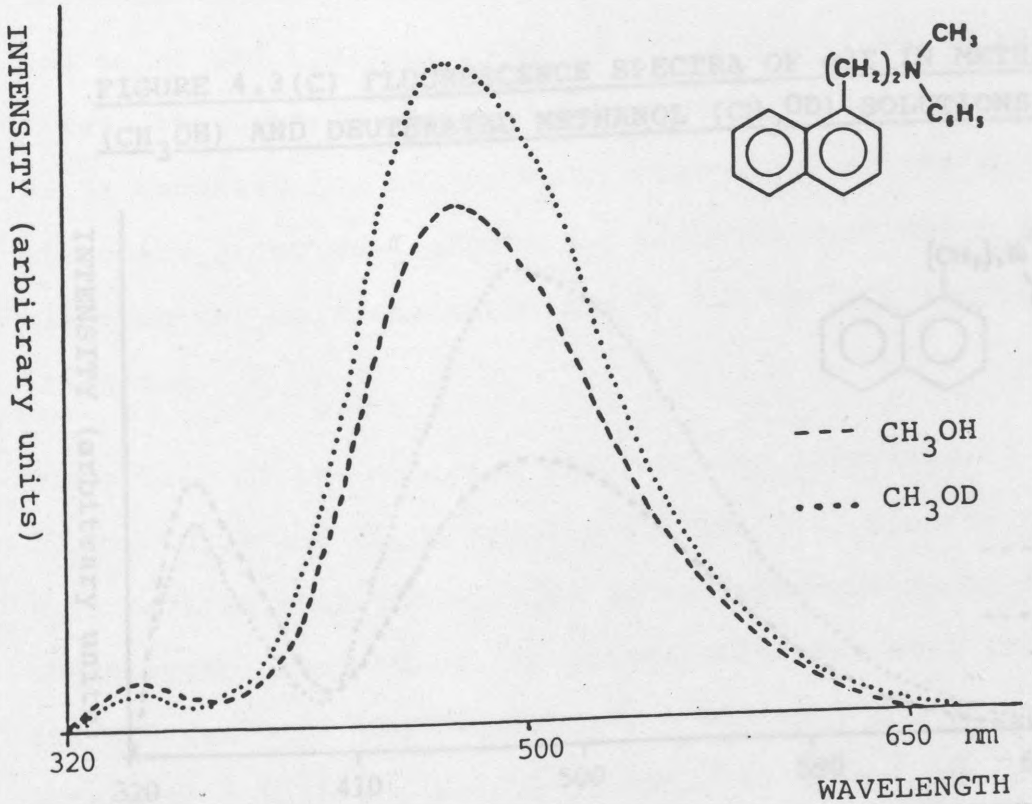


FIGURE 4.3(B) FLUORESCENCE SPECTRA OF α2N IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

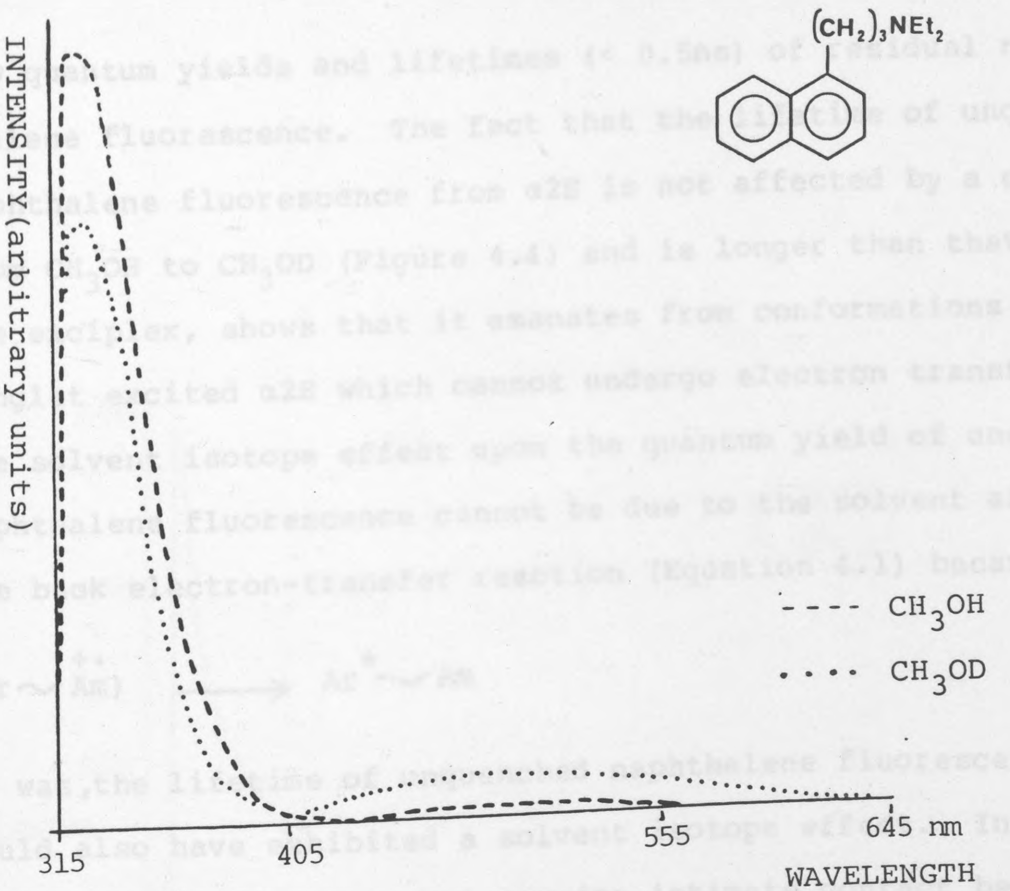


FIGURE 4.3(C) FLUORESCENCE SPECTRA OF α3E IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

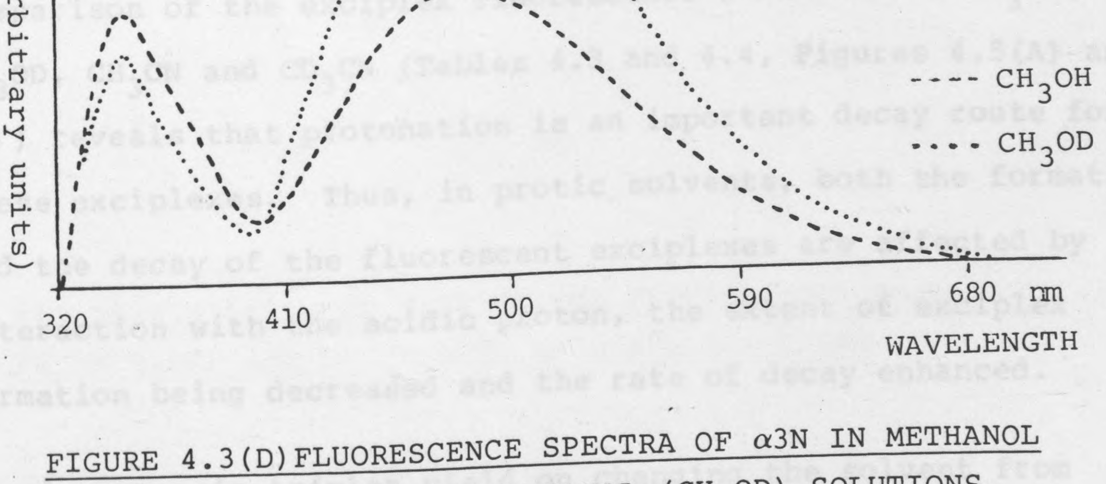


FIGURE 4.3(D) FLUORESCENCE SPECTRA OF α3N IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

low quantum yields and lifetimes (< 0.5ns) of residual naphthalene fluorescence. The fact that the lifetime of unquenched naphthalene fluorescence from α2E is not affected by a change from CH_3OH to CH_3OD (Figure 4.4) and is longer than that of the exciplex, shows that it emanates from conformations of the singlet excited α2E which cannot undergo electron transfer. The solvent isotope effect upon the quantum yield of unquenched naphthalene fluorescence cannot be due to the solvent affecting the back electron-transfer reaction (Equation 4.1) because if

$$(\overset{\overline{\bullet}}{Ar} \sim \overset{+\bullet}{Am}) \longrightarrow Ar^{*} \sim Am \qquad (4.1)$$

it was,the lifetime of unquenched naphthalene fluorescence would also have exhibited a solvent isotope effect. In polar solvents quenching does not require intimate contact between the amine and the aryl group so for a change of solvent to affect the quantum yield of fluorescent exciplex formation, as is observed for CH_3OD/CH_3OH, the nature of the bonding to the amine group must affect the distance over which the electron can be transferred and/or the conformational distribution.

Comparison of the exciplex fluorescence lifetimes in CH_3OH, CH_3OD, CH_3CN and CD_3CN (Tables 4.3 and 4.4, Figures 4.5(A) and (B)) reveals that protonation is an important decay route for these exciplexes. Thus, in protic solvents, both the formation and the decay of the fluorescent exciplexes are affected by interaction with the acidic proton, the extent of exciplex formation being decreased and the rate of decay enhanced.

The increase in triplet yield on changing the solvent from

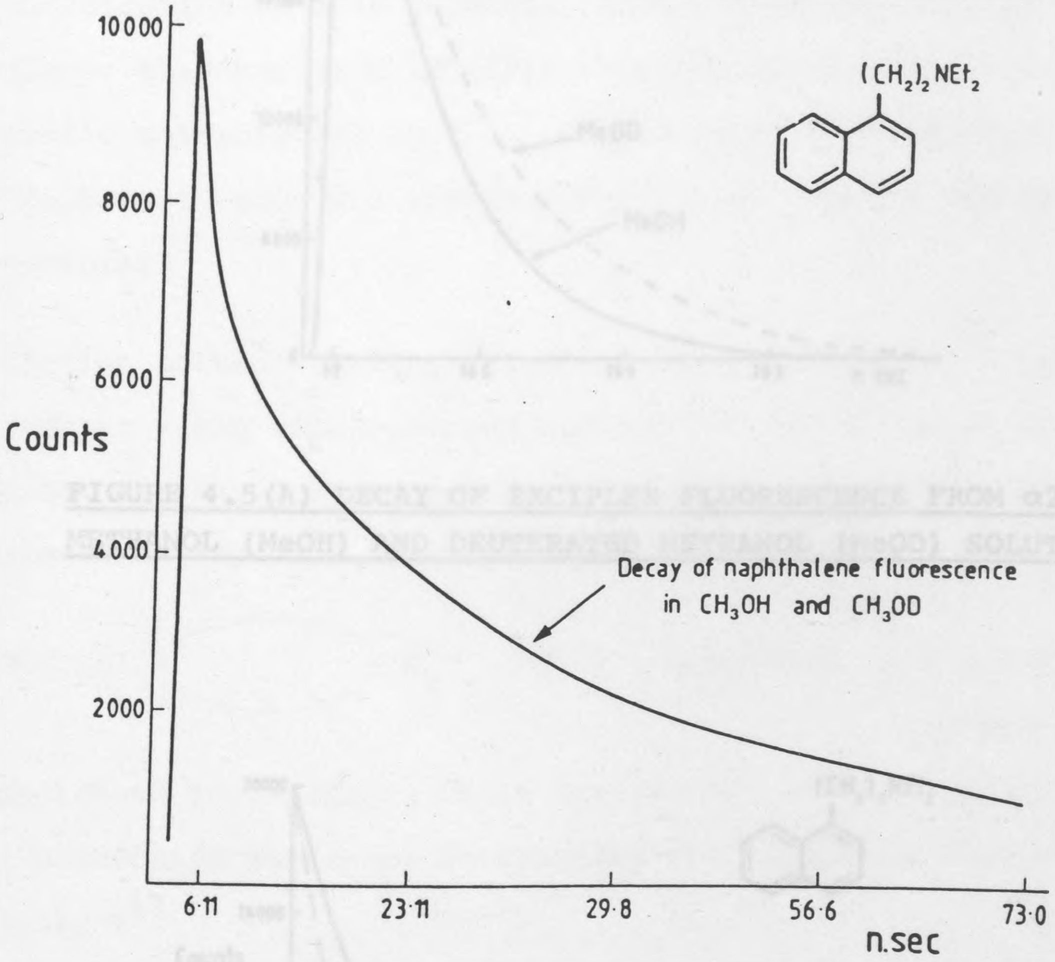


FIGURE 4.4 DECAY OF NAPHTHALENE FLUORESCENCE FROM 2E IN METHANOL AND DEUTERATED METHANOL SOLUTIONS

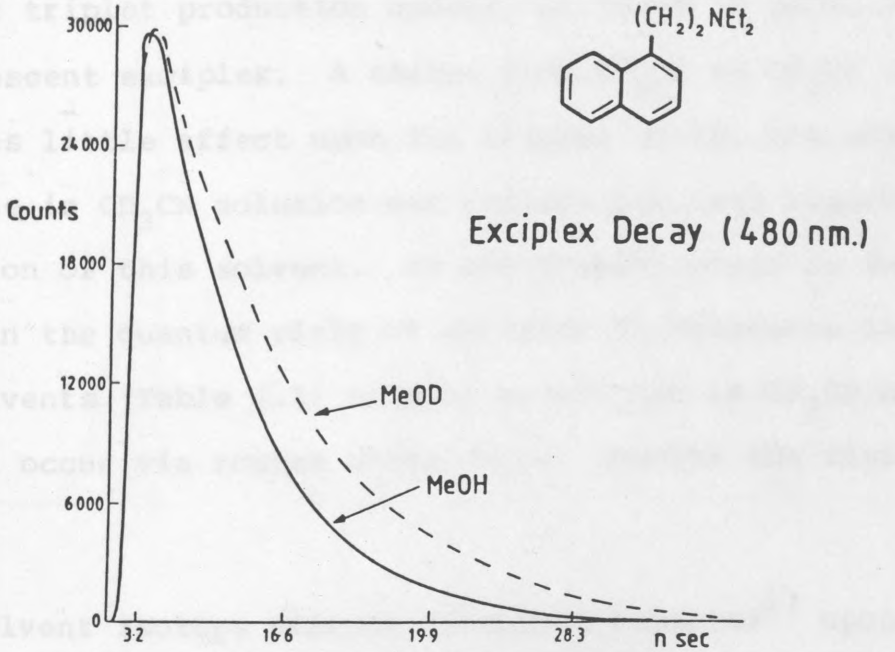


FIGURE 4.5(A) DECAY OF EXCIPLEX FLUORESCENCE FROM α2E IN METHANOL (MeOH) AND DEUTERATED METHANOL (MeOD) SOLUTIONS

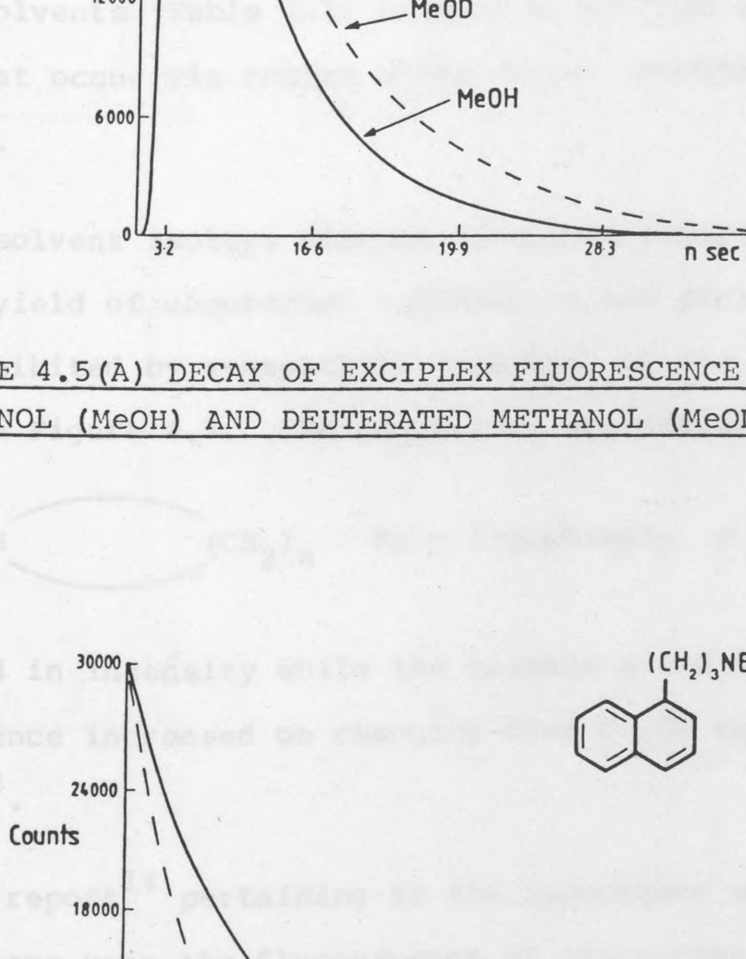
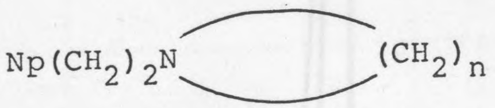


FIGURE 4.5(B) DECAY OF EXCIPLEX FLUORESCENCE FROM α3E IN METHANOL (MeOH) AND DEUTERATED METHANOL (MeOD) SOLUTIONS

methanol to deuterated methanol (Table 4.3 and Figure 4.6) shows that triplet production occurs, at least in part, via the fluorescent exciplex. A change from CH_3CN to CD_3CN as solvent has little affect upon the triplet yield, the slightly lower value in CD_3CN solution may reflect the less rigorous purification of this solvent. As the triplet yield is far higher than the quantum yield of exciplex fluorescence in protic solvents (Table 4.3) triplet production in CH_3OD and CH_3OH must occur via routes which do not involve the fluorescent exciplex.

Similar solvent isotope effects have been reported[13] upon the quantum yield of unquenched naphthalene and exciplex fluorescence exhibited by α-naphthylalkylamines of the type illustrated in Figure 4.7. The unquenched naphthalene fluorescence

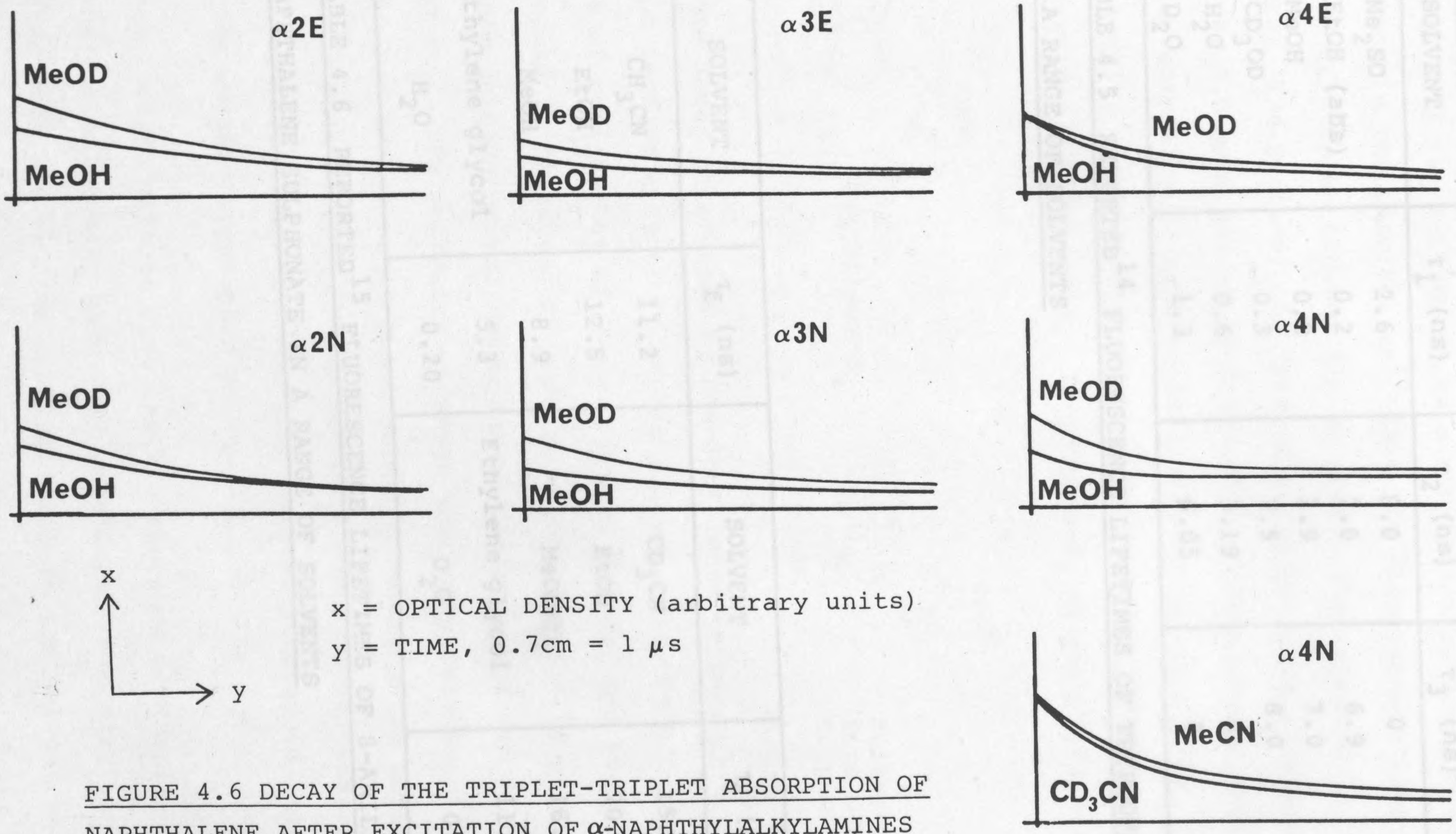


Np = 1-naphthyl; n = 4,5,6,8,12

Figure 4.7

decreased in intensity while the quantum yield of exciplex fluorescence increased on changing from CH_3OH to CH_3OD as solvent[13].

A recent report[14] pertaining to the importance of solvent interactions upon the fluorescence of tryptophan is also in agreement with the results presented in this chapter. The fluorescence lifetimes of the two shorter-lived components (Table 4.5) are considerably longer in dimethylsulphoxide (DMSO) than in protic solvents, and are longer when acidic hydrogen atoms are replaced by deuterium. The authors suggested that the zwitterionic form of tryptophan is the species



x = OPTICAL DENSITY (arbitrary units)
y = TIME, 0.7cm = 1 μs

FIGURE 4.6 DECAY OF THE TRIPLET-TRIPLET ABSORPTION OF NAPHTHALENE AFTER EXCITATION OF α-NAPHTHYLALKYLAMINES IN BOTH DEUTERATED AND NON-DEUTERATED SOLVENTS

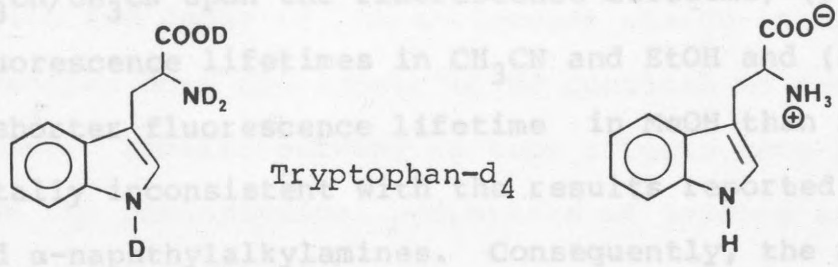
SOLVENT	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
Me_2SO	2.6	8.0	0
EtOH (abs)	0.2	2.0	6.9
MeOH	0.2	1.9	7.0
CD_3OD	0.3	2.5	8.0
H_2O	0.6	3.19	0
D_2O	1.3	6.05	0

TABLE 4.5 REPORTED[14] FLUORESCENCE LIFETIMES OF TRYPTOPHAN IN A RANGE OF SOLVENTS

SOLVENT	τ_f (ns)	SOLVENT	τ_f (ns)
CH_3CN	11.2	CD_3CN	15.3
EtOH	12.5	EtOD	20.6
MeOH	8.9	MeOD	16.5
Ethylene glycol	5.3	Ethylene glycol	11.1
H_2O	0.20	D_2O	0.5

TABLE 4.6 REPORTED[15] FLUORESCENCE LIFETIMES OF 8-ANILINO-1-NAPHTHALENE SULPHONATE IN A RANGE OF SOLVENTS

responsible for these emissions. On the basis of our results protonation of the zwitterion, as a non-radiative decay route could explain the observation[14] that the fluorescence lifetimes of tryptophan are shorter in protic than aprotic solvents. The zwitterionic form of tryptophan, as illustrated in Figure 4.8 must not be confused with intramolecular charge-transfer complexes, e.g. α-naphthylalkylamine exciplexes, in which singlet electron transfer has taken place between two groups within the molecule. Tryptophan-d_4 (Figure 4.8) has



Tryptophan-d_4

Zwitterionic form of tryptophan

Figure 4.8

the same decay parameters as non-deuterated tryptophan so the solvent isotope effects in protic solvents are not a consequence of replacement of N-H and O-H by N-D and O-D bonds when tryptophan is dissolved in a deuterated solvent. In protic solvents a longer-lived component of fluorescence was identified (τ_3), the intensity of which increased relative to the short-lived component in basic solution, whereas the addition of acetic acid (7×10^{-4}M) to methanol quenched it totally. This long-lived component was therefore attributed to emission from the excited tryptophan anion.

Solvent isotope effects upon the fluorescence of 8-anilino-1-naphthalene sulphonate have been attributed[15] to electron transfer from its excited singlet state to the solvent being coupled with intramolecular O-H or O-D vibrations of the solvent. In aprotic solvents, e.g. CH_3CN, the ejected electron is solvated by a polar CN group, whereas in protic solvents the electron can couple with the vibrational mode of the hydroxyl group. The importance of the hydroxyl group was confirmed by the finding that the fluorescence lifetime in methanol solution is not affected by replacement of C-H bonds by C-D whereas replacement of O-H bonds by O-D has a marked influence. Some of their results are shown in Table 4.6. The observations of (i) a solvent isotope effect in CD_3CN/CH_3CN upon the fluorescence lifetime, (ii) similar fluorescence lifetimes in CH_3CN and EtOH and (iii) a shorter fluorescence lifetime in MeOH than in EtOH, are totally inconsistent with the results reported for tryptophan and α-naphthylalkylamines. Consequently, the results in Table 4.6 cannot be explained on the basis of protonation (deuteration) being a non-radiative decay route for 8-anilino-1-naphthalene sulphonate.

In Chapter 7 results are presented which reveal that indoles have higher quantum yields of fluorescence and triplet production in MeOD than MeOH and a wide range of pyrazoline derivatives have higher quantum yields and longer lifetimes of fluorescence in MeOD compared with MeOH solution. All these compounds show considerable charge transfer character in their excited singlet states, so the results can be explained in the same way as solvent effects, in protic solvents, upon intramolecular exciplex formation by α-naphthylalkylamines.

4.1.3 Conclusions

For a range of α-naphthylalkylamines, a change of solvent from methanol (CH_3OH) to deuterated methanol (CH_3OD) leads to an increase in the quantum yield and lifetime of exciplex fluorescence, a decrease in the quantum yield of unquenched naphthalene fluorescence and an increase in the quantum yield of naphthalene triplets. The solvent effect is explained by the relative abilities of the two solvents to form hydrogen (deuterium) bonds to the amine groups and to protonate (deuterate) the fluorescent exciplex.

The ability of hydrogen bonding solvents to affect the formation and decay of intramolecular charge-transfer complex formation does not appear to be confined to α-naphthylalkylamines. Similar solvent isotope effects have been observed upon the photophysical properties of indoles and substituted pyrazoline compounds.

A method which is commonly employed for demonstrating the intermediacy of radical ions, involves carrying out the reaction in the presence of a deuterated protic solvent. If deuterium incorporation into the products is observed it is concluded that the intermediate radical anions have been deuterated by the solvent (see Chapter 3). On the basis of the above results the possibility arises that deuterium incorporation may be a consequence of deuteration of exciplex intermediates and/or radical ions. Therefore, it can only be concluded that radical ions are intermediates in reactions exhibiting deuterium incorporation into the products if fluorescent exciplexes either cannot be observed or have very short lifetimes.

Solvent isotope effects upon singlet oxygen mediated photo-oxidation reactions are interpreted on the assumption that the photophysical properties, e.g. the quantum yield of triplet production, of the sensitiser are unaffected by a change from a non-deuterated to a deuterated solvent (see Chapter 5, Section 3.4(ii)). In the light of the results presented in this chapter it would appear that such an assumption should not be made when using protic solvents if the sensitiser, in its ground or excited states, can undergo hydrogen (deuterium) bonding with, and/or be protonated (deuterated) by, the solvent.

4.2 Solvent isotope effects upon twisted intramolecular charge-transfer complexes

In Chapter 2,4-dimethylaminobenzonitrile was used as an example of a compound which forms a twisted intramolecular charge-transfer (TICT) complex upon excitation. The TICT excited state is a highly polar state in which the donor and acceptor moieties are mutually twisted by 90°. Lippert and co-workers[16] were the first to discover that fluorescent emission from 4-dimethylaminobenzonitrile occurs from two different excited states, one of which is highly polar. Various theories have been proposed in order to account for the experimental results including formation of excimers[17a], formation of exciplexes with polar solvent molecules[17b,c], proton transfer[17d] and high polarisability of the excited state[17e]. The model which is now gaining widespread support involves the amine group being twisted by 90° with respect to the plane of the aromatic ring[18a] and full electron transfer[18b] from the amine group to the aromatic ring (Figure 4.10). Many donor-

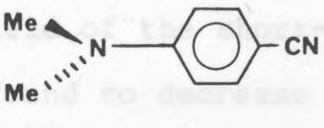


Figure 4.10

acceptor molecules exhibiting similar behaviour have since been identified[19a,b], some of which have been the subject of a recent review[19b]. Other molecules which have non-polar or weakly polar ground states emit from a state characterised by full intramolecular charge transfer even though they are not able to undergo rotation about the donor-acceptor bond, e.g. the compound illustrated in Figure 4.11. Minimum overlap

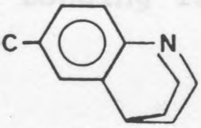


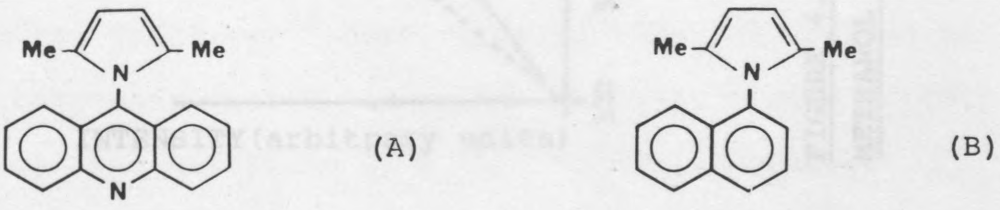
Figure 4.11

between the donor and acceptor molecular orbitals involved in the electron transfer appears to be a structural requirement for the formation of TICT and analagous intramolecular charge-transfer excited states. Consequently, TICT excited states may be considered as being intramolecular exciplexes with certain structural requirements which prevent them from acquiring a sandwich-type conformation. On the basis of the results in Section 4.1 TICT states, which show considerable charge-transfer character, would be expected to be affected by a change from a protic solvent to its deuterated analogue.

4.2.1 Results and discussion

The fluorescence spectrum of 4-dimethylaminobenzonitrile was recorded in methanol (CH_3OH) and deuterated methanol (CH_3OD) solutions. As observed for the α-naphthylalkylamines (Table 4.3) the quantum yield of the short-wavelength (λ_{max} 370nm) emission band was found to decrease on replacement of CH_3OH by CH_3OD as solvent whereas the long-wavelength component (λ_{max} 465nm) increased in intensity. The solvent isotope effects upon the short-wavelength emission and the emission believed to emanate from a TICT state were 0.6 and 1.23 respectively (Figure 4.12). These results can be explained on the basis of hydrogen bonding to the amine moiety, by the solvent, resulting in an increase in the ionisation potential of the amine. Consequently, charge-transfer from the amine to the aromatic ring will be disfavoured in CH_3OH relative to CH_3OD because hydrogen bonding is more efficient than deuterium bonding.

In order to ascertain the effect of steric hindrance of the nitrogen atom on the ability with which it can undergo hydrogen bonding, with the solvent, similar studies are to be carried out on compounds such as compound (A) in Figure 4.13 which is currently being synthesised. Compounds of the type illustrated in Figure 4.13 (B) are known[9] to exhibit TICT complex formation so the effects of protic solvents upon their fluorescence quantum yields and lifetimes are also of interest.



(A)

(B)

Figure 4.13

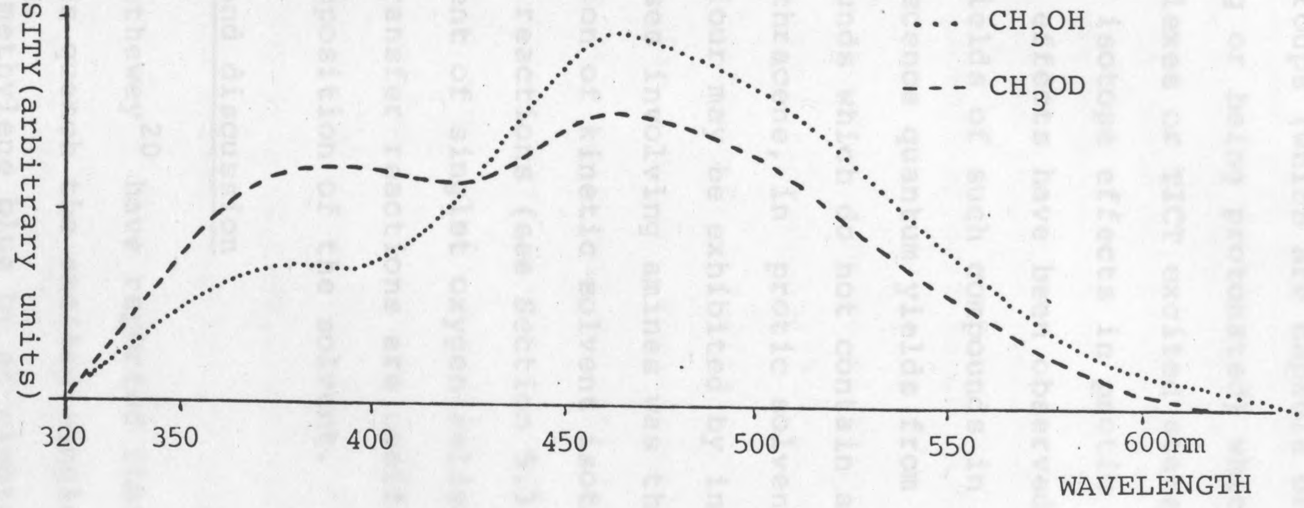


FIGURE 4.12 FLUORESCENCE SPECTRA OF 4-DIMETHYLAMINOBENZONITRILE IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

4.3 Solvent isotope effects upon intermolecular electron transfer reactions

Intramolecular electron transfer reactions of compounds which contain amine groups (which are capable of taking part in hydrogen bonding or being protonated) which lead to the formation of exciplexes or TICT excited states have been shown to exhibit solvent isotope effects in protic solvents. No solvent isotope effects have been observed upon the fluorescence quantum yields of such compounds in aprotic solvents or upon the fluorescence quantum yields from the excited singlet states of compounds which do not contain amine groups, e.g. 9,10-dimethylanthracene, in protic solvents. The possibility that such behaviour may be exhibited by intermolecular electron transfer processes involving amines was therefore investigated. The interpretation of kinetic solvent isotope effects upon photo-oxidation reactions (see Section 5.3.4(ii)) as evidence of the involvement of singlet oxygen relies on the assumption that electron transfer reactions are unaffected by changes in the isotopic composition of the solvent.

4.3.1 Results and discussion

Davidson and Trethewey[20] have reported that many amines and related compounds quench the excited singlet states of both rose bengal and methylene blue by an electron transfer mechanism. The solvent isotope effects upon the quantum yields of fluorescence of methylene blue in MeOH/MeOD and D_2O/H_2O were found to be negligible (<1.1).[21] Consequently, any observed solvent isotope effects upon the quenching of methylene blue fluorescence by electron transfer processes must be due to solvent isotope effects on these reactions because the fluorescence of methylene blue is independent of the isotopic composition of the solvent. The results in Table 4.7 reveal that negligible solvent isotope effects were observed upon the quenching of methylene blue by three of the reported quenchers of methylene blue fluorescence. These results are consistent with the finding by Foote and co-workers[22] that the methylene blue sensitised photo-oxidation of t-stilbene, which is believed to involve an electron transfer mechanism, does not exhibit kinetic solvent isotope effects in CD_3CN/CH_3CN.

As sulphides are known to undergo electron transfer reactions with cyano-aromatic hydrocarbons[23a,b] the quenching of 1-cyanonaphthalene fluorescence by 1,3-dithiane is expected to involve an electron transfer process. Consequently, it was of interest to determine whether there were solvent isotope effects upon this quenching process when protic solvents were used. It was found that the addition of 1,3-dithiane, at a concentration of 10^{-2}M, caused a 55% decrease in the quantum yield of 1-cyanonaphthalene fluorescence in CH_3CN/D_2O (5:1 v/v) solution and of 53% in a CH_3CN/H_2O (5:1 v/v) solvent mixture. The solvent isotope effect upon the fluorescence quenching in MeOD/MeOH was also found to be negligible (i.e. 1.00).

On the basis of these preliminary results it can be seen that solvent isotope effects upon intermolecular electron transfer reactions, which involve groups capable of hydrogen bonding to the solvent, are not necessarily substantial. In order to determine whether such solvent isotope effects are generally negligible it will be necessary to investigate a wider range

QUENCHER	SOLVENT	K_{SV} (M^{-1})	SOLVENT ISOTOPE EFFECT
Sodium azide	MeOH/H_2O (1:4 v/v)	4.24	1.02
" "	MeOH/D_2O (1:4 v/v)	4.34	
3-Methylindole	MeOH	21.2	1.04
"	MeOD	22.1	
1,3-dimethylindole	MeOH	2.21	1.02
"	MeOD	2.26	

TABLE 4.7 STERN VOLMER QUENCHING CONSTANTS (K_{SV}), IN DEGASSED SOLUTION, FOR THE INTERACTION OF A RANGE OF COMPOUNDS WITH SINGLET EXCITED METHYLENE BLUE

of electron transfer reactions. The isotopic composition of protic solvents will be most likely to have an affect upon electron transfer reactions in which the electron donor readily undergoes hydrogen bonding to the solvent. The longer the lifetime of the intermediate excited complex the greater will be the probability that it can undergo protonation (or deuteration) by the solvent. By careful choice of reactants it should be possible to favour conditions under which hydrogen bonding and protonation can occur. If these reactions exhibit negligible solvent isotope effects it may be concluded that, in general, a change from a protic solvent to its deuterated analogue does not affect electron transfer reactions.

4.4 Summary

Solvent isotope effects have been observed, in protic solvents, upon the formation and decay of intramolecular exciplexes, TICT states and other singlet excited states which exhibit charge-transfer character. All the compounds studied contained groups which could undergo hydrogen bonding with the solvent, and no solvent isotope effects upon the photophysical properties of their excited states were observed in aprotic solvents. Consequently, the results may be explained on the basis of (i) hydrogen bonding to the electron donating group increasing its ionisation potential and disfavouring electron transfer to the acceptor group, and (ii) protonation of the excited species being a non-radiative decay route which is more efficient than deuteration.

No evidence was obtained to suggest that intermolecular electron transfer reactions are affected as a result of the replacement of solvent O-H bonds by O-D bonds. There is insufficient data to determine whether such reactions are, in general, insensitive to the isotopic composition of protic solvents.

The finding that the isotopic composition of protic solvents can affect the photophysical properties of excited states is of particular importance for the interpretation of observed solvent isotope effects upon photo-oxidation reactions. Such solvent isotope effects are used to provide evidence for or against the involvement of singlet oxygen on the assumption that the isotopic composition of the solvent, which affects the lifetime of singlet oxygen (see Chapter 5, Table 5.2), does not affect any other photophysical parameters. In the light of the results presented in this chapter it is clear that such an assumption should not be extended to the photophysical properties of sensitisers (of singlet oxygen) which can undergo hydrogen bonding with the solvent.

Details of the experimental procedures used to obtain the results presented in this chapter are included in Chapter 11.

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PHOTO-OXIDATION REACTIONS

CHAPTER 5

INTRODUCTION TO PHOTO-OXIDATION PROCESSES

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5.1 Introduction

The two most common mechanisms for photo-oxidation reactions are classified as Type I and Type II processes. Oxidation processes in which oxygen scavenges photochemically generated radical intermediates are classified as Type I reactions. In Type II reactions singlet excited molecular oxygen (singlet oxygen) is the oxidizing species. A third mechanism for photo-oxidation reactions involves the use of so-called oxygen transfer reagents.

Since the early 196O's a great deal of attention has been paid to photo-oxidation reactions so consequently there are many excellent reviews[la-m] on this topic. The following sections give an outline of each mechanism, its application and scope and deals with methods of determining which mechanisms are operative in a particular photo-oxidation reaction.

5.2 Type I photo-oxidations

Type I reactions involve the scavenging of radicals by oxygen to yield products as outlined in Scheme 5.1. There are a variety of photochemical methods for the production of radicals which include homolytic bond cleavage, hydrogen abstraction by a molecule in its excited triplet state and reactions of radical ions such as proton transfer. Radical ion formation

$$^{3}\mathrm{Sens}^{*} + \mathrm{RH} \xrightarrow[\text{abstraction}]{\text{hydrogen}} \dot{\mathrm{S}}\mathrm{ensH} + \dot{\mathrm{R}}$$

$$\mathrm{Sens}^{-\cdot} + \mathrm{RH}^{+\cdot} \xrightarrow[\text{transfer}]{\text{proton}} \dot{\mathrm{S}}\mathrm{ensH} + \dot{\mathrm{R}}$$

$$\mathrm{R}\text{---}\mathrm{X} \xrightarrow{h\nu} \dot{\mathrm{R}} + \dot{\mathrm{X}}$$

$$\dot{\mathrm{R}} + {}^{3}\mathrm{O}_2 \longrightarrow \mathrm{R}\dot{\mathrm{O}}_2 \xrightarrow{\dot{\mathrm{H}}} \mathrm{RO_2H}$$

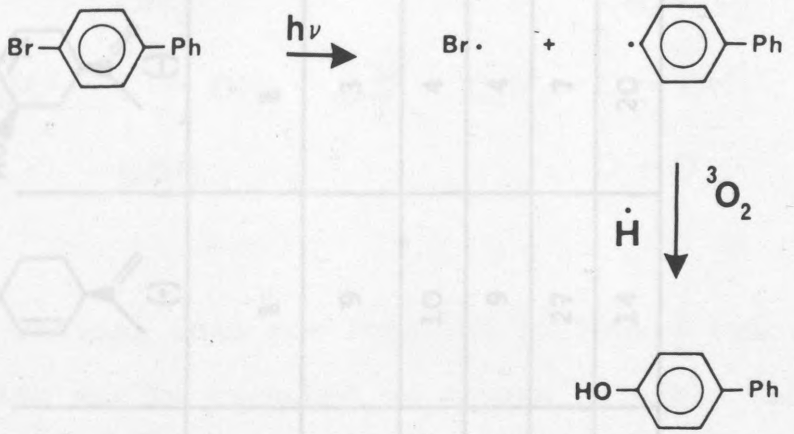
$$\mathrm{HR'}\text{---}\dot{\mathrm{R}} + {}^{3}\mathrm{O}_2 \longrightarrow \mathrm{R'}\!=\!\mathrm{R} + \mathrm{H}\dot{\mathrm{O}}_2$$

Scheme 5.1

as a result of the decay of excited charge-transfer complexes has been dealt with in Chapter 2.

The interaction of oxygen with alkyl radicals may either produce oxidation products via $\mathrm{R}\dot{\mathrm{O}}_2$ or result in the abstraction of a hydrogen atom to produce a double bond and $\mathrm{H}\dot{\mathrm{O}}_2$. The latter can then participate in the oxidation and may disproportionate to form hydrogen peroxide. Once initiated these reactions can become very complex due to the many possible pathways for reaction which are open to the radicals. Evidence for a Type I process can be obtained by trapping of the radical intermediates, esr spectroscopy and from CIDNP studies. Product studies may also prove useful especially if the starting material is optically active because racemic products are indicative of free radical as opposed to Type II photo-oxidations. The concentration of oxygen will determine the efficiency with which oxygen scavenges the various radicals present in the system, whereas Type II reactions are insensitive to changes in oxygen concentration above a certain minimum concentration[2a-c].

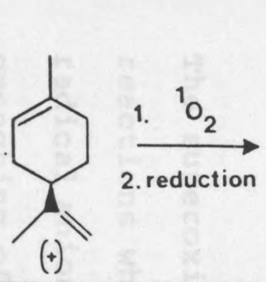
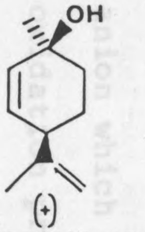
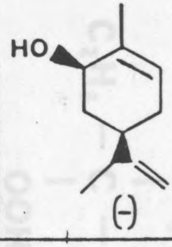
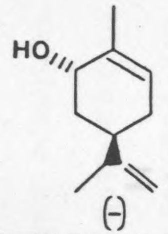
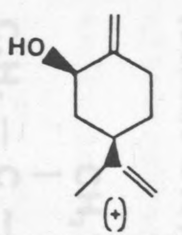
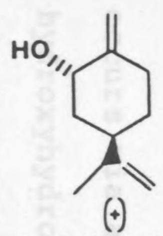
Type I reactions are responsible for many autoxidation processes, e.g. of alkenes, where a solution of the substrate is irradiated directly. Another direct photo-oxidation reaction involving the Type I process is the production of phenols from halogenated biphenyls in the presence of oxygen and a hydrogen donor[3] as outlined in Scheme 5.2.



Scheme 5.2

Many examples of sensitised Type I reactions involve aromatic ketones, e.g. benzophenone, as sensitisers as a consequence of the ability of their triplet excited states to abstract a hydrogen atom and/or undergo electron transfer reactions (Section 5.2.1). The benzophenone sensitised photo-oxidation of (+)-limonene[4a] gives rise to products consistent with the involvement of both singlet oxygen and radical intermediates (Table 5.1), because benzophenone has a sufficiently high triplet energy (68.5 k cal mol^{-1}) to sensitise the production of singlet oxygen and to abstract a hydrogen atom from the alkene.

The benzophenone sensitised photo-oxidation of alcohols[5]

							
SENSITISER	E_T (kcal mol^{-1})	%	%	%	%	%	%
Microwave discharge of $^3O_2$ ^{b}		41	9	3	7	22	18
Methylene Blue ^{c}	34.0	36	10	4	9	21	19
Pyrene^c	48.7	36	9	4	9	20	22
Benzophenone^c	68.5	27	27	7	18	8	13
None^d		16	14	20	26	0	0

a - reference 4b,c

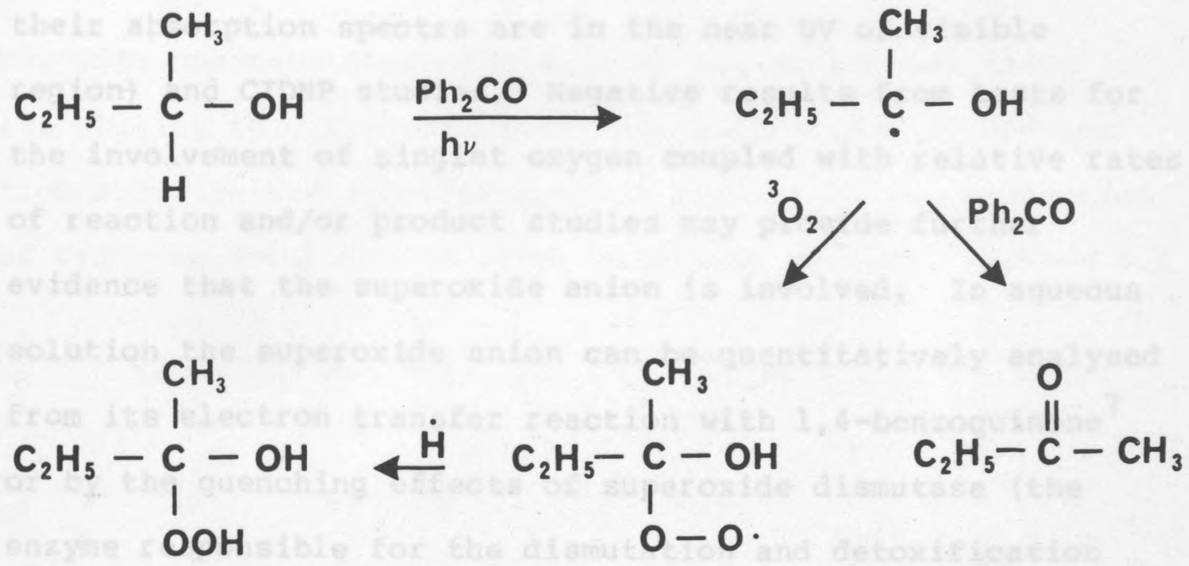
b - reference 4d, MeOH, -50°C

c - reference 4a, MeOH, 20°C

d - reference 4c, MeOH

TABLE 5.1

PRODUCT^a DISTRIBUTIONS FROM THE DIRECT AND SENSITISED PHOTO-OXIDATION (FOLLOWED BY REDUCTION) OF (+)-LIMONENE occurs via a radical mechanism to yield ketones and/or hydroxyhydroperoxides depending on the reaction conditions (Scheme 5.3).



Scheme 5.3

If radical ions are involved in Type I reactions the radical anion may be quenched by oxygen to yield the superoxide anion which can then react with the radical cation to form oxidation products.

5.2.1 Reactions involving the superoxide anion ($O_2^{\cdot-}$)

The superoxide anion may be produced in those photochemical reactions which produce radical ions, by reaction of the radical anions with oxygen or as a result of electron transfer quenching of singlet oxygen. The most convenient chemical method for generating the superoxide anion in protic or aprotic solvents involves the solubilisation of KO_2 by crown ethers[6a]. Electrochemical reduction of oxygen[6b] to generate the superoxide anion in situ has proved useful in studying its reactivity towards various substrates.

Evidence for the presence of the superoxide anion and other radical ions can be obtained from esr spectroscopy, by electrochemical techniques and from flash photolysis (if their absorption spectra are in the near UV or visible region) and CIDNP studies. Negative results from tests for the involvement of singlet oxygen coupled with relative rates of reaction and/or product studies may provide further evidence that the superoxide anion is involved. In aqueous solution the superoxide anion can be quantitatively analysed from its electron transfer reaction with 1,4-benzoquinone[7] or by the quenching effects of superoxide dismutase (the enzyme responsible for the dismutation and detoxification of superoxide anions <u>in vivo</u>). Khan[8a] has proposed that dismutation of the superoxide anion yields singlet oxygen, but Foote and co-workers[8b] undertook a quantitative investigation which revealed that <0.2% of singlet oxygen is produced in the dismutation reaction (Equation 5.1).

$$O_2^{\overset{\bullet}{-}} + O_2^{\overset{\bullet}{-}} + 2H^+ \xrightarrow[\text{dismutase}]{\text{superoxide}} {}^1O_2 + H_2O_2 \qquad (5.1)$$

Careful investigations[9a,b] indicate that there is no quenching activity of superoxide dismutase towards singlet oxygen, contrary to earlier claims[10] where the observed quenching may have been caused by inhibition of superoxide anion rather than by quenching of singlet oxygen.

The range of reactions[1ℓ,m] which the superoxide ion can undergo reflects its ability to behave as a nucleophile[11a,b] and as a strong Brønsted base. The superoxide anion is not a reactive electron transfer oxidant of organic substrates unless the resulting radical anion is stabilised[1ℓ], e.g. by coordination to a metal.

$$O_2^{\overset{-}{\cdot}} + A \longrightarrow \dot{A}\text{–O–O}^{-} + O_2 \qquad (5.2)$$

The most dominant characteristic of the superoxide anion is its ability to disproportionate, via abstraction of protons from solvents and substrates, which results in the production of hydrogen peroxide and other oxidizing species. Scheme 5.4

$$H^{+} + O_2^{\overset{-}{\cdot}} \xrightarrow{a} H\dot{O}_2 \qquad pKa = 4.69^{12}$$

$$O_2^{\overset{-}{\cdot}} + H\dot{O}_2 \xrightarrow{b} O_2 + HO_2^{-}$$

$$2H\dot{O}_2 \xrightarrow{c} O_2 + H_2O_2$$

$$H_2O_2 + O_2^{\overset{-}{\cdot}} \xrightarrow{d} H\dot{O} + OH^{-} + O_2$$

Scheme 5.4

illustrates the principal processes involved. In aqueous solution the conjugate acid ($H\dot{O}_2$) of the superoxide anion will always be formed. Some substrates, e.g. linoleic acid[13] (LH) are oxidized far more readily by perhydroxyl radicals ($H\dot{O}_2$) than by the superoxide anion. The chain initiating reaction involves the formation of a linoleate radical and hydrogen peroxide (Equation 5.3).

$$LH + H\dot{O}_2 \longrightarrow \dot{L} + H_2O_2 \qquad (5.3)$$

In aprotic solvents oxidation of strongly or weakly acidic organic substrates may occur, via initial proton abstraction from the substrate by the superoxide anion, to yield the substrate anion, $H\dot{O}_2$, oxygen and ultimately oxidation products. Basic reducing substrates with readily transferable hydrogen atoms[14], e.g. hydrazines and hydroxylamines, are also oxidized by the superoxide anion as illustrated for N-methylhydrophenazine (Equation 5.4).

$$\dot{M}eNPhenH + O_2^{\bar{\cdot}} \longrightarrow MeNPhen^{\cdot} + HO_2^{\cdot} \qquad (5.4)$$

The superoxide anion can also behave as a strong nucleophile in aprotic solvents, e.g. it oxidizes primary alkyl halides[15] to dialkyl peroxides via an S_N2 mechanism (Scheme 5.5).

$$RX + O_2^{\bar{\cdot}} \longrightarrow RO_2^{\cdot} + X^-$$

$$RO_2^{\cdot} + O_2^{\bar{\cdot}} \longrightarrow RO_2^- + O_2$$

$$RO_2^- + RX \longrightarrow ROOR + X^-$$

Scheme 5.5

(i) <u>Oxygen quenching of radical anions</u>

Davidson and co-workers[16] found that flash photolysis of oxygen-free acetonitrile solutions of tri-p-tolylamine containing benzophenone yielded the amine radical cation and the ketone radical anion, but in the presence of oxygen only the amine radical cation could be detected. These results were explained by a mechanism (Scheme 5.6) involving the formation of the superoxide anion.

$$\begin{tikzcd}
Ph_2CO \arrow[r, "h\nu"] & {}^1Ph_2CO^* \arrow[r, "ISC"] & {}^3Ph_2CO^* \arrow[d, "Ar_3N"] \\
Ph_2CO + O_2^{\bar{\cdot}} & & Ph_2\dot{C}\bar{O} + Ar_3\overset{+\cdot}{N} \arrow[ll, "{}^3O_2"']
\end{tikzcd}$$

Scheme 5.6

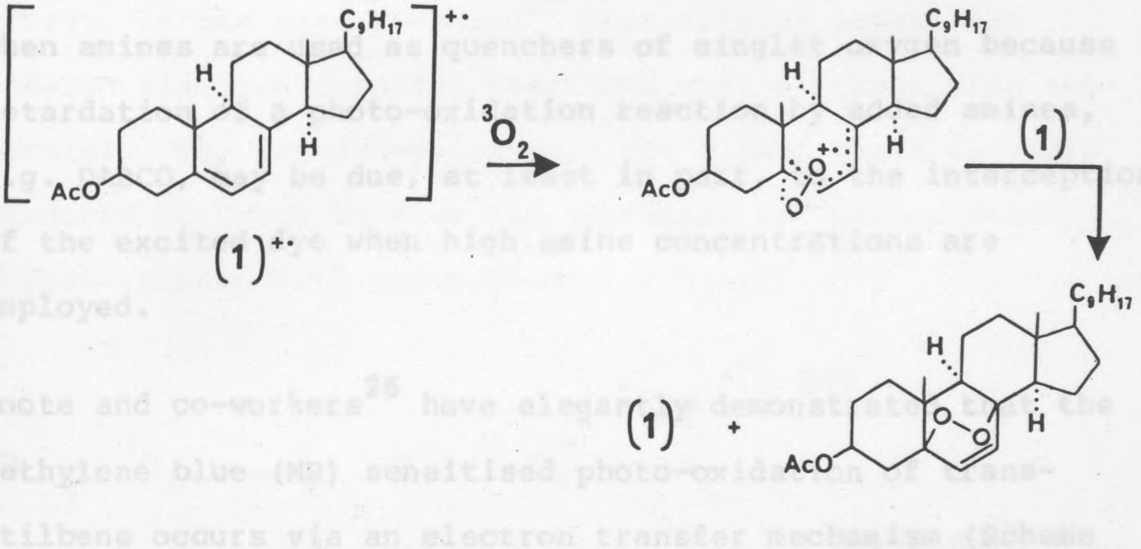
Subsequently, a similar electron transfer process has been proposed by Foote and co-workers[17] in order to account for the 9,10-dicyanoanthracene (DCA) sensitised photo-oxidation of electron rich substrates such as alkenes and sulphides. trans-Stilbene (TS) is an example of a substrate which is unreactive towards singlet oxygen but readily undergoes photo-oxidation in the presence of DCA, light and oxygen[2c] (Scheme 5.7).

$$\begin{tikzcd} \mathrm{DCA} \arrow[r, "h\nu"] & {}^{1}\mathrm{DCA}^{*} \arrow[r, "\mathrm{TS}"] & \mathrm{DCA}^{\bar{\cdot}} + \mathrm{TS}^{+\cdot} \arrow[d, "{}^{3}O_{2}"] \\ & 2\ \mathrm{PhCHO} & \mathrm{TS}^{+\cdot} + O_{2}^{\bar{\cdot}} + \mathrm{DCA} \arrow[l] \end{tikzcd}$$

Scheme 5.7

Recently Foote and co-workers[18] have demonstrated that DCA can sensitise the production of singlet oxygen so it must not be assumed that DCA sensitised reactions occur entirely by non-singlet oxygen mechanisms. In the case of the DCA sensitised photo-oxidation of diphenyl sulphide and diethyl sulphide the former reacts three times as fast as the latter[17] even though diphenyl sulphide is ~2800 times less reactive towards singlet oxygen. However, distinguishing between the two mechanisms is not usually so easy because the ultimate products from electron transfer photo-oxidation, e.g. of vinyl sulphides[19], are often similar to those obtained using singlet oxygen as the oxidizing species. In the DCA sensitised photo-oxidation of 1,4-dimethylnaphthalene[20] the products obtained are consistent with the involvement of both the superoxide anion and singlet oxygen.

Oxygen may react directly with the radical cation to initiate a chain reaction (Scheme 5.8) via the Barton mechanism[21a,b]. This is the process which enables ergosterol acetate to be



Scheme 5.8

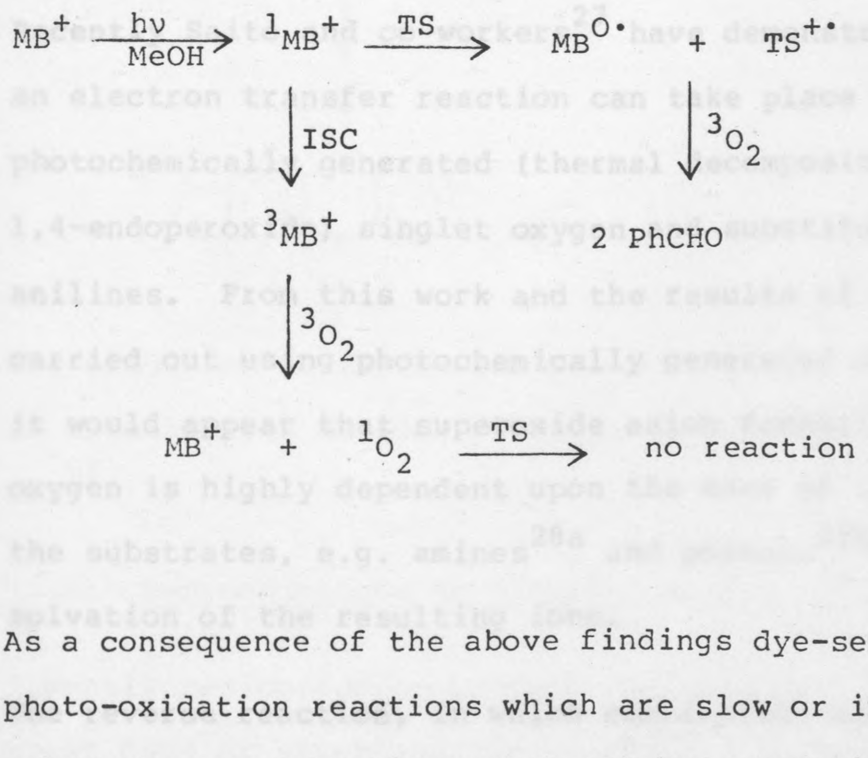
converted into its peroxide by ground state oxygen (a process forbidden by a spin barrier) in the presence of Lewis acids.

The extent to which the presence of oxygen reduces the lifetime of the radical cation[22a] indicates the relative importance of such a mechamism which will obviously be more important in oxygen saturated than in aerated solutions. The Barton mechanism has been ruled out as the major pathway in the DCA sensitised photo-oxidations of several alkenes[22ab].

Dye-sensitised photo-oxidation reactions which are generally regarded as singlet oxygen mediated reactions[23] can also involve electron transfer processes. Srinivasan and co-workers[24] have reported that dyes, e.g. rose bengal, can produce superoxide anions as well as singlet oxygen; in buffered methanol solution the ratio obtained for rose bengal was 23:77.

Davidson and Trethewey[25a-c] found that both aromatic and aliphatic amines can undergo electron transfer reactions with the singlet and triplet excited states of rose bengal and methylene blue. This is an important point to be remembered when amines are used as quenchers of singlet oxygen because retardation of a photo-oxidation reaction by added amines, e.g. DABCO, may be due, at least in part, to the interception of the excited dye when high amine concentrations are employed.

Foote and co-workers[26] have elegantly demonstrated that the methylene blue (MB) sensitised photo-oxidation of trans-stilbene occurs via an electron transfer mechanism (Scheme 5.9) and not via a singlet oxygen mechanism as was previously supposed.

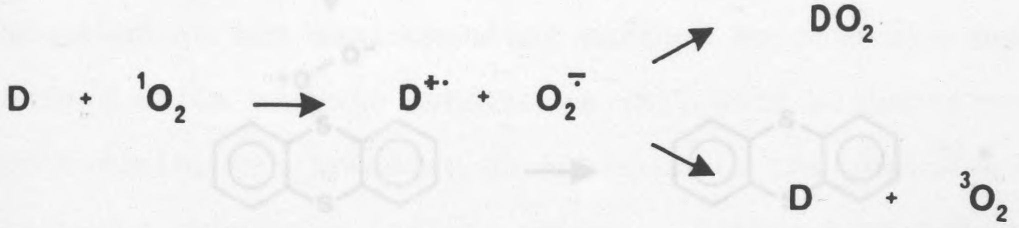


Scheme 5.9

As a consequence of the above findings dye-sensitised photo-oxidation reactions which are slow or involve high substrate concentrations must not be automatically interpreted as being singlet oxygen mediated reactions.

(ii) Electron transfer reactions of singlet oxygen

Since singlet oxygen should have an $E_{\frac{1}{2}}$ 1 V higher than ground state oxygen ($E_{\frac{1}{2}}$ = -0.57V), as a consequence of its excitation energy, it has been proposed[2c] that singlet oxygen can undergo electron transfer reactions with electron rich substrates. The resulting ion-pair can either react to yield products or decay to give the substrate and ground state oxygen (Scheme 5.10 and Section 5.3.5(ii)).



Scheme 5.10

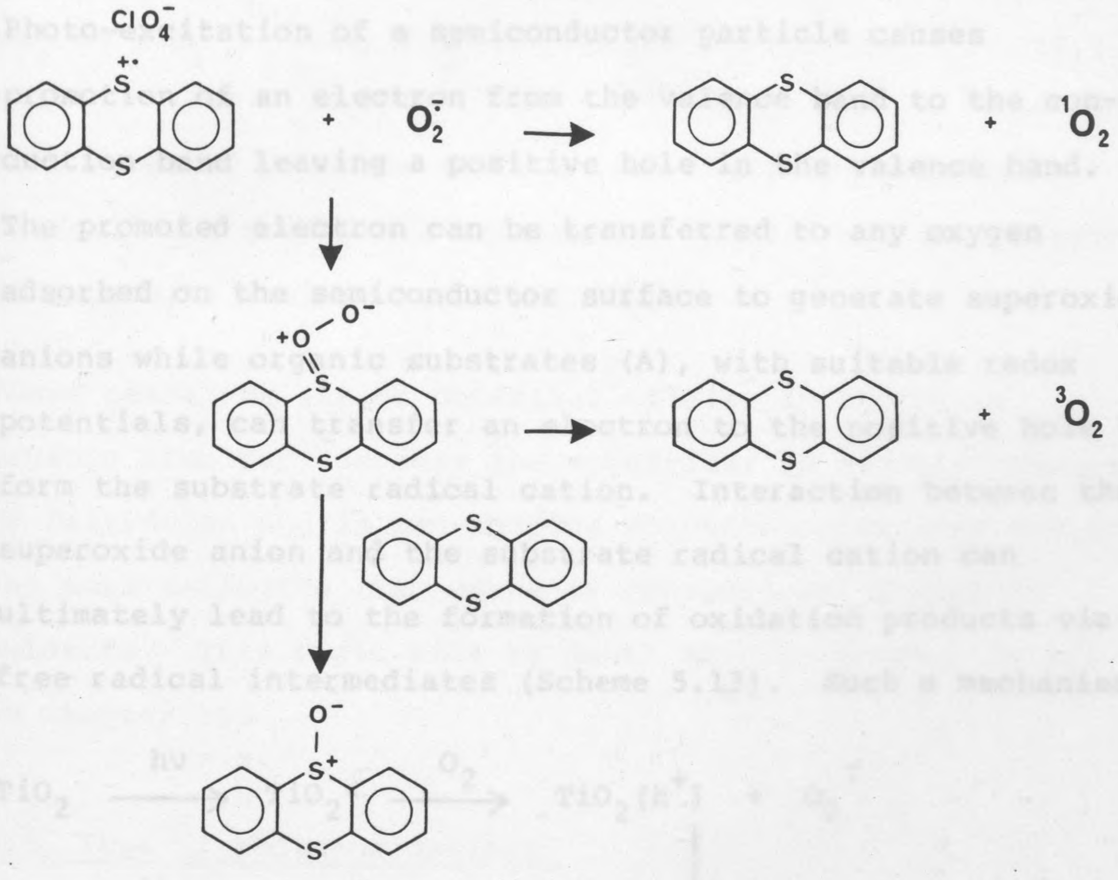
Recently Saito and co-workers[27] have demonstrated that such an electron transfer reaction can take place between non-photochemically generated (thermal decomposition of a 1,4-endoperoxide) singlet oxygen and substituted N,N-dimethylanilines. From this work and the results of experiments[28a-c] carried out using photochemically generated singlet oxygen it would appear that superoxide anion formation from singlet oxygen is highly dependent upon the ease of ionisation of the substrates, e.g. amines[28a] and phenols[28b,c], and the solvation of the resulting ions.

The reverse reaction, in which combination of radical ions produces singlet oxygen or oxidation products (Scheme 5.11), has been proposed by Ando and co-workers[29] as one of the processes resulting from the reaction of the radical cation

$$D^{+\bullet} + O_2^{-\bullet} \longrightarrow (D - O_2)^* \longrightarrow D + {}^1O_2$$

Scheme 5.11

of thianthrene with superoxide anion. The singlet oxygen was identified spectroscopically and indirectly from the results of trapping experiments (Scheme 5.12).



Scheme 5.12

The oxidation of superoxide anion to singlet oxygen requires an oxidant with a redox potential of at least +0.34V vs NHE[1ℓ].

(iii) Semiconductors as sensitisers for the superoxide anion

Recently semiconductor powders and colloids have received a great deal of attention due to their ability to catalyse photo-induced electron transfer oxidation reactions. The semiconductors which have received most attention are titanium dioxide (TiO_2, anatase), zinc oxide (ZnO) and cadmium sulphide (CdS). The mechanistic details of semiconductor catalysed oxidations are the subject of much controversy. However, there is considerable evidence that singlet oxygen is not the oxidising species in these reactions[30a,b].

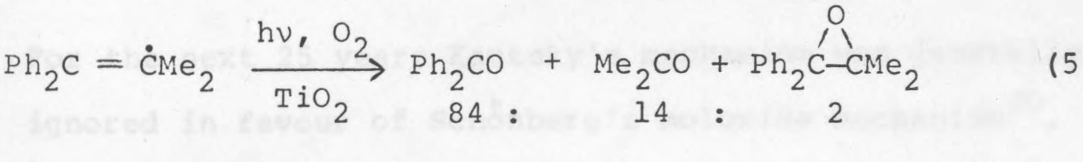
Photo-excitation of a semiconductor particle causes promotion of an electron from the valence band to the conduction band leaving a positive hole in the valence band. The promoted electron can be transferred to any oxygen adsorbed on the semiconductor surface to generate superoxide anions while organic substrates (A), with suitable redox potentials, can transfer an electron to the positive hole to form the substrate radical cation. Interaction between the superoxide anion and the substrate radical cation can ultimately lead to the formation of oxidation products via free radical intermediates (Scheme 5.13). Such a mechanism

$$\begin{tikzcd}
TiO_2 \arrow[r, "h\nu"] & TiO_2^* \arrow[r, "O_2"] & TiO_2(h^+) + O_2^{\bar{\cdot}} \arrow[d, "A"] \\
 & \text{products} & A^{+\cdot} + TiO_2 \arrow[l, "O_2^{\bar{\cdot}}"']
\end{tikzcd}$$

Scheme 5.13

would account for many of the reported oxidations using platinised and metal-free semiconductors. In aqueous solution $H\dot{O}$ radicals are considered to be the major oxidant[31] and their generation has been proposed to involve the Haber-Weiss reaction (Scheme 5.4 path d).

Irradiation of a semiconductor in the presence of alkenes[30a,b,32,33] results in the formation of epoxides, carbonyl compounds, alcohols and in some cases oxidative cleavage to yield ketones also takes place, as in the example below (Equation 5.5). Similarly carboxylic acids undergo decarboxylation, primary and aliphatic amines are oxidized



$$\mathrm{Ph_2C{=}CMe_2} \xrightarrow[\mathrm{TiO_2}]{h\nu,\ \mathrm{O_2}} \underset{84\ :}{\mathrm{Ph_2CO}} + \underset{14\ :}{\mathrm{Me_2CO}} + \underset{2}{\mathrm{Ph_2C\overset{O}{\frown}CMe_2}} \qquad (5.5)$$

to a range of products derived from the aminium radical cation[34] and amides are oxidized to imides[35] in the presence of oxygen, a semiconductor and light.

These reactions are of potential utility in synthetic organic chemistry because the sensitiser is readily removed by filtration and in non-aqueous solution oxidations can be far more selective than ozone or conventional inorganic oxidants. This topic will be dealt with in greater detail in Chapter 10.

5.3 Type II photo-oxidations

Type II photo-oxidations involve the strongly oxidizing species singlet oxygen as the reactive intermediate.

5.3.1 Introduction

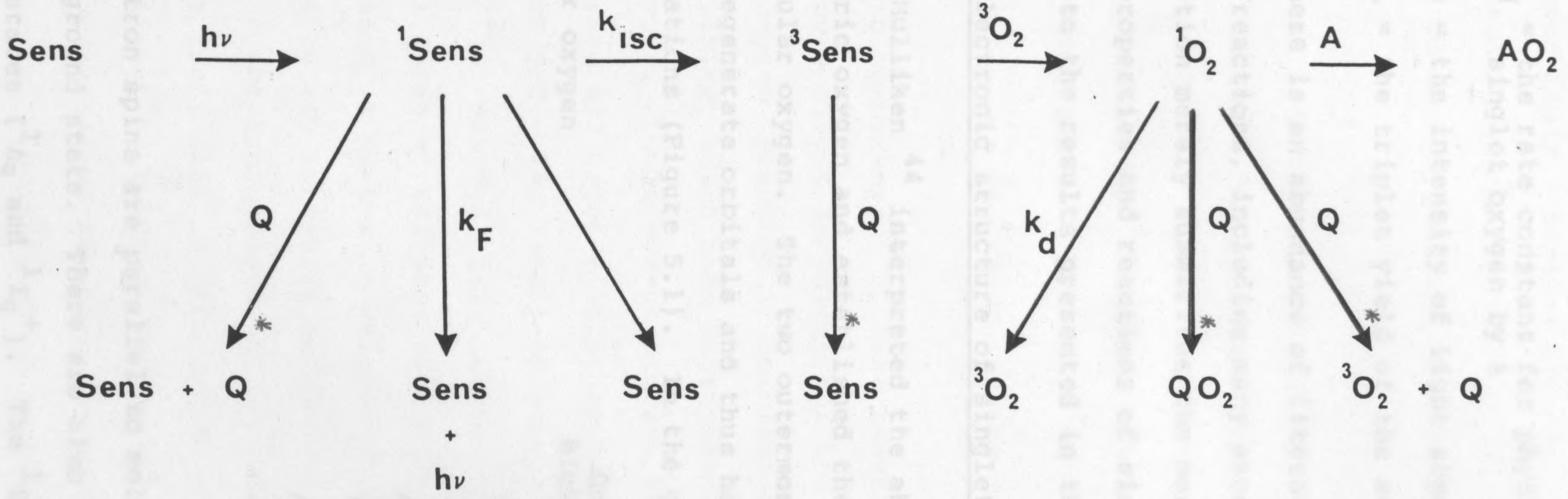
Kautsky and de Bruijn[36] were the first to propose that an excited singlet state of molecular oxygen was the active intermediate in oxidations performed in the presence of a dye, light and oxygen. Spectroscopic studies[37] and the finding that dyes with insufficient triplet energies to sensitise the formation of the $^1\Sigma_g^+$ state of oxygen could be used to sensitise photo-oxidation reactions[38] implicated the first excited singlet state ($^1\Delta_g$) of molecular oxygen (singlet oxygen) in these reactions. Consequently, Kautsky[39] revised his original mechanism, involving the $^1\Sigma_g^+$ state of oxygen, to include the $^1\Delta_g$ state of oxygen.

For the next 25 years Kautsky's mechanism was generally ignored in favour of Schönberg's moloxide mechanism[40]. The latter mechanism involves the formation of an unstable sensitiser-oxygen complex capable of transferring oxygen to an acceptor molecule. Then in 1964 Foote and Wexler[41] reported that oxidation with singlet oxygen produced by the peroxide-hypochlorite reaction yielded identical products to those obtained in dye-sensitised photo-oxidations. Once Kautsky's original proposal had been supported by these and other results[42], where singlet oxygen generated by microwave discharge had been used as the oxidizing species, there was a rapid expansion in interest in the chemistry of singlet oxygen.

The processes in Scheme 5.12 not marked with red arrows are those involved in a Type II photo-oxidation where singlet oxygen, generated by energy transfer from a triplet excited sensitiser (Sens) to ground state oxygen, reacts with an organic molecule (A) to yield oxidation products (AO_2). The following kinetic equation can be derived[43] (see Appendix 5.6) for the rate of consumption of substrate:-

$$\frac{-d(A)}{dt} = \frac{k_r\,[A]\;Ia\phi_T}{(k_d + k_r\,[A])} \qquad (5.6)$$

where k_d = the unimolecular decay constant for singlet oxygen



SCHEME 5.12 OUTLINE OF THE PHOTOSENSITISED PRODUCTION OF SINGLET OXYGEN BY A SENSITISER (Sens) AND THE DECAY ROUTES AVAILABLE FOR THE SINGLET OXYGEN IN THE PRESENCE OF A SUBSTRATE (A) AND A QUENCHER (Q)

k_r = the rate constant for reaction of singlet oxygen with the substrate (A)

k_q = the rate constant for physical quenching of singlet oxygen by A

Ia = the intensity of light absorbed by the sensitiser

ϕ_T = the triplet yield of the sensitiser.

Since there is an abundance of literature on singlet oxygen and its reactions, including many excellent reviews[1a-k], this section merely summarises the most important aspects of the properties and reactions of singlet oxygen with respect to the results presented in this thesis.

5.3.2 Electronic structure of singlet oxygen

In 1928 Mulliken[44] interpreted the absorption bands of atmospheric oxygen and established the electronic structure of molecular oxygen. The two outermost electrons are located in two degenerate orbitals and thus have three possible configurations (Figure 5.1). In the ground state ($^3\Sigma_g^-$) the electron spins are parallel so molecular oxygen has a triplet ground state. There are also two low lying excited singlet states ($^1\Delta_g$ and $^1\Sigma_g^+$). The $^1\Sigma_g^+$, $^1\Delta_g$ and $^3\Sigma_g^-$

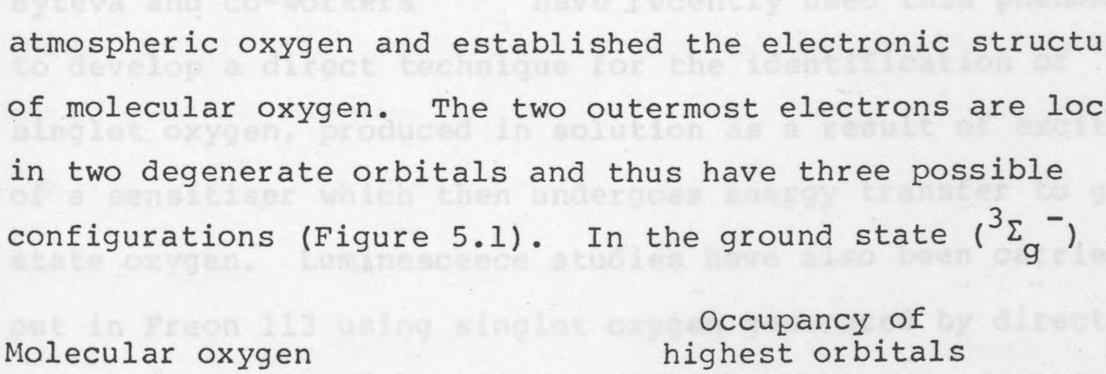


Figure 5.1

states have almost identical binding energies and dissociate to a common limit. Because the $^1\Sigma_g^+$ state relaxes rapidly, by collisional quenching, to the $^1\Delta_g$ state the latter is believed to be the reactive species present in the condensed phase.

Transitions from the ground state ($^3\Sigma_g^-$) to the excited singlet state are highly forbidden, but transitions from $^1\Delta_g$ to $^3\Sigma_g^-$ do give rise to singlet oxygen phosphorescence at 1270nm and 1580nm[45a-c] which has been observed in both the gas phase and in solution.

$$\begin{array}{lcll} ^1\Delta_g\,(\nu=0) & \longrightarrow & ^3\Sigma_g^- & (\nu=0)\ 1270\text{nm} \\ \,(\nu=0) & & & (\nu=1)\ 1580\text{nm} \end{array} \qquad (5.7)$$

Byteva and co-workers[46a,b] have recently used this phenomenon to develop a direct technique for the identification of singlet oxygen, produced in solution as a result of excitation of a sensitiser which then undergoes energy transfer to ground state oxygen. Luminescence studies have also been carried out in Freon 113 using singlet oxygen generated by direct excitation (Nd - YAG laser) of molecular oxygen under high pressure[46c]. However, this latter technique is limited by the small range of suitable solvents. The quantum yield of luminescence is so low in solution that a high intensity light source and sensitive photo-detectors are required. Studies of the luminescence of singlet oxygen have now yielded a great deal of information on the lifetime of singlet oxygen in solution (see Section 5.3.4) and have enabled quantitative determinations of the quantum yield of singlet oxygen production from sensitisers[47].

5.3.3 Generation of singlet oxygen

The most widely used methods for the generation of singlet oxygen can be classified under the following headings:- energy transfer, peroxide decomposition and electrical discharge, as outlined below.

(i) Energy transfer

By far the most widely used technique for the generation of singlet oxygen in solution involves the quenching of triplet excited states by ground state molecular oxygen as illustrated in Scheme 5.14.

$$^1M \xrightarrow{h\nu} {}^1M^* \xrightarrow{ISC} {}^3M^* \xrightarrow{^3O_2} (M\text{-}O_2)^*$$

where $(M\text{-}O_2)^*$ can have the following multiplicities and break down as shown:-

$$^1(M\text{-}O_2) \xrightarrow{\mathbf{a}} {}^1M + {}^1O_2$$

$$^3(M\text{-}O_2) \xrightarrow{\mathbf{b}} {}^3M^* + {}^3O_2$$

$$^5(M\text{-}O_2) \xrightarrow{\mathbf{c}} {}^3M^* + {}^3O_2$$

Scheme 5.14

The quenching is believed to occur via an excited complex $(M\text{-}O_2)^*$ and usually occurs to yield singlet oxygen at ~$^1/10$ the diffusion controlled rate. A factor of $^1/9$ can be explained by the probability of the complex decaying to yield singlet oxygen (path a) rather than following paths b or c[1d]. Any charge transfer character in the $(M\text{-}O_2)^*$ complex increases the efficiency with which singlet oxygen is produced.

Excited sensitiser triplet states are usually produced by the use of continuous or pulsed light sources. The most commonly used photosensitisers for singlet oxygen production are dyes, e.g. rose bengal and methylene blue, but almost any compound with a high quantum yield of triplet formation can be used. The sensitiser and the wavelength of the irradiating light are carefully chosen to ensure that the sensitiser is selectively excited. Consequently, this technique is very versatile and has found widespread applications.

It is well known that molecular oxygen quenches the fluorescence of many organic molecules with diffusion controlled rate constants, but the mechanism of the quenching remains controversial (see Chapter 8). Provided the singlet-triplet splitting of the organic molecule exceeds the excitation energy of singlet oxygen (94.5kJ mol^{-1}) generation of the latter (Scheme 5.15 path a) is a feasible process. However,

$$^{1}M^{*} + {}^{3}O_{2} \longrightarrow (M - O_{2})^{*}$$

$$^{3}(M - O_{2})^{*} \xrightarrow{\mathbf{a}} {}^{3}M^{*} + {}^{1}O_{2}$$

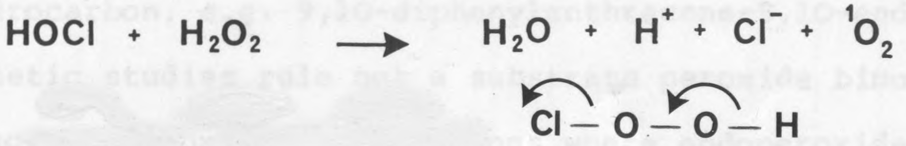
$$\xrightarrow{\mathbf{b}} {}^{3}M^{*} + {}^{3}O_{2}$$

Scheme 5.15

there is considerable debate about the ability of path a to compete with oxygen enhanced inter-system crossing (path b). The generation of singlet oxygen from highly fluorescent aromatic hydrocarbons such as rubrene (which has been used as a sensitiser for the photo-oxidation of 2,5-dimethylfuran[48]) occurs via this process.

(ii) Peroxide decomposition

The addition of an aqueous hypochlorite solution[49a] or the bubbling of gaseous chlorine or bromine[49b] through an alkaline solution of hydrogen peroxide produces singlet oxygen. It can be seen from Scheme 5.16 that spin-pairing requires the oxygen produced to be in a singlet state.



Scheme 5.16

Optimum yields (up to 80%) of singlet oxygen are obtained in methanolic solution by direct production and via relaxation of the $^1\Sigma_g^+$ state of oxygen which is also a product of the reaction. This technique is limited by the reactivity of hydrogen peroxide, free radical side reactions and the low solubility of the reagent in organic solvents.

Doubt[50a] has been cast upon the proposal[49b] that the decomposition of organic peracids in aqueous alkaline solution gives rise to significant yields of singlet oxygen.

Organic phosphites, e.g. triphenyl phosphite, react with ozone to form adducts which are stable at very low temperatures, but break down on warming to yield phosphates and singlet oxygen. The usefulness of this reaction has been increased by the discovery that in the presence of methanol and pyridine, triphenyl phosphite ozonide decomposes at temperatures as low as -100°C[50b]; in their absence it decomposes at -15°C. The rate with which singlet oxygen is liberated is increased by an order of magnitude for each substitution of a phenyl group by a methyl group. Such substitutions occur in the presence of methanol and pyridine thereby causing the observed acceleration in singlet oxygen production[50c].

Polycyclic aromatic endoperoxides undergo concerted thermal decomposition to yield singlet oxygen and the parent aromatic hydrocarbon, e.g. 9,10-diphenylanthracene-9,10-endoperoxide[51a,b]. Kinetic studies rule out a substrate peroxide bimolecular reaction in oxidation reactions where endoperoxides are used to generate singlet oxygen.

Transition metal-oxygen complexes, such as potassium perchromate, decompose in aqueous solution to yield singlet oxygen (Equation 5.8), but other oxidants may be involved. A review[52] of the decomposition of such complexes provides

$$4\ CrO_8{}^{3-} + 2H_2O \longrightarrow 4\ CrO_4{}^{2-} + 7\ O_2 + 4\ OH^- \qquad (5.8)$$

many more examples of their use as sources of singlet oxygen.

(iii) Electrical discharge

Microwave discharges at 2450 MHz through gaseous oxygen produce oxygen in both its $^1\Delta_g$ and $^1\Sigma_g{}^+$ states[53]. This method is a convenient non-chemical source of singlet oxygen, but is unreliable for kinetic studies due to the simultaneous production of reactive species other than singlet oxygen.

5.3.4 Lifetime of singlet oxygen in solution

The relatively long lifetime ($^1/k_d$) of singlet oxygen in solution (Table 5.2) is one reason why it is such an important

SOLVENT	INDIRECT TECHNIQUES		DIRECT TECHNIQUES	
	τ(μs)	τ_D/τ_H	τ(μs)	τ_D/τ_H
C_6H_6	23.8^{a}, 27^{b}, 28.2^{c}	16.8^{d}, 35^{c}	32^{f}, 26.7^{g}, 28^{h}	21.9^{f}, 20.6^{g}
C_6D_6	1000^{c}		700^{f}, 550^{g}, 628^{h}	22.4^{h}
CH_3CN	30.3^{a}, 57.0^{b}, 92^{c}	8.7^{d}, 7.2^{d}	61^{f}, 54.4^{g}, 69^{h}, 58^{j}	7.2^{f}, 11.0^{g},
CD_3CN	1250^{c}	13.4^{c}	440^{f}, 600^{g}, 621^{h}, 950^{j}	16.4^{h}, 9.0^{j}
$CHCl_3$	60^{a}, 415^{c}	15.6^{d}, 10.4^{d}	265^{f}, 160^{k}	2.4^{f}, 22.5^{k}
$CDCl_3$	885^{c}	9.8^{d}, 2.13^{c}	640^{f}, 3600^{k}	
Me_2CO	26.3^{a}, 42^{b}, 55^{c}	19.9^{d}, 17.0^{d}	51^{f}, 46.5^{g}, 51^{h}, 39^{j}, 65.3^{k}	12.5^{f}, 14.8^{g}
$(CD_3)_2CO$	760^{c}	17.8^{d}, 13.8^{c}	640^{f}, 690^{g}, 588^{h}, 770^{j}, 838^{k}	11.5^{h}, 19.7^{j}, 12.8^{k}
CH_3OH	7^{a}, 11.4^{e}, 10^{e}			
CH_3OD			37^{f}	
CD_3OD				22.0^{h}

where *a* to *k* represent the following references:- *a* - 54, *b* - 55, *c* - 56, *d* - 57, *e* - 58, *f* - 59a, *g* - 59b, *h* - 60, *j* - 61, *k* - 62.

TABLE 5.2 LIFETIMES OF SINGLET MOLECULAR OXYGEN ($^1\Delta_g$) IN SOLUTION AND SOLVENT ISOTOPE EFFECTS UPON THE LIFETIMES, AS DETERMINED BY DIRECT AND INDIRECT METHODS intermediate in many photo-oxidation reactions. From the results in Table 5.2 it can be seen, despite the discrepancy in results obtained from various laboratories, that the lifetime of singlet oxygen is markedly dependent upon the

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g^-) \qquad (5.9)$$

nature of the solvent and increases dramatically as a consequence of replacement of solvent hydrogen atoms by deuterium.

(i) Measurement of the lifetime of singlet oxygen

The lifetime of singlet oxygen was first investigated by an indirect technique which involved determining the rates of product formation (or loss of substrate) as a result of photo-oxidation of a substrate (A) in the presence of singlet oxygen (generated by energy transfer from an excited triplet state sensitiser to molecular oxygen). Slope/intercept ratios for plots of the reciprocal of the quantum yield of photo-oxidation ΦAO_2^{-1} vs $[A]^{-1}$ yielded β values ($\beta = k_d/k_A$).

$$^1O_2 + A \xrightarrow{k_A} AO_2 \qquad (5.10)$$

In the presence of a quenching molecule (Q) slope/intercept ratios for plots of ΦAO_2^{-1} vs $[Q]$ yielded values for k_q/k_A (where k_q is the rate constant for the quenching of singlet oxygen by Q) enabling the determination of relative rate constants for the reaction of A and various species Q with singlet oxygen. Consequently, although solvent effects upon the ratio k_d/k_A were available, no conclusions could be drawn about solvent effects upon the lifetime of singlet oxygen.

The time-resolved technique pioneered by Adams and Wilkinson[54a,b, 63] represented a major advance in determining the lifetime of singlet oxygen in solution because it yielded absolute values for k_d and k_A. In this technique, which was modified by Young and co-workers[58], the time-resolved bleaching of 1,3-diphenylisobenzofuran (DPBF) is monitored at 415nm, after production of singlet oxygen via pulsed laser excitation of methylene blue. DPBF, which absorbs strongly at 415nm, is rapidly oxidized by singlet oxygen to yield intermediates and products which do not absorb at 415nm. A plot of $\ln(D_t - D_\infty)$, where D_t and D_∞ are respectively the optical densities of DPBF at time t and at completion of the quenching event, against time has a slope k' (Equation 5.10). Plots of k' against [DPBF] in the absence of quencher yield k_d and k_A while plots of k'

$$k' = k_d + k_A[\mathrm{DPBF}] + k_q[\mathrm{Q}] \qquad (5.11)$$

against [Q] at fixed DPBF concentration yield k_q. These results enabled relative rate constants, determined by steady state techniques, to be placed on an absolute basis. Using Young's technique inaccurate values may be obtained if the lifetime of singlet oxygen greatly exceeds 100μs.

These indirect techniques have since been supplemented by direct techniques in which the weak singlet oxygen phosphorescence at 1270nm is measured (following pulsed laser excitation of a sensitiser) using an intrinsic germanium photo-diode. Direct techniques have the advantage of not requiring the addition of any potential singlet oxygen quenchers other than the sensitiser. Although the measured lifetime is dependent upon the sensitiser concentration and the laser power, extrapolation to zero sensitiser concentration and zero laser power does give reproducible estimates of the lifetime of singlet oxygen. Values obtained by direct methods are generally longer than those obtained by indirect methods[64].

(ii) Factors affecting the lifetime of singlet oxygen in solution

The lifetime of singlet oxygen, in a wide range of solvents, varies very little with temperature[63,64,65] indicating that observed temperature effects upon singlet oxygen reactions are due to the effect of temperature upon the addition of singlet oxygen to the substrate.

The nature and isotopic composition of the solvent has a marked affect upon the lifetime of singlet oxygen (Table 5.2). The lifetime of singlet oxygen in a "collision-free" environment is of the order of 45 minutes[66] whereas in solution the lifetime varies from one to several hundred microseconds. The first explanation for the observed solvent effects upon the lifetime of singlet oxygen was proposed by Merkel and Kearns[54b,c]. They found a correlation between the intensities of the solvent absorption bands in the energy regions corresponding to the O→O and O→1 oxygen $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition energies and the observed lifetime of singlet oxygen (Equation 5.12). On the basis of this a mechanism

$$\tau(^1O_2) = \left[0.5\ (OD)_{O-O} + 0.05\ (OD)_{O-1} + \ldots . \right] \quad (5.12)$$

involving electronic to vibrational energy transfer was proposed. With the advent of direct techniques for determining the lifetime of singlet oxygen it became clear that this explanation, although it gave a qualitative agreement with the experimental data, was inadequate in explaining observed solvent effects quantitatively[57,59a,b,62].

Recently, Ogilby and Foote[64] have extended Merkel and Kearns' original equation to take into account the fact that the solvent can induce the transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ as well as behaving as an energy sink. The term K_{solv} in Equation 5.13 is a constant, characteristic of each solvent, which expresses the ability of the solvent to induce this transition.

$$\tau(^1O_2) = K_{solv}\left(a(OD)_{0-0} + b(OD)_{0-1} + c(OD)_{0-2}\right) \qquad (5.13)$$

Integration of the absorption spectra of the solvents over a range of wavelengths centred on each transition gave closer agreement with experimental results but even this treatment does not provide quantitative correlations. Generally, for solvents with large optical densities in regions corresponding to $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transitions in the oxygen molecule (mainly due to the presence of C-H and O-H bonds) the lifetime of singlet oxygen will be relatively short. Solvent isotope effects can be explained on the basis of the different IR absorption properties of O-H and C-H bonds compared with their deuterated counterparts and solvent deuteration changing the particular contribution that specific vibrational modes make to the energy transfer process (i.e. the relative magnitudes of a, b and c).

Because solvent deuteration only causes a minor perturbation in the properties of the solvent, but has a marked affect upon the lifetime of singlet oxygen (Table 5.2), the observation of a solvent isotope effect upon the rate of a photo-oxidation reaction is often used as evidence for the involvement of singlet oxygen. This diagnostic test for singlet oxygen was developed by Merkel and Kearns and first used to demonstrate the participation of singlet oxygen in the photo-sensitised oxidation of free amino acids[67], e.g. tryptophan.

The majority of singlet oxygen reactions are insensitive to the nature of the solvent so k_d is the only term in Equation 5.4 which will be affected when a reaction is carried out in a deuterated solvent rather than its non-deuterated analogue. Consequently, observed solvent isotope effects upon the rate of a Type II photo-oxidation reaction of a substrate $[A]$ will be given by Equation 5.14 (see

$$\frac{\mathrm{RATE}_D}{\mathrm{RATE}_H} = \frac{k_d + (k_r + k_q)[A]}{k_d' + (k_r + k_q)[A]} \qquad (5.14)$$

Appendix 5.6). If maximal solvent isotope effects are to be observed the reaction with singlet oxygen must involve a diffusional process and the concentration of the substrate should be kept as low as possible in order that $k_d > (k_r + k_q)[A]$.

It must be stressed that solvent isotope effects upon photo-oxidation reactions are interpreted on the assumption that the behaviour of the sensitiser and the other rate constants of the system are essentially unaffected by a change from a non-deuterated solvent to its deuterated counterpart. These assumptions have not, in general, been put to the test.

5.3.5 Quenching of singlet oxygen

Quenching of singlet oxygen may be physical, to give ground state oxygen, or chemical (leading to oxidation products) in nature. Physical quenching can either involve energy transfer or charge transfer and will be dealt with in this section, whereas chemical quenching will be covered in Section 5.3.6.

Scheme 5.12 illustrates the possible routes (red arrows) by which an added quencher of singlet oxygen can interfere with a photosensitised singlet oxygen reaction. Since any quencher of singlet oxygen is a potential quencher of the excited states of the sensitiser[25a-c] caution must be taken when interpreting the effects of an added quencher upon the rate of a photo-oxidation reaction[68].

(i) Energy transfer quenching

This is the reverse of the process by which singlet oxygen is generated from a triplet excited sensitiser molecule by energy transfer to ground state oxygen (see Section 5.3.3 (i)). The triplet state of the quencher must be similar, or lower, in energy than the singlet oxygen for quenching to be efficient. This mechanism has been well documented for the diffusion controlled quenching of singlet oxygen by β-carotene[69a,b], but not clearly demonstrated for any other cases. It is probably the mechanism by which certain dyes[64,70a-c], triplet excited sensitisers[71] and compounds with extensive conjugated systems, which have low triplet energies, quench singlet oxygen.

(ii) Charge transfer quenching

This mechanism is more general than energy transfer and is the process by which amines, sulphides, azides, superoxide anion[72] and other electron rich compounds quench singlet oxygen. The rate of quenching is a function of the oxidation potential of the donor, the reduction potential and the excitation energy of singlet oxygen. In some cases, e.g. quenching by sulphides, decay of the intermediate charge transfer complex can also lead to product formation, i.e. chemical quenching as well as physical quenching. Therefore, quenching by sulphides, phenols and azide ions will be dealt with in the sections on their reactivity with singlet oxygen.

Amines which do not possess an abstractable hydrogen atom, e.g. 1,4-diazabicyclo[2.2.2]octane are purely physical quenchers of singlet oxygen[73a,b] and have consequently been used to test for the intermediacy of singlet oxygen in photo-oxidation reactions. Primary aliphatic amines are very inefficient quenchers of singlet oxygen, whereas electron rich aromatic amines quench at rates approaching $10^{9} M^{-1} sec^{-1}$[74].

5.3.6 Tests for the involvement of singlet oxygen in photo-oxidation reactions

(i) If reaction of a substrate with singlet oxygen, generated by non-photochemical methods, gives rise to the same products and product ratios as obtained in a photo-oxidation reaction of the same substrate it may be concluded that singlet oxygen may be the reactive species in the latter reaction.

(ii) Product studies may indicate the involvement of singlet oxygen because unlike many radical oxidation processes the addition of singlet oxygen to organic substrates is often regio or stereospecific, e.g. in the photo-oxidation of (+)-limonene (Table 5.1) radical oxidation processes give rise to racemic products, whereas the reaction with singlet oxygen yields optically active products and results in very different product ratios.

(iii) Inhibition of photo-oxidation by added singlet oxygen quenchers, e.g. DABCO, is indicative of the involvement of singlet oxygen provided the quencher does not interact with the excited states of the sensitiser. The effect of added chemical quenchers of singlet oxygen, e.g. alkenes, can also prove useful in determining the rôle of singlet oxygen. In such cases the isolated products may indicate that singlet oxygen has indeed been trapped.

(iv) From Equation 5.4 it can be seen that the rate of photo-oxidation via a singlet oxygen mechanism will be independent of oxygen concentration above a critical minimum concentration[2a-c]. In contrast to Type II processes the concentration of oxygen in Type I reactions will determine the efficiency with which the radicals present are scavenged by oxygen.

(v) Since the lifetime of singlet oxygen is considerably longer in a deuterated solvent than its non-deuterated counterpart (but the other properties of the solvent are hardly affected) the observation of a solvent isotope effect upon the rate of a photo-oxidation reaction is often used as evidence for the involvement of singlet oxygen.

(vi) Observation of singlet oxygen luminescence at 1270 nm provides evidence that singlet oxygen is present in solution, but little indication of whether it is the reactive species responsible for oxidation. If quenching of singlet oxygen luminescence by the substrate is independent of the method used to generate the singlet oxygen and associated with product formation it can be inferred that the photo-oxidation reaction under investigation involves a Type II mechanism.

5.3.7 Some examples of Type II reactions

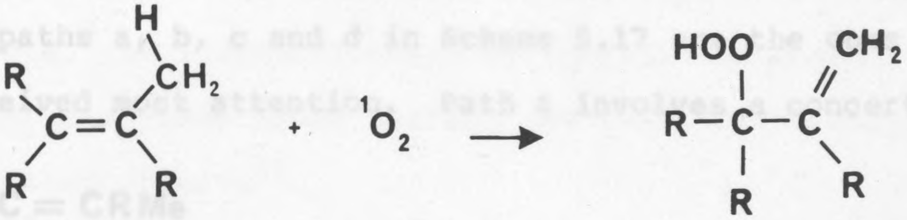
Singlet oxygen is a highly reactive species which is capable of oxidizing a wide range of organic compounds. As the ground state of oxygen is a triplet its reaction with organic compounds in their singlet ground states is spin forbidden, whereas no such spin-barrier hinders the interaction between oxygen in its excited singlet states and ground state organic compounds. The following sections give some indication of the variety of reactions in which singlet oxygen is involved.

(i) Reactions of singlet oxygen with alkenes

Singlet oxygen behaves as an electrophile towards alkenes, undergoing addition reactions to yield hydroperoxides, dioxetanes or endoperoxides depending on the nature of the alkene. The ultimate products are determined by the reactivity of these initially formed species under the reaction conditions.

(a) The ene reaction

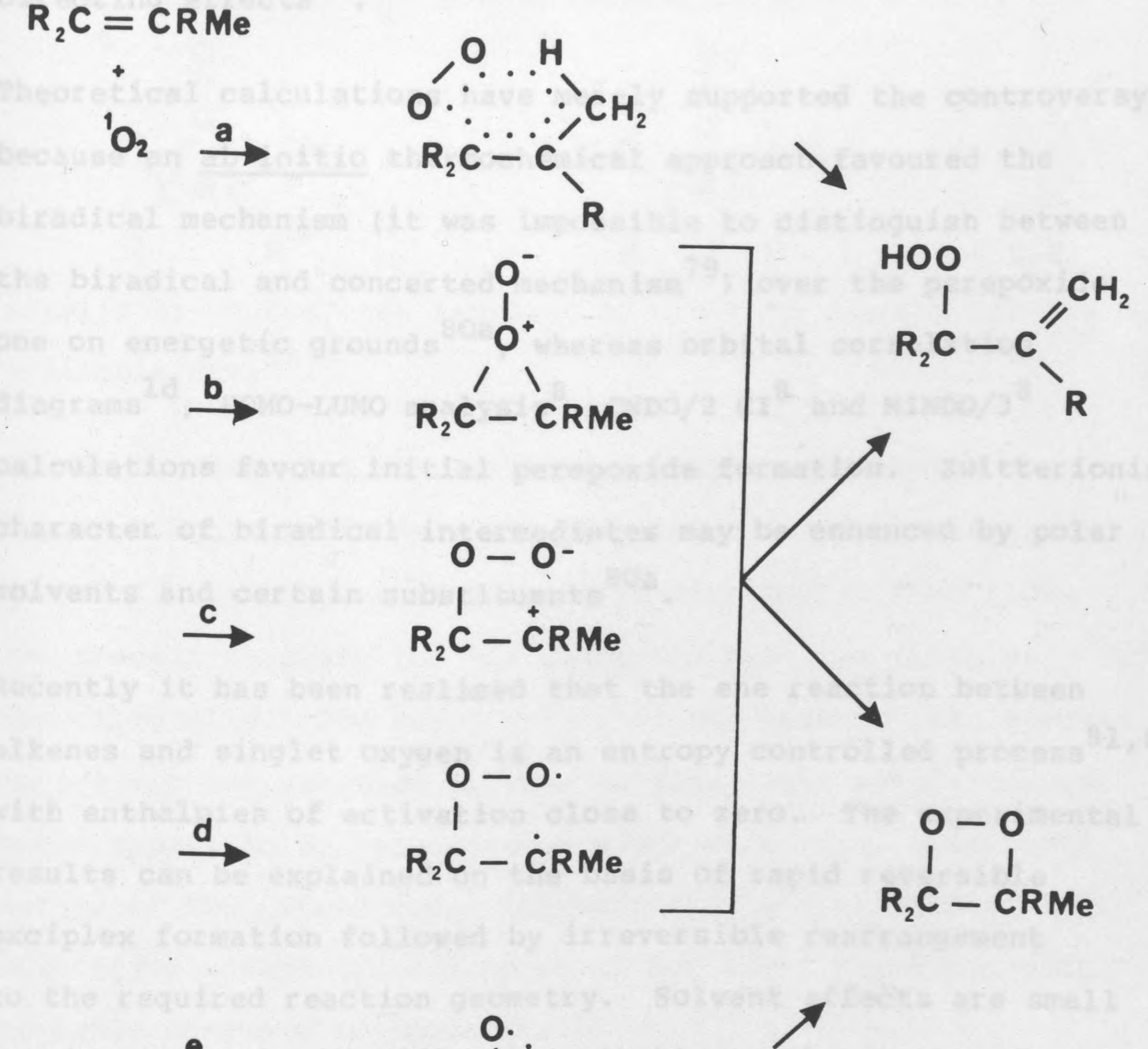
The ene-type process by which singlet oxygen reacts with alkenes to yield allylic hydroperoxides with a rearranged double bond (Equation 5.15) was first discovered by Schenk in 1943[75]. This reaction has proved useful in synthetic



(5.15)

organic chemistry because the product allylic hydroperoxides are readily converted to allylic alcohols in the presence of reducing agents, e.g. $NaBH_4$. The rearranged double bond sometimes distinguishes the ene reaction from autoxidation processes. In the case of optically active alkenes, e.g. (+)-limonene (Table 5.1) the ene reaction gives rise to optically active products, whereas the radical reaction produces racemic products and a different product distribution.

The ene reaction is fairly insensitive to the nature of the solvent[76], but sensitive to steric, conformational and electronic effects. Electronic effects determine the locospecificity of the ene reaction and indicate that singlet oxygen is behaving as an electrophilic species[77a,b]. For alkenes with more than one double bond it is the one with the lowest ionisation potential which reacts preferentially or even exclusively, e.g. the most substituted double bond of (+)-limonene reacts exclusively (Table 5.1). The high exothermicity of the ene reaction and the low enthalpies of activation favour a highly ordered transition state which closely resembles the reactants. The low primary deuterium isotope effects are consistent with such a transition state[78a-c]. Despite all the numerous investigations of stereochemical and electronic effects, which have been the subject of a comprehensive review[76], the mechanism of the ene reaction is still the subject of controversy. The four mechanisms represented by paths a, b, c and d in Scheme 5.17 are the ones which have received most attention. Path a involves a concerted six-



Scheme 5.17 Possible structures for the intermediate species in both the ene and the dioxetane forming reactions between alkenes and singlet oxygen.

membered transition state typical of the classical ene reaction, path b is via a perepoxide which is closely related to the intermediate in path c, and finally path d involves a biradical intermediate. The strongest arguments against the intermediacy of zwitterions and biradicals as intermediates have been based on the lack of solvent polarity effects, the ineffectiveness of radical scavenges, the absence of any cis-trans isomerization and the lack of Markovnikov-directing effects[76].

Theoretical calculations have merely supported the controversy because an <u>ab initio</u> thermochemical approach favoured the biradical mechanism (it was impossible to distinguish between the biradical and concerted mechanism[79]) over the perepoxide one on energetic grounds[80a], whereas orbital correlation diagrams[1d], HOMO-LUMO analysis[8], CNDO/2 CI[8] and MINDO/3[8] calculations favour initial perepoxide formation. Zwitterionic character of biradical intermediates may be enhanced by polar solvents and certain substituents[80a].

Recently it has been realised that the ene reaction between alkenes and singlet oxygen is an entropy controlled process[81,82] with enthalpies of activation close to zero. The experimental results can be explained on the basis of rapid reversible exciplex formation followed by irreversible rearrangement to the required reaction geometry. Solvent effects are small but in some cases significant, probably as the result of solvation entropy requirements at the transition state leading from the exciplex to products. The tendency for dioxetane formation to be favoured over allylic hydroperoxide formation with increasing solvent polarity probably reflects the higher polarity of the latter transition state[82]. Although there is a correlation between ionization potential and reactivity towards singlet oxygen for cis-alkenes and for trans-alkenes, cis and trans-alkenes with identical ionization potentials may have widely differing reactivities[81]. As cis-alkenes are usually more reactive than their trans counterparts two representations of the favoured transition state[83a,b] (Figure 5.2), with the oxygen loosely directed towards the allylic hydrogens, are required in order to explain all the available data[81].

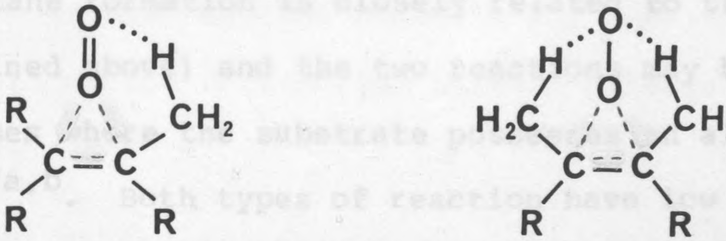
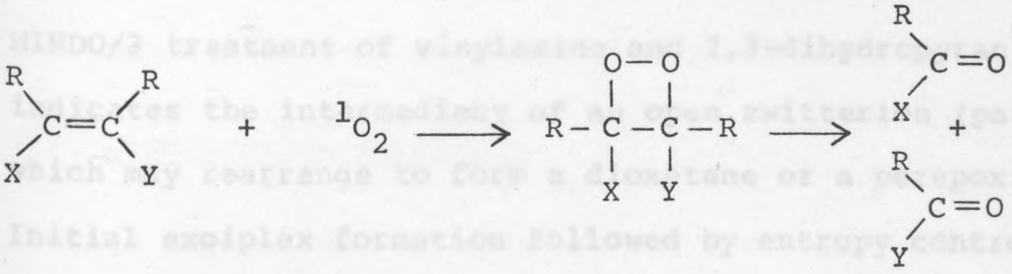


Figure 5.2

It can be seen that the transition states represented in Figure 5.2 are related to the perepoxide intermediate (path b) and it will be very difficult to distinguish them from the transition state for the concerted reaction (path a) experimentally. The exact nature of the intermediate species in a given ene reaction between an alkene and singlet oxygen would appear to be dependent upon the structural characteristics of the alkene under investigation and efforts to identify a unique transition state for these reactions will probably continue to prove fruitless.

(b) Dioxetane formation

Trans 1,3-dienes and alkenes with electron donating substituents at the double bond, e.g. enamines[84] and vinyl ethers[85a,b] react with singlet oxygen to form intermediate 1,2-dioxetanes (Equation 5.16) which decomposes to yield products in which

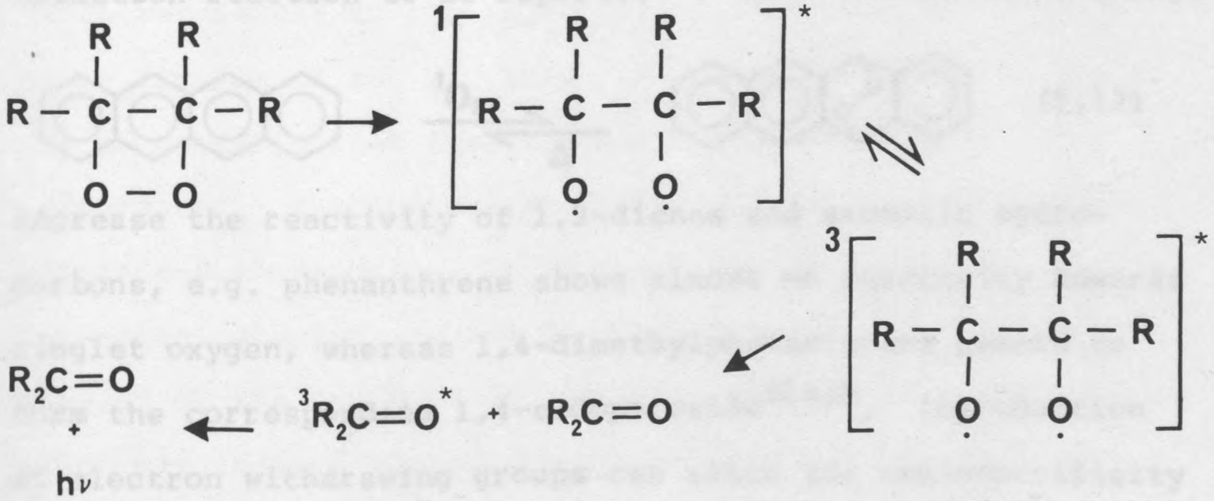


(5.16)

the double bond has been cleaved[86].

Dioxetane formation is closely related to the ene reaction (outlined above) and the two reactions may be competitive in cases where the substrate possesses an allylic hydrogen atom[87a,b]. Both types of reaction have low activation energies, but polar solvents tend to favour dioxetane formation over the ene reaction. Bartlett and co-workers[86, 87a] were the first to succesfully isolate a 1,2-dioxetane from the 1,2-cycloaddition of singlet oxygen to an alkene (cis-diethoxyethylene). Although spectroscopic and product studies have provided evidence for the intermediacy of 1,2-dioxetanes which have proved to be difficult to isolate, the exact mechanism of dioxetane formation remains controversial. Mechanistic discussions (Scheme 5.16) have centred around a concerted mechanism involving a 4-membered transition state (path e) and mechanisms (paths b, c and d) involving common intermediates to those proposed for the ene reaction. Path e, which involves concerted $({}_{\pi}2_a + {}_{\pi}2_s)$ addition must be antarafacial with respect to oxygen as illustrated. Concerted ${}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition is only allowed if the alkene HOMO is higher in energy than the singlet oxygen LUMO[1d]. Theoretical calculations based on an *ab initio* thermodynamical approach suggest a biradical intermediate common to both the ene and dioxetane reactions[80a]. Molecular orbital calculations for simple alkenes favour perepoxide formation[80b], whereas a MINDO/3 treatment of vinylamine and 2,3-dihydropyran[80c] indicates the intermediacy of an open zwitterion (path c) which may rearrange to form a dioxetane or a perepoxide. Initial exciplex formation followed by entropy controlled rearrangement to the transition state leading to products, as described for the ene reaction, has recently been proposed[82] as the reaction sequence for dioxetane formation as a result of the interaction between alkenes and singlet oxygen.

Interest in 1,2-dioxetanes was intensified when McCapra[89] suggested that these strained, high energy peroxides might decompose to form electronically excited products which would emit light as is observed in various chemi- and bioluminescent reactions. All dioxetanes decompose, at elevated temperatures, with the emission of light probably by a biradical mechanism



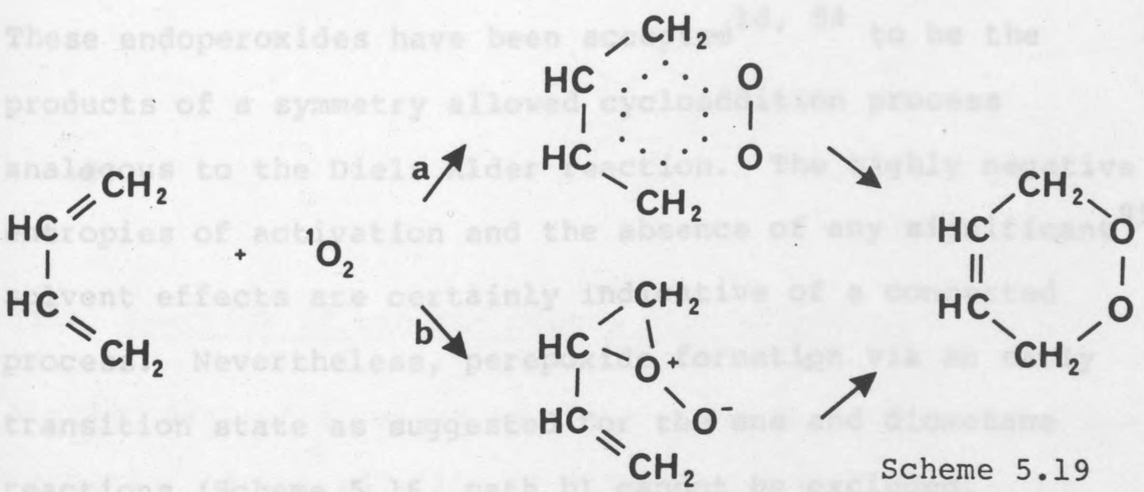
Scheme 5.18

in which inter-system crossing takes place within the biradical

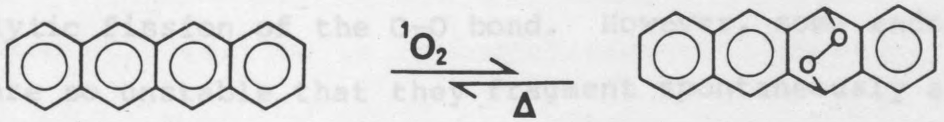
(Scheme 5.18). An alternative mechanism has been proposed[90] which involves spin-inversion as an integral part of the concerted cleavage. There are several reviews[86, 91a-c] of the chemiluminescent decomposition of dioxetanes.

(c) Endoperoxide formation

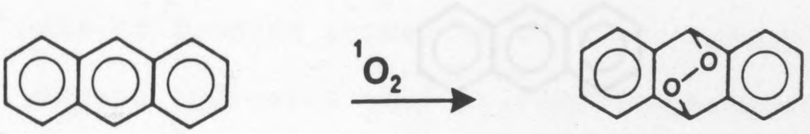
Singlet oxygen adds to conjugated π systems, e.g. cisoid 1,3-dienes and aromatic hydrocarbons, to yield endoperoxides (Scheme 5.19). The 1,4-addition of singlet oxygen to naphthalene (Equation 5.17) was the first example of a photo-oxidation reaction to be reported[92]. Electron donating groups increase the reactivity of 1,3-dienes and aromatic hydrocarbons, e.g. phenanthrene shows almost no reactivity towards singlet oxygen, whereas 1,4-dimethylphenanthrene reacts to form the corresponding 1,4-endoperoxide[51a,b]. Introduction of electron withdrawing groups can alter the regiospecificity of the 1,4-addition, e.g. addition of singlet oxygen to anthracene yields the 9,10-endoperoxide (Equation 5.18)



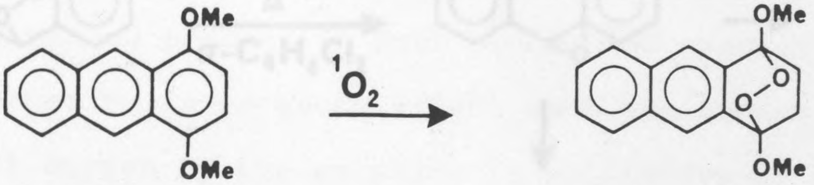
Scheme 5.19



(5.17)

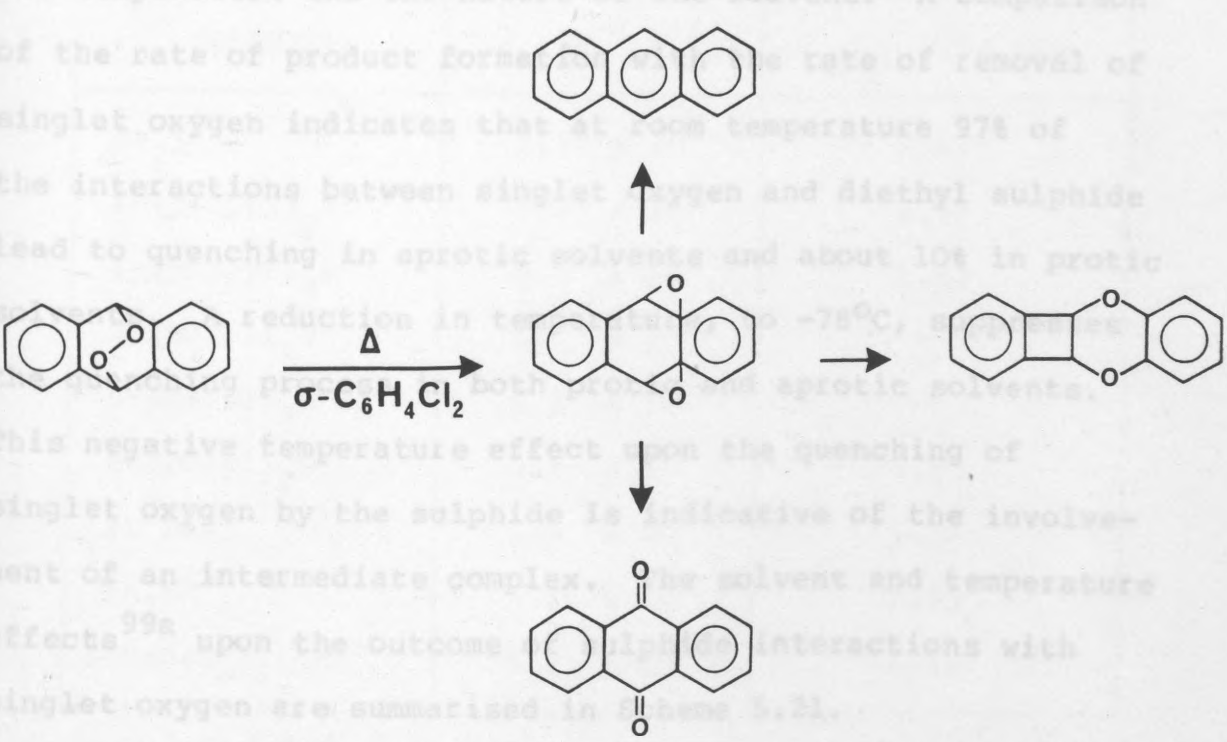

(5.18)

whereas the analogous reaction of 1,4-dimethoxyanthracene yields the 1,4-endoperoxide exclusively[93] (Equation 5.19).


(5.19)

These endoperoxides have been accepted[1d, 94] to be the products of a symmetry allowed cycloaddition process analogous to the Diels Alder reaction. The highly negative entropies of activation and the absence of any significant[95] solvent effects are certainly indicative of a concerted process. Nevertheless, perepoxide formation via an early transition state as suggested for the ene and dioxetane reactions (Scheme 5.16, path b) cannot be excluded.

The action of heat upon endoperoxides causes fragmentation which may result in the regeneration of reactants or homolytic fission of the O-O bond. However, some endoperoxides are so unstable that they fragment spontaneously at room temperature. The thermal decomposition of 9,10-diphenylanthracene-9,10-peroxide, in benzene, has been used as a convenient chemical source of singlet oxygen[51a]. Homolytic fission of the O-O bond of endoperoxides yields bisepoxides, which may undergo further reaction[96], e.g. themolysis of anthracene-9,10-peroxide in σ-dichlorobenzene[97] (Scheme 5.20).



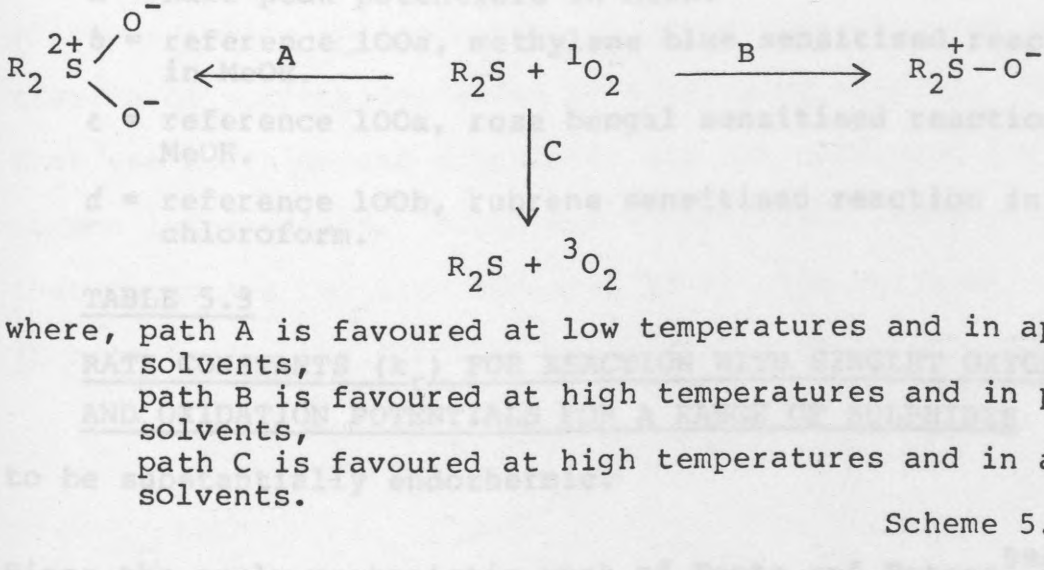
Scheme 5.20

(ii) Reaction of singlet oxygen with sulphides

A great deal of interest has been shown in ascertaining the mechanism of the addition of singlet oxygen to sulphides since the photo-oxidation of sulphides was first reported by Schenck and co-workers[98] in 1963. The products of the reaction are sulphoxides and sulphones (Equation 5.20) but product formation is in competition with physical quenching

$$R_2S \xrightarrow{{}^1O_2} R_2SO + R_2SO_2 \qquad (5.20)$$

of singlet oxygen by the sulphide. Foote and co-workers[99a,b] have shown that although the rate of removal of singlet oxygen is relatively independent of solvent and temperature the rate of product formation shows a marked dependence upon the temperature and the nature of the solvent. A comparison of the rate of product formation with the rate of removal of singlet oxygen indicates that at room temperature 97% of the interactions between singlet oxygen and diethyl sulphide lead to quenching in aprotic solvents and about 10% in protic solvents. A reduction in temperature, to -78°C, suppresses the quenching process in both protic and aprotic solvents. This negative temperature effect upon the quenching of singlet oxygen by the sulphide is indicative of the involvement of an intermediate complex. The solvent and temperature effects[99a] upon the outcome of sulphide interactions with singlet oxygen are summarised in Scheme 5.21.



where, path A is favoured at low temperatures and in aprotic solvents,
path B is favoured at high temperatures and in protic solvents,
path C is favoured at high temperatures and in aprotic solvents.

Scheme 5.21

The addition of methyl groups α to the sulphur causes a decrease in the rate of oxidation of ~ 10 for each pair of methyl groups added symmetrically[100a,b] (Table 5.3). This cannot be explained by the change in oxidation potential so must be due to steric crowding, a similar effect is caused by replacement of alkyl by phenyl groups. Complete electron transfer from sulphides to singlet oxygen has been calculated[100a]

SULPHIDE	k_r (M^{-1} s^{-1})	$E_{p/2}$, V vs SCE
Et_2S^b	1.71×10^7	1.65
$i\text{-(propyl)}_2S^c$	2.51×10^6	1.63
$i\text{-(propyl)}_2S^d$	2.2×10^6	1.63
$n\text{-(butyl)}_2S^d$	2.3×10^7	-
$s\text{-(butyl)}_2S^d$	1.8×10^6	-
$t\text{-(butyl)}_2S^d$	1.3×10^5	1.65
Ph SMe^c	2.0×10^6	1.51
Ph_2S^c	$\sim 1 \times 10^5$	1.65
$\rho\text{-MeO}(C_6H_4)SMe^c$	5.3×10^6	1.13

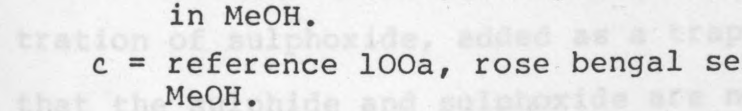
a = half-peak potentials in MeCN.
b = reference 100a, methylene blue sensitised reaction in MeOH.
c = reference 100a, rose bengal sensitised reaction in MeOH.
d = reference 100b, rubrene sensitised reaction in chloroform.

TABLE 5.3

RATE CONSTANTS (k_r) FOR REACTION WITH SINGLET OXYGEN AND OXIDATION POTENTIALS FOR A RANGE OF SULPHIDES

to be substantially endothermic.

Since the early mechanistic work of Foote and Peters[99a] the following oxidizing species (Figure 5.3) have been considered


$R_2\overset{+}{S}\text{-}OO^-$ A

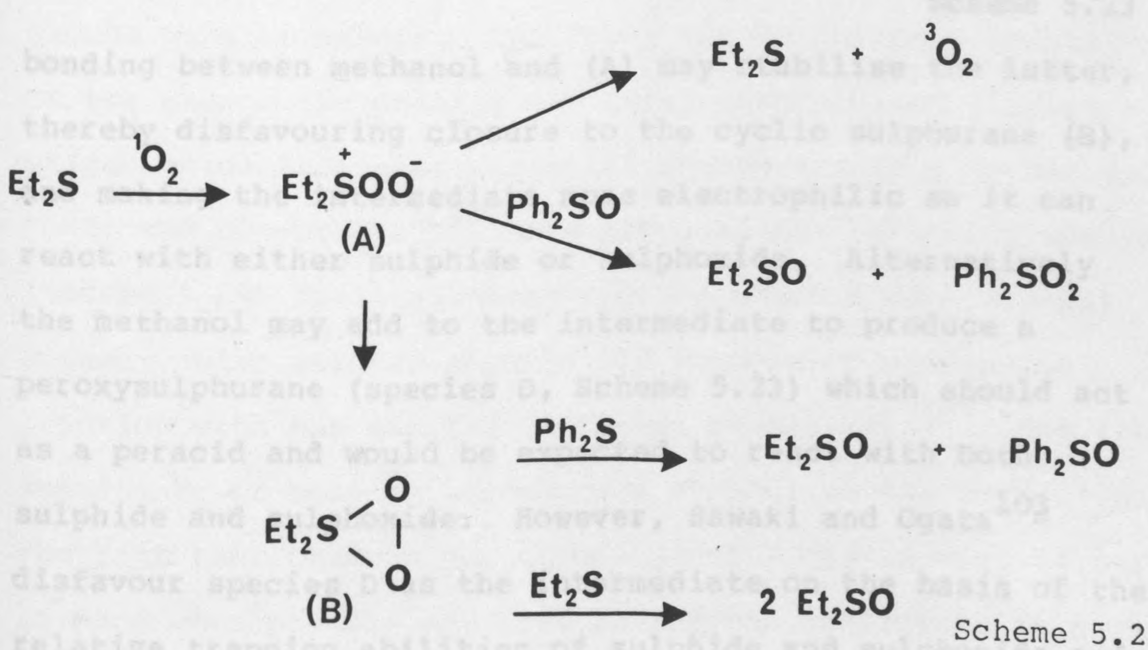
$R_2\dot{S}\text{-}O\dot{O}$ B

C

Figure 2.3

as the most likely intermediates in the sensitised photo-oxidation of sulphides. Determining whether the intermediate is a zwitterion (A), a diradical (B) or a cyclic peroxide (C) has been achieved by trapping experiments. Diphenyl sulphide and diphenyl sulphoxide, both of which are relatively inert to singlet oxygen, are oxidized by intermediates in the sensitised photo-oxidation of diethyl sulphide to yield diphenyl sulphoxide and diphenyl sulphone respectively[99a,101]. Diaryl sulphides have been shown by Ando and co-workers[102] to act as nucleophiles when used as trapping agents (quenching was observed to be enhanced by the presence of electron donating groups), whereas Sawaki and Ogata[103] have shown that sulphoxides act as electrophiles towards the intermediate.

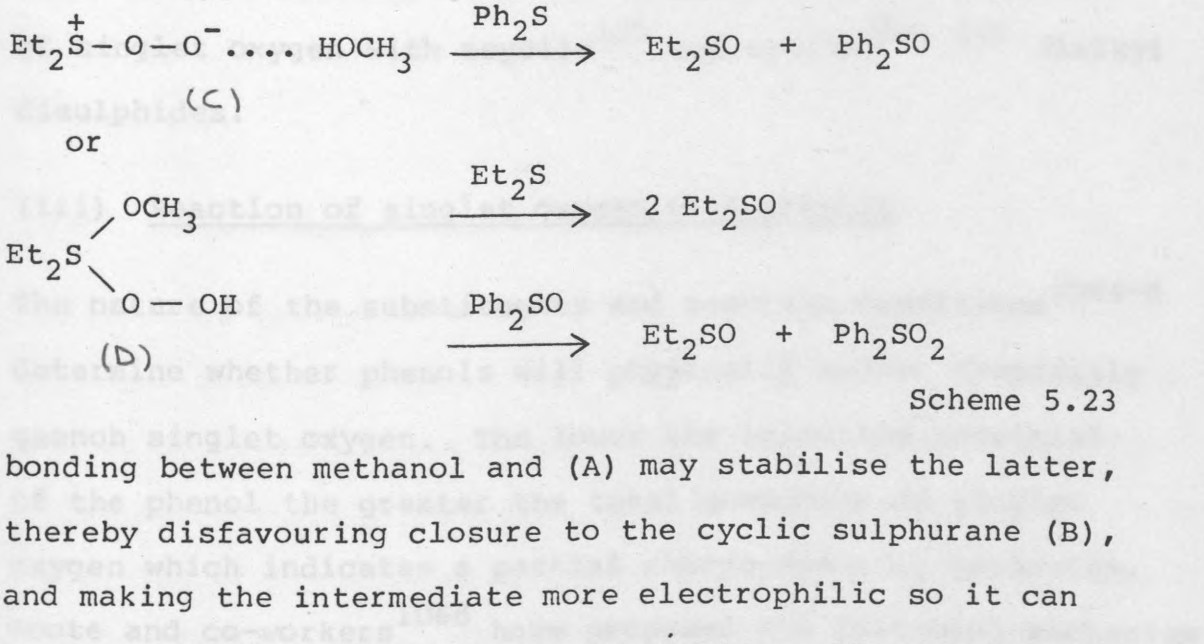
These observations coupled with the fact that the fraction of product formation, in aprotic solvents, is independent of the sulphide concentration but dependent upon the concentration of sulphoxide, added as a trapping species, indicate that the sulphide and sulphoxide are not competing for a common intermediate. Foote and co-workers[104] have proposed that there are two intermediates in aprotic solvents (Scheme 5.22), the first of which (A) is an electrophilic



Scheme 5.22

species which can dissociate to the sulphide and ground state oxygen, be trapped by sulphoxides, rearrange to form a sulphone or collapse to a second intermediate (B) which can be trapped by sulphides. The proposed structures for A and B are based on kinetic evidence alone so are not considered as definitive, but seem to be the most reasonable on the basis of their reactivity.

In methanol there is no physical quenching of singlet oxygen by the sulphide and quenching of the intermediate by sulphide is competitive with quenching by sulphoxide. Foote and co-workers[99a, 104] have proposed two possible explanations for these observations (Scheme 5.23). Firstly, hydrogen



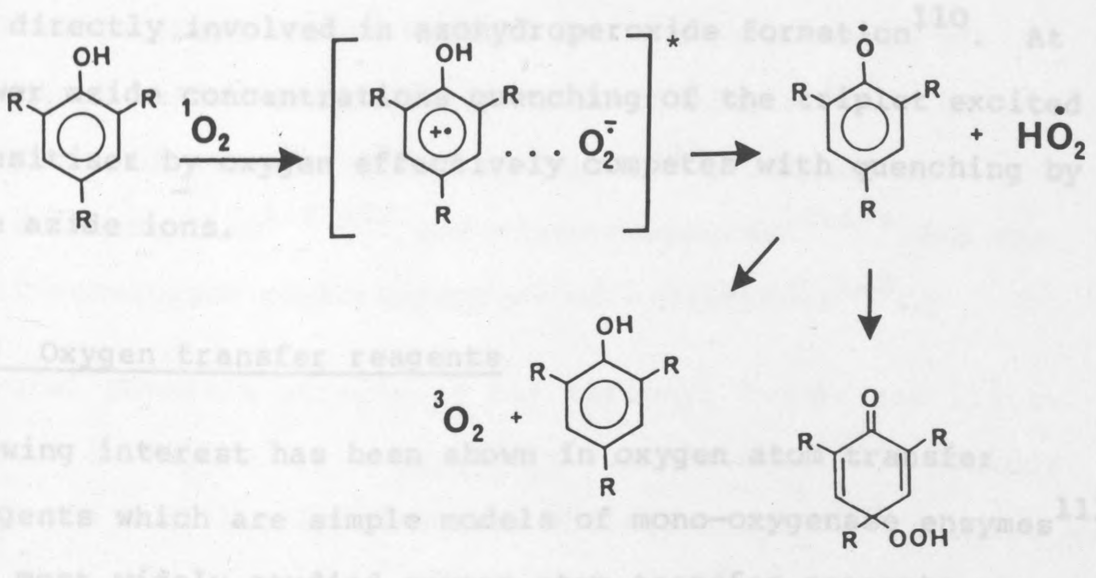
Scheme 5.23

bonding between methanol and (A) may stabilise the latter, thereby disfavouring closure to the cyclic sulphurane (B), and making the intermediate more electrophilic so it can react with either sulphide or sulphoxide. Alternatively the methanol may add to the intermediate to produce a peroxysulphurane (species D, Scheme 5.23) which should act as a peracid and would be expected to react with both sulphide and sulphoxide. However, Sawaki and Ogata[103] disfavour species D as the intermediate on the basis of the relative trapping abilities of sulphide and sulphoxide and positive ρ values, none of which were consistent with peracid oxidation.

Rearrangement of the intermediates (in the sensitised photo-oxidation of sulphides whose sulphoxides are unreactive towards the intermediate, e.g. diethyl sulphide) to form sulphones, in the absence of any trapping species, accounts for the higher ratio of sulphone to sulphoxide obtained using low concentrations of sulphide[99a]. In protic solvents the stabilisation of the intermediate, which disfavours breakdown to give the sulphide and ground state oxygen, also appears to disfavour its rearrangement to sulphone[99a]. Similar intermediates have been proposed for the reaction of singlet oxygen with acyclic[105] and cyclic[99a, 105] dialkyl disulphides.

(iii) Reaction of singlet oxygen with phenols

The nature of the substituents and reaction conditions[106a-d] determine whether phenols will physically and/or chemically quench singlet oxygen. The lower the oxidation potential of the phenol the greater the total quenching of singlet oxygen which indicates a partial charge-transfer mechanism. Foote and co-workers[106d] have proposed the following mechanism (Scheme 5.24) for the interaction of phenols with singlet oxygen. Like amines, phenols are capable of undergoing reaction with the excited states of sensitisers[107], but the importance of such an interaction depends on the conditions[106d]. The fact that phenols can quench singlet oxygen must be borne in mind when phenols are used as radical inhibitors to deter-



Scheme 5.24

mine whether a photo-oxidation is occurring via a Type I mechanism. By using low concentrations of phenols (e.g. 2,6-di-tert-butyl phenol) as radical quenchers their influence upon the rate of any Type II mechanism can be minimised.

(iv) Reaction of singlet oxygen with azide ions

Azide ions have been shown to react with singlet oxygen to produce azido hydroperoxides (AO_2HN_3)[108] so earlier experiments in which azide ions were added to ene reactions on the basis that any azidohydroperoxides were formed as a result of azide trapping of the intermediates in the ene reaction were based upon a fallacy. Spin-trapping studies[109] have provided evidence for the participation of azide radicals in the quenching of singlet oxygen by azides (Equation 5.21). Under

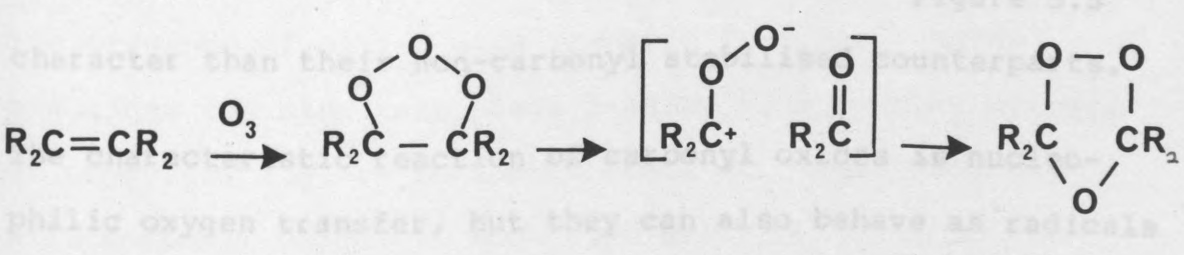
$$N_3^- + {}^1O_2 \longrightarrow \left(\dot{N}_3 \ldots . O_2^{\bar{\cdot}}\right) \longrightarrow \dot{N}_3 + O_2^{\bar{\cdot}} \quad (5.21)$$

conditions where the azide concentration is sufficiently high (>0.3M) the sensitising dye, e.g. methylene blue, may be directly involved in azohydroperoxide formation[110]. At lower azide concentrations quenching of the triplet excited sensitiser by oxygen effectively competes with quenching by the azide ions.

5.4 Oxygen transfer reagents

Growing interest has been shown in oxygen atom transfer reagents which are simple models of mono-oxygenase enzymes[111]. The most widely studied oxygen atom transfer reagents are carbonyl oxides. Other oxygen transfer reagents which have received attention are pyridine N-oxides[112, 113], heterocyclic S-oxides (e.g. persulphoxides (see Section 5.3.7(ii)) and persulphones[103]) selenium oxides[114] and phosphite ozonides, e.g. triphenylphosphite ozonide[115a-c]. Although phosphite ozonides readily decompose to yield phosphates and singlet oxygen they have been observed to oxidize alkenes at temperatures well below those required for unimolecular decomposition[115a-c].

As early as 1949 Criegee[116a,b] explained the reaction of alkenes with ozone, to yield 1,2,4-trioxalanes, by the following mechanism:-



Scheme 5.25

Since then the intermediate carbonyl oxides, which can be trapped by added aldehydes, have been the subject of many investigations. Other methods for the preparation of carbonyl oxides include ozonolysis of alkynes[117], the addition of singlet oxygen to furans[118], sulphur or pyridinium ylids[119,120] and diazo compounds[121a-c] and the self-sensitised photo-oxidation of α-diketones[122].

Several possible structures for carbonyl oxides are illustrated in Figure 5.4. Ab-initio calculations[123a,b] favour C as the most likely structure whereas MINDO/3[124] studies suggest

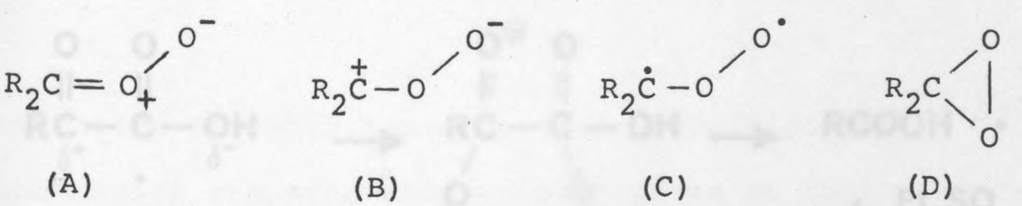


Figure 5.4

that A will be the most stable. The reactivity of carbonyl oxides towards a wide range of substrates is consistent with the actual structure being a resonance hybrid between A and C. Carbonyl stabilised carbonyl oxides have three zwitterionic resonance structures[118,120] (Figure 5.5) and consequently exhibit a higher degree of zwitterionic

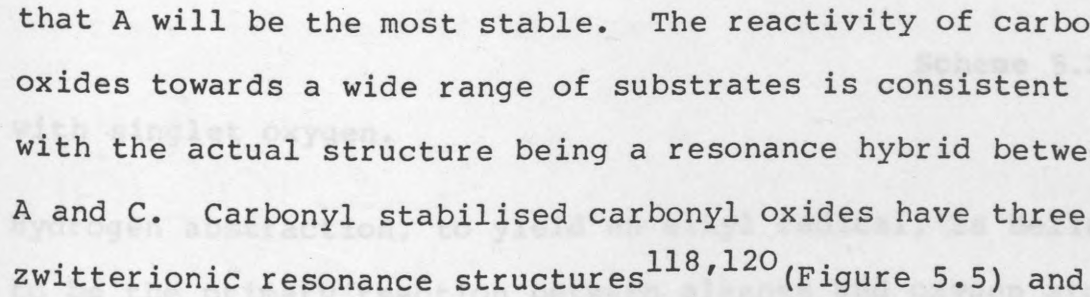
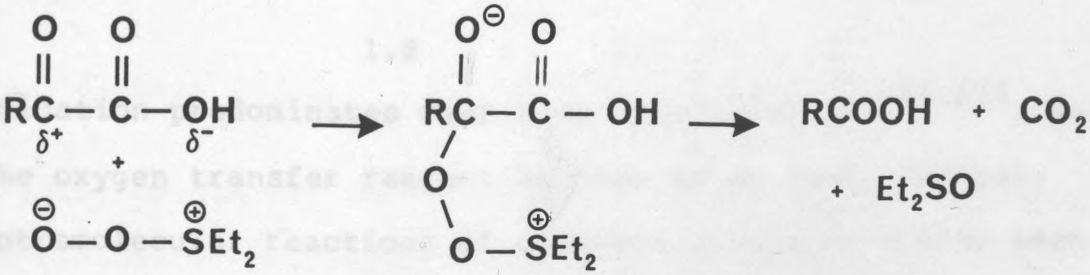


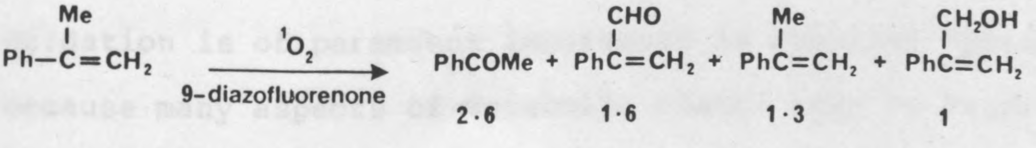
Figure 5.5

character than their non-carbonyl stabilised counterparts. The characteristic reaction of carbonyl oxides is nucleophilic oxygen transfer, but they can also behave as radicals and abstract a hydrogen atom, undergo radical oxygen atom transfer and act as poor electrophilic oxidants. The type of behaviour exhibited by carbonyl oxides is therefore markedly dependent upon the nature of the substrate. Nucleophilic oxygen atom transfer by carbonyl oxides leads to the oxidation of sulphides to sulphoxides, sulphoxides to sulphones[124,119] and silyl compounds to silyloxides[125]. Ando and co-workers[126] have recently reported that α-ketocarboxylic acids can undergo oxidative decarboxylation in the presence of diethylpersulphoxide (Scheme 5.26), which is an intermediate in the reaction of diethyl sulphide with singlet oxygen.



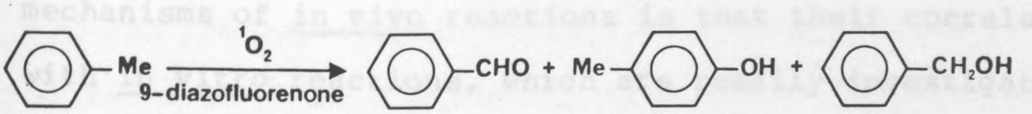
Scheme 5.26

Hydrogen abstraction, to yield an alkyl radical, is believed to be the primary reaction between alkanes and oxygen atom transfer reagents. The ultimate products are alcohols and carbonyl compounds, e.g. cyclohexane is oxidized to cyclohexanol and cyclohexanone[127]. In contrast to alkanes, alkenes undergo C-C bond cleavage as the major reaction in the presence of oxygen atom transfer reagents. Other reactions can also take place leading to a complex mixture of products, e.g. as in the reaction of α-methylstyrene with carbonyl oxides[124] (Equation 5.22).



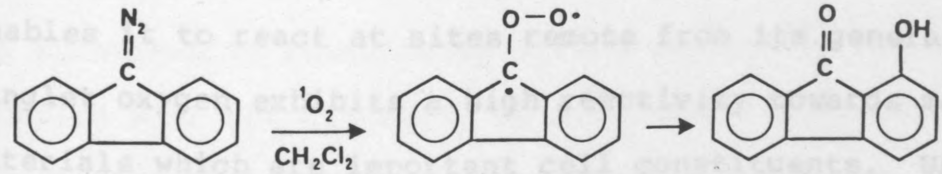
$$\mathrm{Ph{-}\overset{Me}{C}{=}CH_2 \xrightarrow[\text{9-diazofluorenone}]{^1O_2} \underset{2\cdot6}{PhCOMe} + \underset{1\cdot6}{Ph\overset{CHO}{C}{=}CH_2} + \underset{1\cdot3}{Ph\overset{Me}{C}{=}CH_2} + \underset{1}{Ph\overset{CH_2OH}{C}{=}CH_2}} \qquad (5.22)$$

Aromatic hydrocarbons react with oxygen transfer reagents to yield epoxide intermediates and ultimately products in which the aromatic ring has been hydroxylated. The ratio of α to β-naphthols (17:3) obtained from naphthalene is indicative of a radical mechanism[128]. For alkyl substituted aromatic hydrocarbons, e.g. toluene (Equation 5.23), side chain oxidation predominates over ring hydroxylations[113,124], i.e. the oxygen transfer reagent behaves as an ionic radical. Intramolecular reactions of carbonyl oxides have also been reported; an example is illustrated in Equation 5.24.



(5.23)

1.8 : 1.3 : 1



(5.24)

Evidence for the involvement of an oxygen transfer reagent in a photo-oxidation reaction can be obtained from trapping experiments and relative reactivities of the oxidizing species towards a variety of substrates. If the order of reactivity is inconsistent with the intermediacy of singlet oxygen, peroxy acids or acylperoxy radicals an oxygen transfer reagent may be the oxidizing species.

5.5 Biological significance of oxidizing species

Oxidation is of paramount importance in cellular systems because many aspects of metabolic change rely on oxidation steps. Excessive or inefficient oxidation is therefore potentially toxic. Biological systems have a range of enzymatic and non-enzymatic lines of defence against oxygen toxicity[130a]. Photo-oxidation has been studied on a molecular scale in aqueous solution and in vivo in multicellular animals. One of the major drawbacks in determining the mechanisms of in vivo reactions is that their correlation with in vitro reactions, which are readily investigated, is unknown.

(i) Singlet oxygen

Singlet oxygen has been considered as a potential intermediate in biological oxidations because of its relatively long lifetime in condensed phases and selective reactivity, which enables it to react at sites remote from its generation[131]. Singlet oxygen exhibits a high reactivity towards many materials which are important cell constituents. Until recently evidence for the participation of singlet oxygen has been based on product studies, solvent isotope effects in D_2O/H_2O and the observed effects of added quenchers of singlet oxygen, e.g. β-carotene. The ability to detect the weak luminescence of singlet oxygen has therefore represented a major advance in the determination of whether or not singlet oxygen is involved in model and/or actual biological media[132]. Unfortunately, confirmation that singlet oxygen is produced in a particular system does not neccesarily mean that it is the species responsible for the observed photodynamic activity. However, this technique has been used with model microheterogeneous aqueous systems, which mimic some aspects of cellular assemblies, to demonstrate that singlet oxygen produced from an albumin bound sensitiser can survive encounters with the protein and escape into the aqueous medium. The formation of singlet oxygen may account for such diverse phenomenon as the light sensitivity in certain porphyrias (which can be treated by oral administration of β-carotene[133]) and the hematoporphyrin sensitised destruction of tumours by red light[134]. A review of this topic[135] provides numerous examples of damage caused to plants and animals which are believed to be due to the detrimental effects of singlet oxygen.

(ii) <u>Superoxide anion</u>

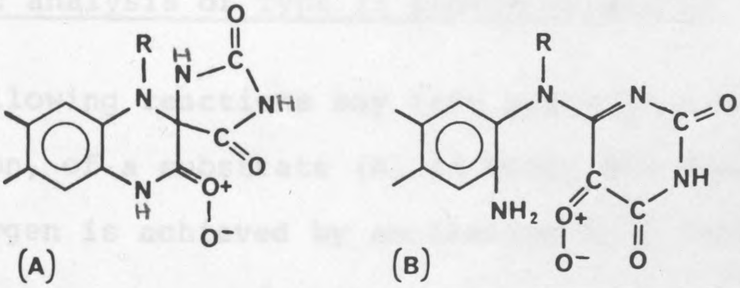
In 1969 superoxide anions were detected, by esr spectroscopy, in an enzymatic reaction involving oxygen[136]. This observation coupled with the discovery of metalloproteins which catalyse the disproportionation of superoxide anions, i.e. superoxide dismutases[137] opened up the possibility that superoxide anions may be important intermediates in aerobic life. Under biological conditions superoxide anions can be produced as a result of many reactions including the reduction of ground state oxygen by reduced flavins in oxygenated aqueous media[137,138]. Due to the inherent instability of the superoxide anion in aqueous solution $H\dot{O}_2$, $H\bar{O}_2$, H_2O_2 and $\dot{O}H$ all have to be considered as possible reactive intermediates in the many biological systems in which superoxide anions are generated. The toxicity of these secondary species may in some cases exceed that of the superoxide anion itself, e.g. $\dot{H}O_2$ and they may be instrumental in initiating radical reactions[13].

The biological function of superoxide dismutases is believed to be the protection of living cells against the toxic effects of superoxide anions. Indeed, superoxide dismutases have proved to be beneficial in the treatment of conditions ranging from radiation burns to osteoarthritis of the knee joint[139]. Sadly, irradiation of pheomelanin (the dominant melanin in the skin of red-haired people) with UV light yields superoxide anions which can lead to cell damage and possibly carcinogenisis. However, not all the effects of the superoxide anion and its derivatives are toxic, too little superoxide anion can be just as detrimental and result in conditions such as chronic granulomatous disease.

A recent conference report[139] reveals some of the scope of the superoxide anion as an initiator of biological oxidation reactions. Superoxide anions have undoubtedly superceded singlet oxygen as the in vogue oxidizing species <u>in vivo</u>.

(iii) Oxygen transfer reagents

Carbonyl oxides have received considerable attention as chemical models for mono-oxygenase enzymes which accomplish oxygen atom transfer reactions. 4α-Hydroperoxy flavins are important intermediates in oxygen activation in biochemical systems which in their free[140] or enzyme-bound states[141] are capable of oxidizing sulphides, alkenes and secondary and tertiary amines at rates exceeding those for alkyl hydroperoxides by many orders of magnitude[142]. Although the intermediates are believed to be flavin derived carbonyl oxides their exact nature, which has been the subject of some debate, remains to be resolved. For example, Mager[143] has proposed structure (A) for the above reactions whereas Keay and Hamilton[144] favour a carbonyl stabilised carbonyl oxide (B) as the intermediate in the flavoenzyme catalysed hydroxylations of phenols (Figure 5.6). The model systems



(A) (B)

Figure 5.6

have shown high reactivity and some selectivity towards alkanes, alkenes and aromatic hydrocarbons. However, evidence for their involvement in photo-oxidation reactions has relied on the negative results of tests for other oxidizing species and relative reactivities towards various substrates, which makes them difficult to identify as the reactive species in biological oxidations.

5.5.2 Conclusions

Photo-oxidation reactions can involve singlet oxygen, radical or moloxide mechanisms none of which are mutually exclusive. Elucidating which mechanisms are operative in a given reaction is rarely straightforward as the results of diagnostic tests may be ambiguous. In organic synthesis careful choice of the reaction conditions can favour one type of mechanism in order to maximize the yield of the desired products.

The importance of photo-oxidation reactions in biological systems is considerable; they are essential for the preservation of life, but in excess any oxidizing species is potentially highly toxic.

5.6 Appendix

Kinetic analysis of Type II photo-oxidations

The following reactions may take place in a photo-oxidation reaction, of a substrate (A), in which the formation of singlet oxygen is achieved by excitation of a sensitiser (S):-

$$S_{S_0} \xrightarrow{Ia} S_{S_1} \xrightarrow{k_F} S_{S_0} + h\nu$$

$$S_{S_0} \xleftarrow{k_T} S_{T_1} \xleftarrow{k_{ISC}} S_{S_1} \xrightarrow{k_{IC}} S_{S_0}$$

$$S_{T_1} + {}^3O_2 \xrightarrow{k_O} S_{S_0} + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} {}^3O_2$$

$$AO_2 \xleftarrow{k_r} {}^1O_2 + A \xrightarrow{k_q} {}^3O_2 + A$$

Scheme 5.27

The rate of disappearance of substrate is given by Equation 5.25

$$\frac{-\,d[A]}{dt} = k_r\,[A]\,[{}^1O_2] \qquad (5.25)$$

Using the steady state approximation for the singlet and triplet excited states of the sensitiser Equation 5.26 is obtained

$$[S_{T_1}] = Ia\ \phi_T\ /(k_T + [^3O_2]k_O) \tag{5.26}$$

where the quantum yield of triplets $\phi_T = k_{ISC}/(k_F + k_{IC} + k_{ISC})$.

Using the steady state approximation for singlet oxygen:-

$$[S_{T_1}]\ [^3O_2]k_O = [^1O_2]\ (k_d + [A]\ (k_q + k_r)) \tag{5.27}$$

Substituting Equation 5.26 into Equation 5.27 gives Equation 5.28.

$$[^1O_2] = \frac{Ia\ \phi_T\ [^3O_2]k_O}{(k_d + [A]\ (k_q + k_r))\ ([^3O_2]\ k_O + k_T)} \tag{5.28}$$

Provided $k_T << [^3O_2]\ k_O$ the rate of disappearance of substrate, obtained by substituting Equation 5.28 into Equation 5.25, is given by Equation 5.6.

$$\frac{-\ d[A]}{dt} = k_r\ [A]\ Ia\ \phi_T\ /\ (k_d + [A]\ (k_q + k_r)) \tag{5.6}$$

If k_r is the only rate constant which changes when a deuterated solvent is used in place of its non-deuterated counterpart the solvent isotope effect will be given by Equation 5.14.

$$\frac{-\ d[A]}{dt}\ /\ \frac{-\ d[A]_H}{dt} = \frac{k_d + [A]\ (k_q + k_r)}{k_d' + [A]\ (k_q + k_r)} \tag{5.14}$$

where k_d' = the unimolecular decay constant for singlet oxygen in the deuterated solvent.

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* JACS = J. Amer. Chem. Soc.

Tet. Letts. = Tetrahedron Letters

CHAPTER 6

DECARBOXYLATION REACTIONS OF α-KETO-CARBOXYLIC ACIDS AND ESTERS

CHAPTER 6

DECARBOXYLATION REACTIONS OF α-KETO-CARBOXYLIC ACIDS AND ESTERS

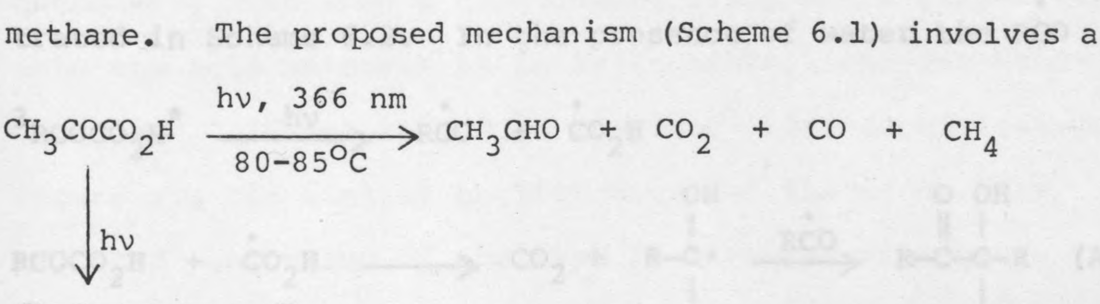
6.1 Introduction

The mechanisms of the direct and dye-sensitised photo-oxidation of α-keto-carboxylic acids have received a great deal of attention but are still the subject of controversy. By contrast α-keto-carboxylic esters have received much less attention, although there is some debate as to whether they undergo photo-induced fragmentation via a Norrish Type I or Type II process.

6.2 Photo-induced decarboxylation of α-keto-carboxylic acids

6.2.1 Introduction

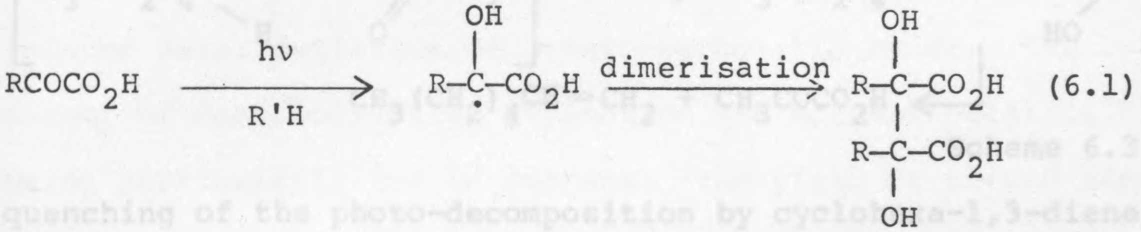
In 1964 Vesley and Leermakers[1] reported that the vapour phase photo-oxidation of pyruvic acid yielded carbon dioxide, quantitatively, and trace amounts of carbon monoxide and methane. The proposed mechanism (Scheme 6.1) involves a



Scheme 6.1

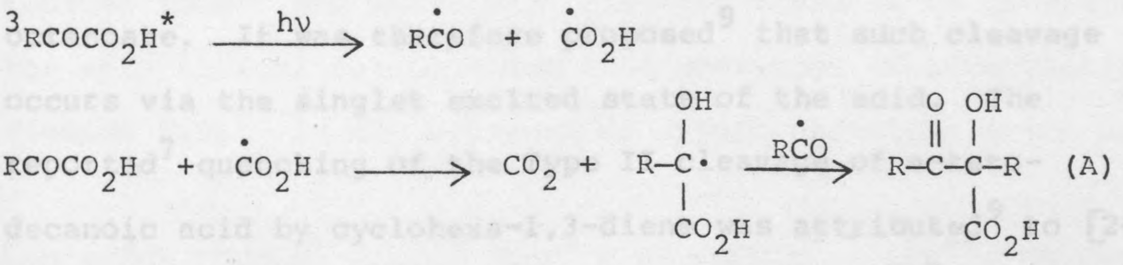
concerted transition state in which hydrogen bonding is maximised. Rearrangement of the intermediate hydroxy carbene could give rise to the observed production of acetaldehyde.

Photo-reduction is an important pathway for the decomposition of pyruvic[2a-c] and other α-keto-carboxylic acids[3] in deoxygenated hydrogen-donating solvents. Reaction is believed to occur via intermediate ketyl radicals, identified by esr spectroscopy[4], which dimerise to yield derivatives of tartaric acid (Equation 6.1). CIDNP studies[5] suggested that the triplet state is responsible for the photo-reduction of pyruvic acid by ethanol in acetonitrile solution because naphthalene, a known triplet quencher, inhibited the formation of ketyl radicals[5].



$$RCOCO_2H \xrightarrow[R'H]{h\nu} R-\overset{OH}{\underset{\bullet}{C}}-CO_2H \xrightarrow{\text{dimerisation}} \begin{array}{l} R-\overset{OH}{C}-CO_2H \\ R-\underset{OH}{C}-CO_2H \end{array} \quad (6.1)$$

In non-reducing polar solvents decarboxylation of α-keto-carboxylic acids has been proposed[2a-c] to take place via Norrish Type I cleavage[6] (unimolecular cleavage of the carbonyl-carboxy bond) of the triplet excited acid as illustrated in Scheme 6.2. In the presence of water the $R\dot{C}O$ radical may abstract a hydrogen atom to yield the corresponding aldehyde, e.g. as observed in the decarboxylation of phenylglyoxylic acid[2b], or the product (A) can undergo acid catalysed hydrolysis, e.g. pyruvic acid undergoes



$$^3RCOCO_2H^* \xrightarrow{h\nu} R\dot{C}O + \dot{C}O_2H$$

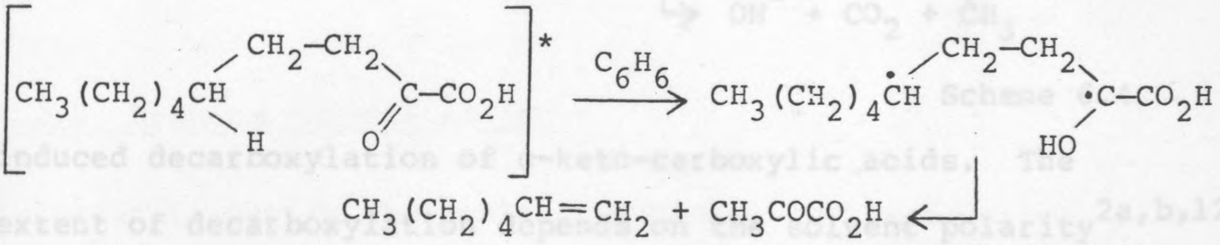
$$RCOCO_2H + \dot{C}O_2H \longrightarrow CO_2 + R-\overset{OH}{\underset{CO_2H}{C}}\bullet \xrightarrow{R\dot{C}O} R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CO_2H}{C}}-R \quad (A)$$

where R = alkyl or aryl

Scheme 6.2

photo-induced decarboxylation in aqueous solution to yield acetoin as the major product[2a,b].

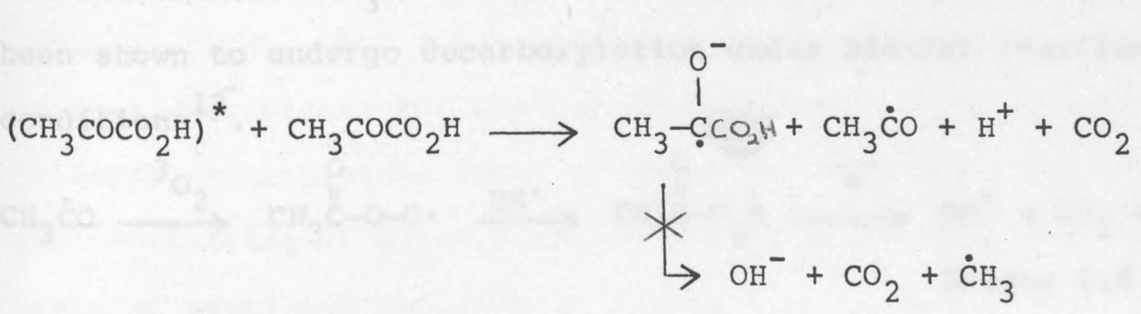
For long-chain α-keto-carboxylic acids the possibility arises that they can undergo Norrish Type II elimination[6,7] as illustrated for α-keto-decanoic acid in Scheme 6.3. Observed[7]



Scheme 6.3

quenching of the photo-decomposition by cyclohexa-1,3-diene led to the proposal that the entire reaction occurs via the triplet excited α-keto-decanoic acid - in contrast to aliphatic ketones which undergo Norrish Type II reactions via both their singlet and triplet excited states[8]. However, Davidson and co-workers[9] have observed that the Norrish Type II cleavage of α-keto-octanoic acid is insensitive to the presence of oxygen and naphthalene, which are known triplet quenchers, even when a naphthalene group was incorporated into the acid molecule as in 2-(2-naphthyl)ethyl-α-keto-octanoate. It was therefore proposed[9] that such cleavage occurs via the singlet excited state of the acid. The reported[7] quenching of the Type II cleavage of α-keto-decanoic acid by cyclohexa-1,3-diene was attributed[9] to [2+2] cycloaddition between the diene and the singlet excited α-keto-carboxylic acids. For those α-keto-carboxylic acids which undergo Norrish Type II cleavage, decarboxylation of the resultant pyruvic acid is thought to be responsible for the observed carbon dioxide production[10].

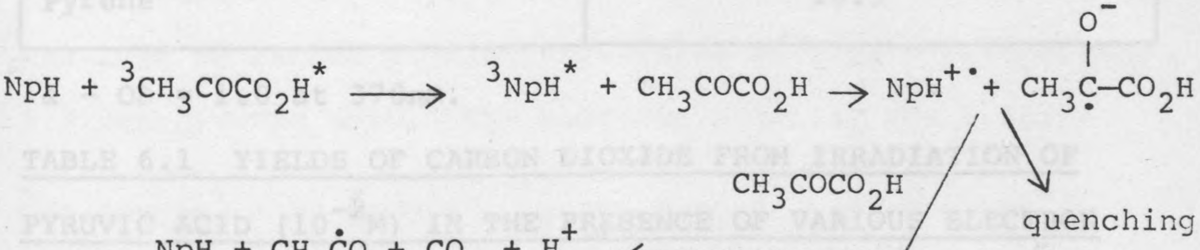
Evidence has been accumulating[11,12] in favour of a bimolecular electron transfer mechanism (Scheme 6.4) for the direct photo-induced decarboxylation of α-keto-carboxylic acids. The extent of decarboxylation depends on the solvent polarity[2a,b,12], being particularly low in benzene. The yield of carbon dioxide when benzene is used as the solvent can be enhanced by the addition of pyridine, which can aid radical ion formation. Use of ^{14}C labelled pyruvic acid[9] revealed that decarboxylation, in degassed solution, only occurs from the C_1 position of this α-keto-carboxylic acid. The presence of the triplet quencher, naphthalene, has been found[11] to enhance the carbon dioxide production from irradiation of α-keto-carboxylic acids. A mechanism has been proposed which involves quenching of the triplet acid by naphthalene to yield radical ions[11] and subsequent electron transfer to generate the acid radical cation which then undergoes decarboxylation (Scheme 6.5). In the presence of oxygen, decarboxylation occurs from both the C_1 and C_2 positions of pyruvic acid[9]. The second mole of carbon dioxide is believed to emanate from the



$$(CH_3COCO_2H)^* + CH_3COCO_2H \longrightarrow CH_3-\overset{O^-}{\underset{\bullet}{C}}CO_2H + CH_3\dot{C}O + H^+ + CO_2$$

$$\not\longrightarrow OH^- + CO_2 + \dot{C}H_3$$

Scheme 6.4

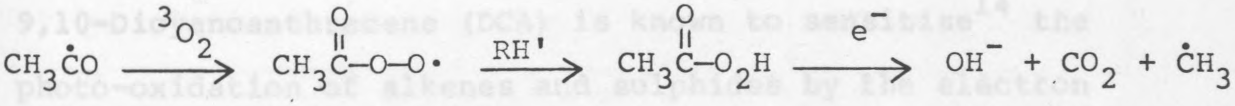


$$NpH + {}^3CH_3COCO_2H^* \longrightarrow {}^3NpH^* + CH_3COCO_2H \rightarrow NpH^{+\bullet} + CH_3\overset{O^-}{\underset{\bullet}{C}}-CO_2H$$

$$NpH^{+\bullet} \xrightarrow{CH_3COCO_2H} NpH + CH_3\dot{C}O + CO_2 + H^+$$

Scheme 6.5

decomposition of per-acids formed from oxygen scavenging of the intermediate $CH_3\dot{C}O$ radicals (Scheme 6.6). Per-acids have been shown to undergo decarboxylation under similar reaction conditions[13].



$$CH_3\dot{C}O \xrightarrow{^3O_2} CH_3\overset{O}{\overset{\|}{C}}\text{—}O\text{—}O\cdot \xrightarrow{RH'} CH_3\overset{O}{\overset{\|}{C}}\text{—}O_2H \xrightarrow{e^-} OH^- + CO_2 + \dot{C}H_3$$

Scheme 6.6

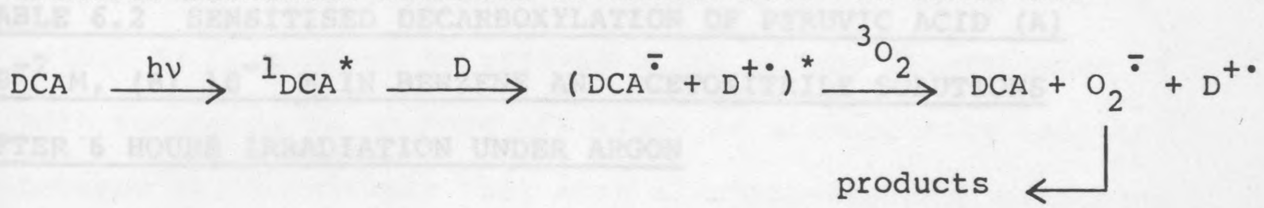
6.2.2 Results and discussion

In order to verify the mechanism leading to the decarboxylation of α-keto-carboxylic acids, in degassed solution, the effects of added electron acceptors upon the decarboxylation of pyruvic acid were determined. The results in Table 6.1 reveal that photo-decarboxylation of pyruvic acid in acetonitrile solution is markedly enhanced in the presence of a wide range

ELECTRON ACCEPTOR	YIELD OF CARBON DIOXIDE (%)
None	17.7
1-Cyanonaphthalene	28.0
Dichlorodicyanobenzoquinone	20.9
9,10-Dicyanoanthracene[a]	43.0
Tetracyanoethylene	37.6
Pyrene	18.5

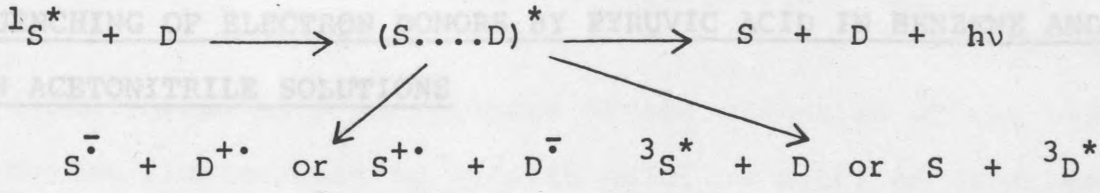
a - OD = 1.0 at 370nm.

TABLE 6.1 YIELDS OF CARBON DIOXIDE FROM IRRADIATION OF PYRUVIC ACID (10^{-2}M) IN THE PRESENCE OF VARIOUS ELECTRON ACCEPTORS (10^{-2}M) IN ACETONITRILE SOLUTION, UNDER ARGON, FOR 4 HOURS of electron acceptors. The concentrations of the electron acceptors are such that they preferentially absorb the incident light. The electron acceptors are therefore being used as sensitisers for the decarboxylation of pyruvic acid. 9,10-Dicyanoanthracene (DCA) is known to sensitise[14] the photo-oxidation of alkenes and sulphides by the electron transfer mechanism outlined in Scheme 6.7. In order for electron donors to sensitise the decarboxylation of pyruvic acid, in degassed solution, the acid must be capable of quenching the singlet excited sensitiser. The intermediate exciplex can decay via radiative and/or non-radiative processes, the latter may result in the formation of radical ions or triplets, as oultined in Scheme 6.8. A summary of the other decay routes open to exciplexes can be found in Chapter 2. Generation of the triplet excited acid or its radical cation can lead to carbon dioxide production as outlined in Scheme 6.9 for pyruvic acid. The electron affinity and triplet



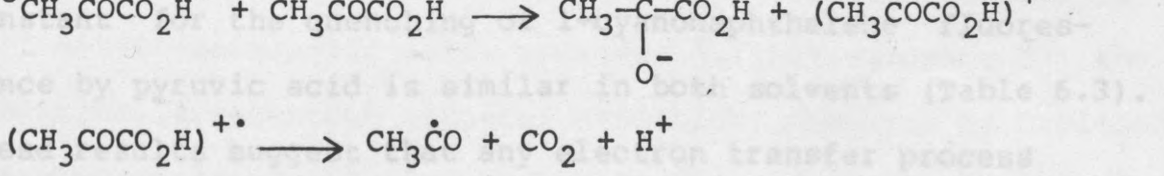
$$DCA \xrightarrow{h\nu} {}^{1}DCA^{*} \xrightarrow{D} (DCA^{\overline{\cdot}} + D^{+\cdot})^{*} \xrightarrow{{}^{3}O_2} DCA + O_2^{\overline{\cdot}} + D^{+\cdot} \rightarrow \text{products}$$

Scheme 6.7



$$
\begin{aligned}
{}^{1}S^{*} + D &\longrightarrow (S....D)^{*} \longrightarrow S + D + h\nu \\
(S....D)^{*} &\longrightarrow S^{\overline{\cdot}} + D^{+\cdot} \text{ or } S^{+\cdot} + D^{\overline{\cdot}} \\
(S....D)^{*} &\longrightarrow {}^{3}S^{*} + D \text{ or } S + {}^{3}D^{*}
\end{aligned}
$$

Scheme 6.8



$$
\begin{aligned}
{}^{3}CH_3COCO_2H^{*} + CH_3COCO_2H &\longrightarrow CH_3\!-\!\dot{C}(O^{-})\!-\!CO_2H + (CH_3COCO_2H)^{+\cdot} \\
(CH_3COCO_2H)^{+\cdot} &\longrightarrow CH_3\dot{C}O + CO_2 + H^{+}
\end{aligned}
$$

Scheme 6.9

SENSITISER 10^{-2} M	YIELD OF CARBON DIOXIDE (%)			
	C_6H_6 (A)	CH_3CN	C_6H_6 (B)	CH_3CN
None	15.8	18.9	4.7	16.0[b]
1-Cyanonaphthalene	52.6	28.0	21.0	10.3
2,6-Dimethylnaphthalene	*a*	*a*	34.5	7.3[b]

a - not determined *b* - reference 11

TABLE 6.2 SENSITISED DECARBOXYLATION OF PYRUVIC ACID (A) 10^{-2} M, (B) 10^{-1} M IN BENZENE AND ACETONITRILE SOLUTIONS AFTER 6 HOURS IRRADIATION UNDER ARGON

ELECTRON DONOR	K_{SV} (M^{-1})	
	C_6H_6	MeCN
1-Cyanonaphthalene	187	185
2,6-Dimethylnaphthalene	500	485

TABLE 6.3 STERN-VOLMER CONSTANTS (K_{SV}) FOR THE FLUORESCENCE QUENCHING OF ELECTRON DONORS BY PYRUVIC ACID IN BENZENE AND IN ACETONITRILE SOLUTIONS

energy of the sensitiser as well as the polarity of the solvent will determine the relative importance of the decay routes open to the sensitiser/α-keto-carboxylic acid exciplex. 1-Cyanonaphthalene sensitises the photo-oxidation of pyruvic acid far more effectively in benzene than in acetonitrile solution (Table 6.2), whereas the Stern-Volmer constant for the quenching of 1-cyanonaphthalene fluorescence by pyruvic acid is similar in both solvents (Table 6.3). These results suggest that any electron transfer process between pyruvic acid and the aromatic hydrocarbons leads to a decrease in the efficiency of decarboxylation. As the pyruvate radical cation can undergo decarboxylation, but the corresponding radical anion cannot, it would appear that the combination of ($S^{+\cdot}$ and $D^{\overline{\cdot}}$) is more stable than ($S^{\overline{\cdot}}$ and $D^{+\cdot}$) in acetonitrile solution. The fluorescence of 2,6-dimethylnaphthalene, which is a stronger electron acceptor than 1-cyanonaphthalene, is more effectively quenched by pyruvic acid. As quenching, by pyruvic acid, of the fluorescence of both compounds is no more efficient in acetonitrile than in benzene it is unlikely that much electron-transfer quenching is taking place in addition to energy transfer quenching. The possibility therefore arises that the electron transfer reaction occurs from the triplet state of the pyruvic acid (generated by inter-system crossing of the singlet excited state formed as a consequence of the quenching of the hydrocarbon fluorescence by pyruvic acid) as outlined in Scheme 6.10.

$$\begin{tikzcd}
{}^{1}S^{*} + CH_3COCO_2H \arrow[r, "\text{energy}", "\text{transfer}"'] & S + {}^{1}CH_3COCO_2H^{*} \arrow[r, "ISC"] & {}^{3}CH_3COCO_2H^{*} \arrow[dl, "S"] \\
 & S^{+\cdot} + ({}^{3}CH_3COCO_2H)^{\overline{\cdot}} &
\end{tikzcd}$$

Scheme 6.10

Naphthalene is known[12] to quench the fluorescence of pyruvic acid by an electron transfer process and has a similar triplet energy to 2,6-dimethylnaphthalene and 1-cyanonaphthalene.

6.2.3 Conclusions

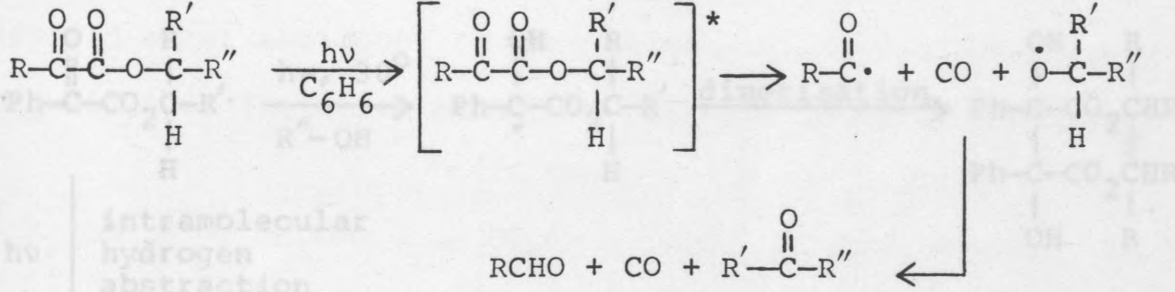
The finding that electron acceptors can promote decarboxylation of α-keto-carboxylic acids provides further evidence for the bimolecular electron transfer mechanism, proposed by Davidson and co-workers[11,12], for the photo-induced fragmentation of these compounds.

6.3 Photo-induced decarboxylation of α-keto-carboxylic esters

6.3.1 Introduction

In 1965 Leermakers and co-workers[15] reported that ethyl and isopropyl pyruvates undergo decarboxylation in the gas phase to yield acetaldehyde and acetone respectively as the major products (Equation 6.2). In solution the photochemical reactions of α-keto-carboxylic esters are markedly dependent upon the reaction conditions. Evidence has accumulated[16,17] in favour of the excited triplet state of the ester being responsible for the observed decomposition. Leermakers and co-workers[17], on the basis of the absence of deuterium isotope effects, have proposed that the primary reaction involves photodecarbonylation as illustrated in Scheme 6.11. This radical mechanism has received support from Tominaga and co-workers[18] who studied the decarbonylation of ethyl phenylglyoxylate. These reactions have proved to be of use in synthetic organic chemistry for the conversion of alcohols to ketones[19] as illustrated for the conversion of menthol to menthone in Scheme 6.12.

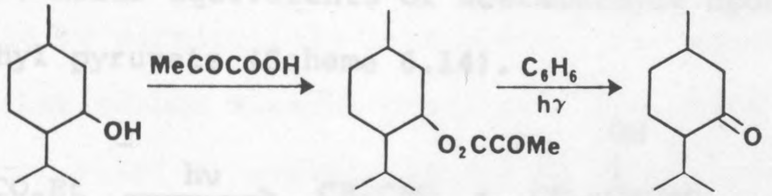
$$CH_3COCO_2R \xrightarrow[55^{\circ}C]{h\nu} CH_3\dot{C}O + CO + \dot{O}R \qquad (6.2)$$



where R = alkyl, aryl

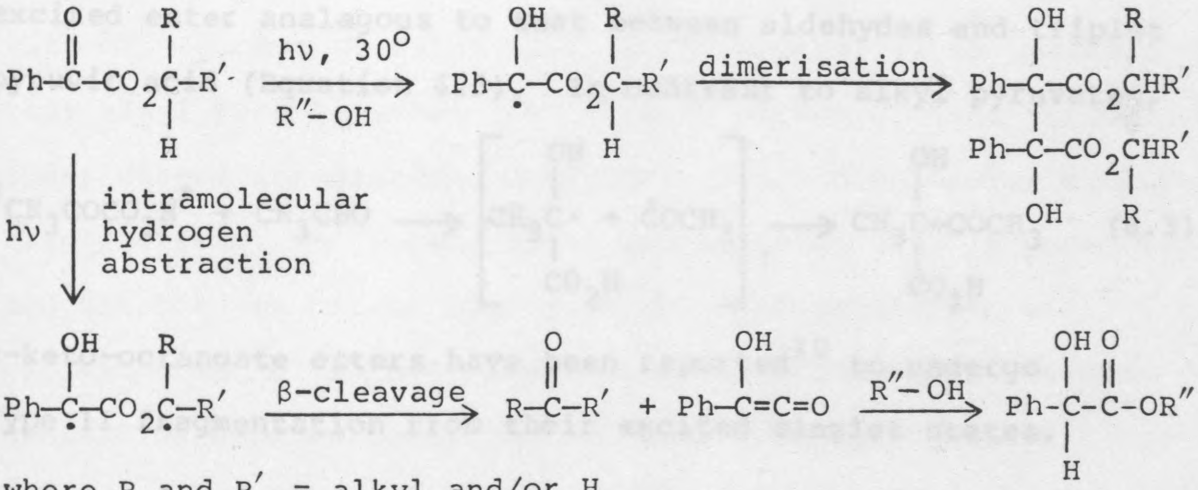
R′ and R″ = alkyl and or hydrogen

Scheme 6.11



Scheme 6.12

By analogy with the α-keto-carboxylic acids it has been found that the corresponding esters undergo intermolecular hydrogen abstraction in hydrogen donating solvents[20,21]. Huyser and Neckers[20] found a temperature dependency upon the nature of the products formed as a result of photolysis of a range of alkyl esters of phenylglyoxylic acid in alcoholic solvents. At low temperatures intermolecular hydrogen abstraction resulted in reductive dimerisation, whereas at higher temperatures intramolecular hydrogen abstraction, followed by β-cleavage, leads to hydroxy ketene formation (Scheme 6.13). Isolation of products[21] which can be attributed to trapping of hydroxy ketenes, by the solvent, have provided evidence for the involvement of these species. Photolytic decarbonylation of an intermediate hydroxy ketene has been proposed to account for the generation of carbon monoxide



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CO_2\underset{H}{\overset{R}{C}}{-}R'} \xrightarrow[R''-OH]{h\nu,\ 30^{o}} \mathrm{Ph{-}\overset{OH}{\dot{C}}{-}CO_2\underset{H}{\overset{R}{C}}{-}R'} \xrightarrow{\text{dimerisation}} \begin{array}{l}\mathrm{Ph{-}\overset{OH}{C}{-}CO_2\overset{R}{C}HR'}\\ \quad | \\ \mathrm{Ph{-}\underset{OH}{C}{-}CO_2\underset{R}{C}HR'}\end{array}$$

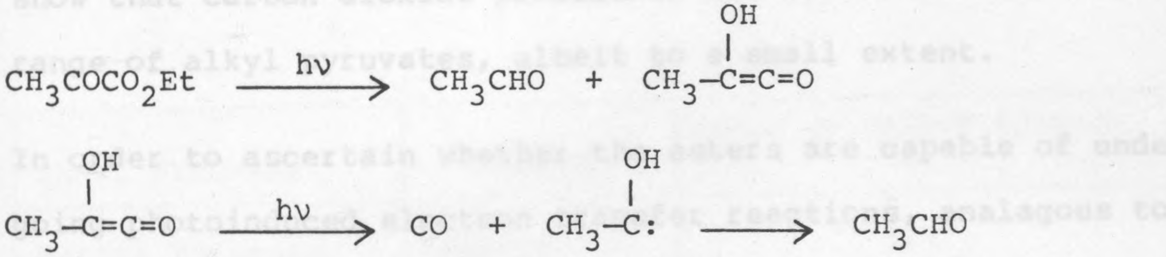
$$\Big\downarrow\ h\nu\ \text{intramolecular hydrogen abstraction}$$

$$\mathrm{Ph{-}\overset{OH}{\dot{C}}{-}CO_2\overset{R}{\dot{C}}{-}R'} \xrightarrow{\beta\text{-cleavage}} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}R'} + \mathrm{Ph{-}\overset{OH}{C}{=}C{=}O} \xrightarrow{R''-OH} \mathrm{Ph{-}\underset{H}{\overset{OH}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OR''}$$

where R and R′ = alkyl and/or H
R″ = ethyl or s-butyl

Scheme 6.13

and two molar equivalents of acetaldehyde upon irradiation of ethyl pyruvate (Scheme 6.14).

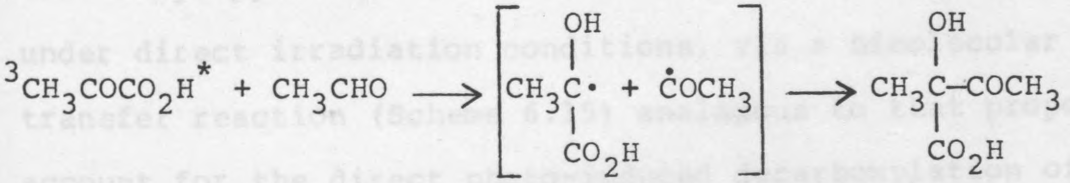


$$\mathrm{CH_3COCO_2Et} \xrightarrow{h\nu} \mathrm{CH_3CHO} + \mathrm{CH_3{-}\overset{OH}{\overset{|}{C}}{=}C{=}O}$$

$$\mathrm{CH_3{-}\overset{OH}{\overset{|}{C}}{=}C{=}O} \xrightarrow{h\nu} \mathrm{CO} + \mathrm{CH_3{-}\overset{OH}{\overset{|}{C}}{:}} \longrightarrow \mathrm{CH_3CHO}$$

Scheme 6.14

Davidson and Goodwin[23] have determined the relative abilities of a range of alkyl pyruvates to undergo photo-induced fragmentation and concluded that these compounds fragment from the triplet state via a Type II and not a Type I process. t-Butyl pyruvate was found to be photostable even though it has a substantially longer triplet lifetime than the photolabile methyl, ethyl, isopropyl and benzyl pyruvates. The low yield of aldehydes from methyl, ethyl and benzyl pyruvates was attributed to reaction of the aldehydes with the triplet excited ester analagous to that between aldehydes and triplet pyruvic acid (Equation 6.3). In contrast to alkyl pyruvates,



$$^{3}\mathrm{CH_3COCO_2H}^{*} + \mathrm{CH_3CHO} \longrightarrow \left[\mathrm{CH_3}\underset{\mathrm{CO_2H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot + \dot{\mathrm{C}}\mathrm{OCH_3}\right] \longrightarrow \mathrm{CH_3}\underset{\mathrm{CO_2H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{-}COCH_3} \qquad (6.3)$$

α-keto-octanoate esters have been reported[10] to undergo Type II fragmentation from their excited singlet states.

6.3.2 Results and discussion

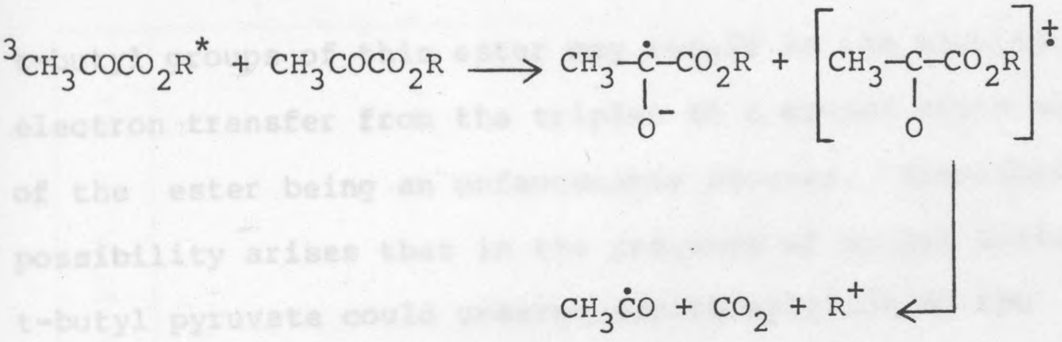
As it has been established that the photoinduced fragmentation of alkyl pyruvates occurs via a Type II process[23] the finding by Hammond and co-workers[16] that irradiation of ethyl pyruvate, in benzene solution, gives rise to small amounts of carbon dioxide is particularly intriguing. The results in Table 6.4 show that carbon dioxide production was found to occur for a range of alkyl pyruvates, albeit to a small extent.

In order to ascertain whether the esters are capable of undergoing photoinduced electron transfer reactions, analagous to those already discussed for the parent α-keto-carboxylic acids, irradiations of several alkyl pyruvates were carried out in the presence of methyl viologen (MV^{2+}). In all cases[13,24] reduced methyl viologen ($MV^{+\cdot}$) was produced and readily characterised by its absorption spectrum. Laser flash photolysis studies indicated that $MV^{+\cdot}$ is not predominantly produced, in the presence of methyl pyruvate, by the reaction of MV^{2+} with the excited states of methyl pyruvate[13]. Although the production of $MV^{+\cdot}$ suggests that alkyl pyruvates must be capable of undergoing electron transfer reactions, formation of $MV^{+\cdot}$ by reaction of a photogenerated biradical with MV^{2+} cannot be ruled out. Consequently, it is possible that alkyl pyruvates can give rise to carbon dioxide production, under direct irradiation conditions, via a bimolecular electron transfer reaction (Scheme 6.15) analagous to that proposed to account for the direct photo-induced decarboxylation of pyruvic acid[12]. Such a mechanism could account for the concentration dependence of the lifetime of triplet methyl pyruvate, which has a self quenching rate constant of ~2 x 10^7 l mol^{-1} s^{-1} in acetonitrile solution[24].

ALKYL PYRUVATE	SOLVENT	YIELD OF CARBON DIOXIDE (%)
Methyl pyruvate	benzene	5.3
Methyl pyruvate	acetonitrile	7
Ethyl pyruvate	acetonitrile	9
Isopropyl pyruvate	acetonitrile	11
t-Butyl pyruvate	benzene	0
t-Butyl pyruvate	acetonitrile	0
n-Hexyl pyruvate[a]	acetonitrile	7

a - 5 x 10^{-2}M, 3 hours irradiation

TABLE 6.4 YIELDS OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION OF ALKYL PYRUVATES (10^{-2}M) FOR 6 HOURS IN DEGASSED SOLUTION



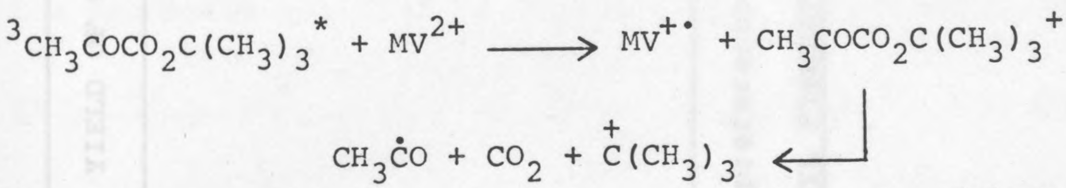
$$ {}^{3}CH_3COCO_2R^{*} + CH_3COCO_2R \longrightarrow CH_3-\underset{\textstyle O^-}{\underset{|}{\dot{C}}}-CO_2R + \left[CH_3-\underset{\textstyle O}{\underset{|}{C}}-CO_2R \right]^{+\cdot} \longrightarrow CH_3\dot{C}O + CO_2 + R^+ $$

where R = CH_3, C_2H_5 or $(CH_3)_2CH$ Scheme 6.15

Although reaction from the excited singlet state cannot be rigorously excluded alkyl pyruvates have low quantum yields of fluorescence and short fluorescence lifetimes and consequently these bimolecular reactions are far more likely to occur from the triplet state[21]. The finding by Hammond and co-workers[16] that benzophenone sensitises carbon dioxide formation from ethyl pyruvate strongly suggests that the triplet state of the ester is responsible for the observed decarboxylation.

The bimolecular electron transfer process illustrated in Scheme 6.14 will be in direct competition with the Type II fragmentation for the degradation of the alkyl pyruvates. The finding that irradiation of n-hexyl pyruvate, in degassed acetonitrile solution, yields both hexanol, via Type II fragmentation, and carbon dioxide illustrates the competition between the two pathways for the degradation of alkyl pyruvates[13].

t-Butyl pyruvate cannot fragment via a Type II process[23] and does not give rise to carbon dioxide production upon direct irradiation[24]. However, t-butyl pyruvate, like the other alkyl pyruvates, was found to be capable of reducing MV^{2+} to $MV^{+\cdot}$ upon irradiation[25]. Steric hindrance by the bulky t-butyl groups of this ester may result in the bimolecular electron transfer from the triplet to a ground state molecule of the ester being an unfavourable process. Therefore, the possibility arises that in the presence of methyl viologen t-butyl pyruvate could undergo decarboxylation by the mechanism outlined in Scheme 6.16. Examination of Table 6.5



$$^{3}CH_3COCO_2C(CH_3)_3^{\,*} + MV^{2+} \longrightarrow MV^{+\bullet} + CH_3COCO_2C(CH_3)_3^{\,+\bullet}$$

$$CH_3\dot{C}O + CO_2 + \overset{+}{C}(CH_3)_3 \longleftarrow$$

Scheme 6.16

reveals that the addition of methyl viologen to a solution of t-butyl pyruvate resulted in decarboxylation taking place upon irradiation. Enhancement of carbon dioxide production was also observed when methyl pyruvate was irradiated in the presence of methyl viologen.

If the bimolecular electron transfer mechanism proposed in Scheme 6.14 is to be considered feasible it should be possible to use electron acceptors as sensitisers for the photo-

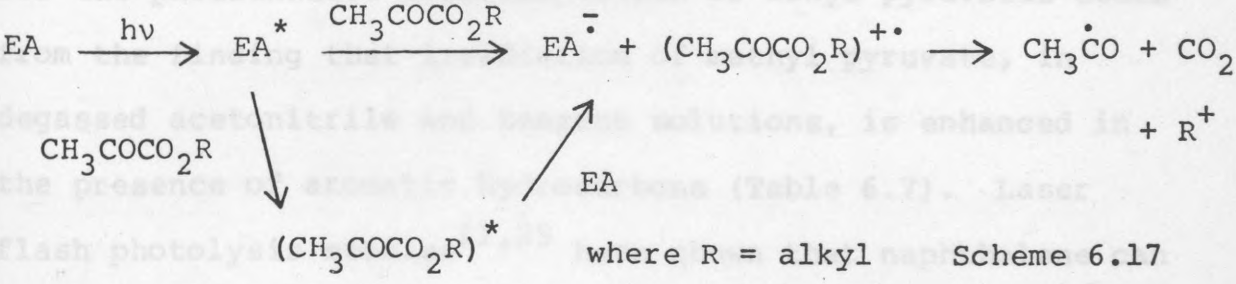
ALKYL PYRUVATE	SOLVENT	YIELD OF CARBON DIOXIDE (%) (A)	(B)
Methyl pyruvate	CH_3CN/H_2O (9:1 v/v)	19	12
t-Butyl pyruvate	CH_3CN/pyridine/H_2O (8:1:1 v/v)	11.4	0

TABLE 6.5 REPORTED YIELDS[13] OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION, FOR 6 HOURS, OF ALKYL PYRUVATES (10^{-2}M) IN DEGASSED SOLUTIONS IN THE PRESENCE (A) AND ABSENCE (B) OF MV^{2+} (10^{-2}M)

ALKYL PYRUVATE	ELECTRON ACCEPTOR	SOLVENT	YIELD OF CARBON DIOXIDE (%)
Methyl pyruvate	1-cyanonaphthalene	benzene	21.5
" "	"	acetonitrile	15.2
" "	dichlorodicyanobenzoquinone	"	11.8
" "	9,10-dicyanoanthracene[a]	"	11.6
" "	tetracyanoethylene	"	12.8
Isopropyl pyruvate	1-cyanonaphthalene	"	23.6
t-Butyl pyruvate	1-cyanonaphthalene	"	14.6
" "	9,10-dicyanoanthracene[a]	"	7.7

a - OD = 1.0 at 370nm in order that it absorbs the incident light in preference to the alkyl pyruvate

TABLE 6.6 YIELDS OF CARBON DIOXIDE AFTER SIX HOURS IRRADIATION OF ALKYL PYRUVATES (10^{-2}M) IN DEGASSED SOLUTIONS CONTAINING ELECTRON ACCEPTORS (10^{-2}M) induced decarboxylation of alkyl pyruvates. Accordingly, irradiations of degassed solutions of electron acceptors containing alkyl pyruvates were performed and the yields of carbon dioxide produced are given in Table 6.6. The observed decarboxylation of the alkyl pyruvates in the presence of electron acceptors (EA) can be rationalised on the basis of the mechanism outlined in Scheme 6.17. As the methyl pyruvate



Scheme 6.17

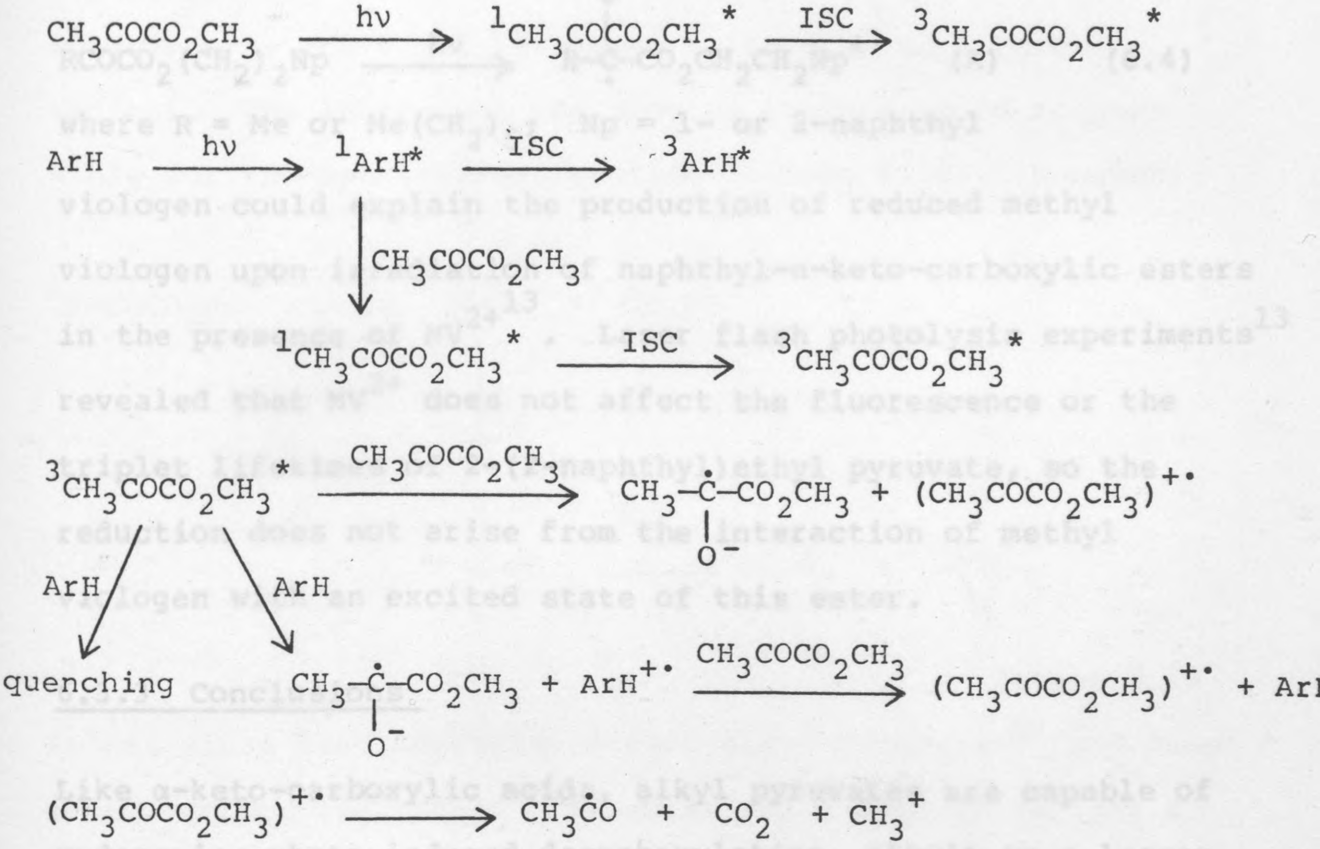
AROMATIC HYDROCARBON	LIGHT ABSORBED[a] (%)	YIELD OF CARBON DIOXIDE (%)	
		C_6H_6	CH_3CN
None		5.3	7.0
Biphenyl	0	11.4	20.9
9,10-dimethylanthracene	100	13.4	22.3
2,6-dimethylnaphthalene	25	7.1	17.5
Naphthalene	7	10.4	12.0
Phenanthrene	70	11.6	11.8
Pyrene	93	*b*	10.2

a - percentage of incident light absorbed by the additive in each case, prior to irradiation.

b - not determined

TABLE 6.7 YIELDS OF CARBON DIOXIDE AFTER 6 HOURS IRRADIATION OF METHYL PYRUVATE (10^{-2}M) IN BENZENE AND ACETONITRILE SOLUTIONS CONTAINING VARIOUS AROMATIC HYDROCARBONS (10^{-2}M), UNDER DEGASSED CONDITIONS quenches the fluorescence of 1-cyanonaphthalene ($k_q = 14.4 \times 10^9\ M^{-1}\ s^{-1}$ in acetonitrile, $k_q = 7.9 \times 10^9\ M^{-1}\ s^{-1}$ in benzene) the electron transfer may either occur directly, from the ester to the excited electron acceptor, or indirectly via the excited ester (Scheme 6.1).

Further evidence in support of an electron transfer mechanism for the photoinduced decarboxylation of alkyl pyruvates comes from the finding that irradiation of methyl pyruvate, in degassed acetonitrile and benzene solutions, is enhanced in the presence of aromatic hydrocarbons (Table 6.7). Laser flash photolysis studies[11,25] have shown that naphthalene can quench the triplet state of methyl pyruvate with the resultant formation of triplet naphthalene. As a consequence the presence of naphthalene would be predicted to quench the decarboxylation of methyl pyruvate which takes place upon irradiation. The observed enhancement of carbon dioxide production in the presence of naphthalene (Table 6.7) therefore suggests the involvement of an electron transfer reaction which leads to carbon dioxide production. The finding that the addition of what should be a quencher for a reaction can lead to enhanced carbon dioxide formation, via electron transfer reactions, is not unique. Such a phenomenon was also observed in the photoinduced decarboxylation of α-keto-carboxylic acids (see Section 6.2.2). It was also found that methyl pyruvate quenches the fluorescence of 2,6-dimethylnaphthalene, the Stern-Volmer constants being 381 M^{-1} and 447 M^{-1} in benzene and acetonitrile solutions respectively. Consequently, the following reactions have to be considered in order to explain the observed decarboxylation of alkyl pyruvates in the presence of aromatic hydrocarbons (Scheme 6.18).



Scheme 6.18

The ester illustrated in Figure 6.1 undergoes photo-induced decarboxylation under the same conditions as the esters in Table 6.4 to yield carbon dioxide in 12.2% yield. For this ester the carboxyl and naphthalene groups are ideally situated for the triplet state of the carboxyl group to be deactivated by the naphthalene moiety and the singlet state of the naphthalene group deactivated by the carboxyl group[10]. Some deactivation via an intramolecular electron transfer

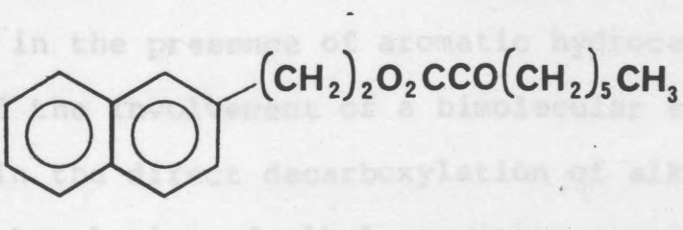
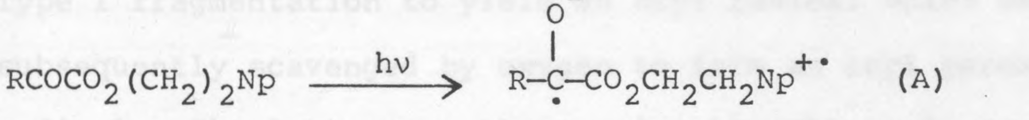


Figure 6.1

process as well as energy transfer is also a possibility (Equation 6.4). The interaction of species (A) with methyl



$$\mathrm{RCOCO_2(CH_2)_2Np} \xrightarrow{h\nu} \mathrm{R{-}\underset{\bullet}{\overset{O^-}{C}}{-}CO_2CH_2CH_2Np^{+\bullet}} \quad (A) \qquad (6.4)$$

where R = Me or Me$(CH_2)_5$; Np = 1- or 2-naphthyl

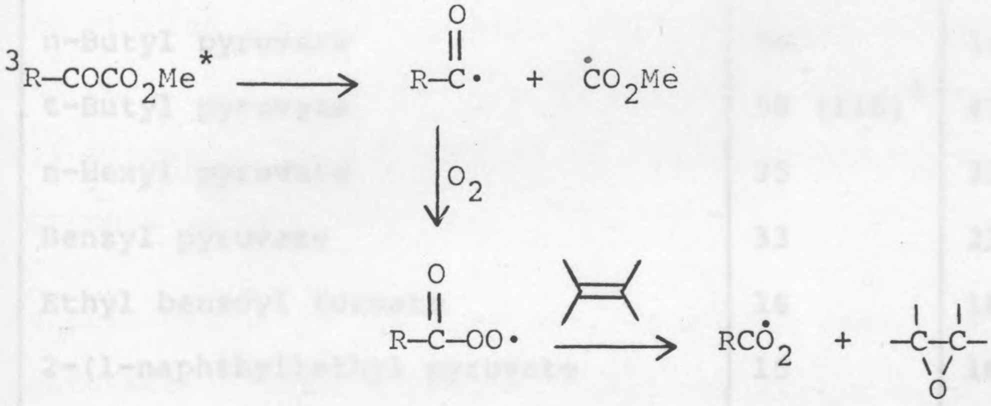
viologen could explain the production of reduced methyl viologen upon irradiation of naphthyl-α-keto-carboxylic esters in the presence of MV^{2+}[13]. Laser flash photolysis experiments[13] revealed that MV^{2+} does not affect the fluorescence or the triplet lifetimes of 2-(2-naphthyl)ethyl pyruvate, so the reduction does not arise from the interaction of methyl viologen with an excited state of this ester.

6.3.3 Conclusions

Like α-keto-carboxylic acids, alkyl pyruvates are capable of undergoing photo-induced decarboxylation, albeit to a lesser extent, under degassed conditions. The observation that such decarboxylation can be sensitised by electron acceptors and enhanced in the presence of aromatic hydrocarbons is indicative of the involvement of a bimolecular electron transfer process in the direct decarboxylation of alkyl pyruvates. The decarboxylation of alkyl pyruvates represents a minor route for fragmentation and is in competition with the Type II reaction for the degradation of these esters.

6.4 Photo-oxidative decarboxylation of α-keto-carboxylic esters

The only report pertaining to the effect of oxygen upon the photo-reactions of α-keto-carboxylic esters in solution concerns the epoxidation of α-methylstyrene by methyl phenylglyoxylate[26]. It was proposed that the ester underwent a Type I fragmentation to yield an acyl radical which was subsequently scavenged by oxygen to form an acyl peroxy radical. The latter was the species thought to be responsible for the epoxidation reaction (Scheme 6.19). However, it has since been appreciated that alkyl pyruvates[23] and other α-keto-carboxylic esters[10] fragment via a Type II and not a Type I process. Consequently, the mechanism of the interaction of oxygen with α-keto-carboxylic esters which leads to carbon dioxide production is of particular interest.



Scheme 6.19

6.4.1 Results and discussion

A wide variety of α-keto-carboxylic esters were found to undergo direct photo-oxidative decarboxylation in oxygenated acetonitrile and benzene solutions (Table 6.8). There are a variety of ways in which oxygen may interact with α-keto-carboxylic esters. For those esters capable of undergoing a Type II fragmentation reaction, oxygen could intercept the intermediate 1,4-biradical[27] to yield a product which collapses to give carbon dioxide. The high yield of hexaldehyde formed via Type II fragmentation of n-hexyl pyruvate on irradiation

α-KETO-CARBOXYLIC ESTER	YIELD OF CARBON DIOXIDE (%)	
	CH_3CN	C_6H_6
Methyl pyruvate	37 (83) [a]	34 (59) [a]
Ethyl pyruvate	63	54
Isopropyl pyruvate	46	23
n-Butyl pyruvate	20	19
t-Butyl pyruvate	58 (116) [b]	47 (82) [b]
n-Hexyl pyruvate	35	33
Benzyl pyruvate	33	23
Ethyl benzoyl formate	16	18
2-(1-naphthyl)ethyl pyruvate	15	18.5
2-(2-naphthyl)ethyl pyruvate	21	11
2-(2-naphthyl)ethyl-α-oxo-octanoate	17	17

a - 20 hours irradiation *b* - 18 hours irradiation

TABLE 6.8 YIELDS OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION OF α-KETO-CARBOXYLIC ESTERS (10^{-2}M), UNDER OXYGEN, IN ACETONITRILE AND BENZENE SOLUTIONS FOR 3 HOURS

CONDITIONS	YIELD OF CARBON DIOXIDE (%)
9,10-Dicyanoanthracene absent	50
9,10-Dicyanoanthracene present	38

TABLE 6.9 YIELD OF CARBON DIOXIDE AFTER 6 HOURS IRRADIATION OF METHYL PYRUVATE (10^{-2}M), IN OXYGENATED ACETONITRILE, IN THE ABSENCE AND PRESENCE OF 9,10-DICYANOANTHRACENE (OD = 1.0 at 370nm in order that 9,10-dicyanoanthracene absorbs most of the incident light)

in oxygenated acetonitrile solution[28] suggested that the 1,4-biradical was not intercepted by oxygen. In fact the presence of oxygen enhanced the yield of hexaldehyde formed from the photo-induced degradation of n-hexyl pyruvate. It was proposed[28] that oxygen suppresses the reduction of triplet n-hexyl pyruvate by hexaldehyde (Equation 6.3) by intercepting the triplet n-hexyl pyruvate. In an earlier report Davidson and co-workers[10] noted that oxygen did not intercept the 1,4-biradical formed by Type II fragmentation of α-keto-octanoic esters.

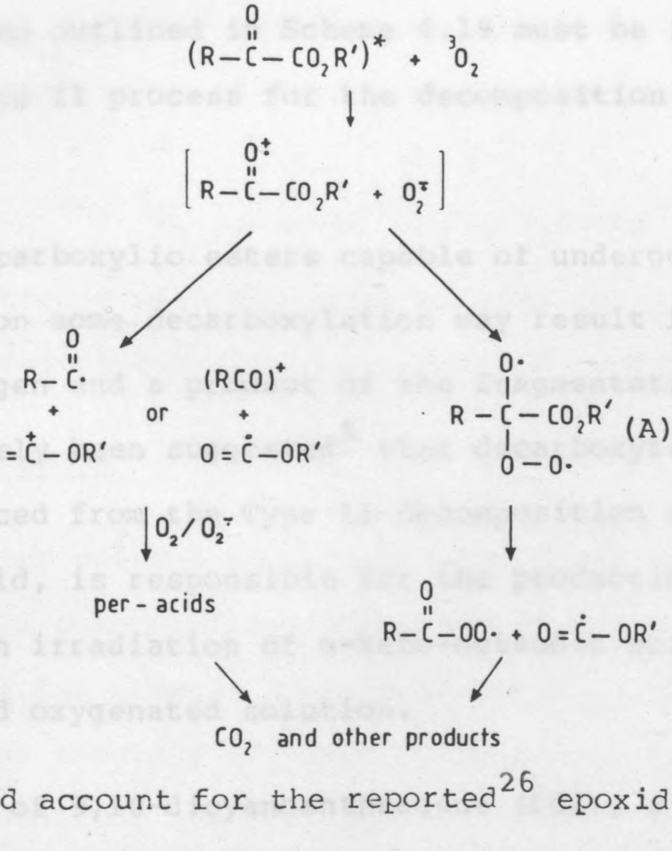
Surprisingly, t-butyl pyruvate, which has been shown to be photo-stable under degassed conditions (Table 6.4) was found to undergo efficient oxidative decarboxylation (Table 6.8). Since this ester does not fragment via either a Type I or a Type II reaction decarboxylation must be the result of a direct reaction between oxygen and the t-butyl pyruvate. A similar direct reaction between oxygen and the esters capable of fragmenting by a Type II process would obviously be in competition with the Type II reaction for degradation of these esters.

As negligible kinetic solvent isotope effects have been reported[28] upon the yield of carbon dioxide from the direct irradiation of methyl and ethyl pyruvates in oxygenated solution it would appear that singlet oxygen plays little, if any, part in these reactions.

Alkyl pyruvates have been shown to reduce methyl viologen via an electron transfer mechanism[13,24] so it is conceivable that electron transfer from the excited ester molecule to ground state oxygen can take place in oxygenated solution (Equation 6.5). Subsequent interaction of the radical ions could then

$$(\text{ester})^{*} + {}^{3}O_2 \longrightarrow (\text{ester})^{+\bullet} + O_2^{\bullet -} \qquad (6.5)$$

lead to carbon dioxide production. Alternatively, the radical cation of the ester may fragment to yield radicals which are then scavenged by oxygen to generate peroxy species which subsequently undergo reactions leading to carbon dioxide production (Scheme 6.20). The formation of peroxy species would account for the reported[26] epoxidation of alkenes during photo-oxidation of methyl phenylglyoxylate. Species similar to (A) in the above scheme have been proposed as intermediates in the direct photo-oxidations of α-keto-carboxylic acids (see Section 6.2), non-conjugated aliphatic ketones[29] and as possible intermediates in the analagous reaction of ρ-benzoquinone[30]. Further evidence for the involvement of peroxy species is the observation[28] that prolonged irradiation of t-butyl pyruvate, in oxygenated



Scheme 6.20

acetonitrile yielded more than one molar equivalent of carbon dioxide (Table 6.8). Peroxy species such as $O=\dot{C}-OC(CH_3)_3$ can either undergo direct decarboxylation or interact with oxygen to form an intermediate which subsequently collapses to yield the second mole of carbon dioxide. In contrast to the t-butyl pyruvate (which cannot undergo a Type II reaction)[23] prolonged irradiation of methyl pyruvate, which is capable of fragmentation via a Type II process did not produce carbon dioxide in greater than 100% yield. Therefore, the mechanism outlined in Scheme 6.19 must be in competition with the Type II process for the decomposition of methyl pyruvate.

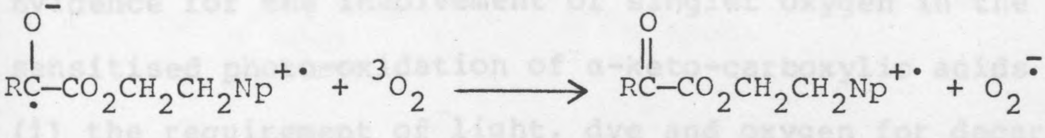
For α-keto-carboxylic esters capable of undergoing Type II fragmentation some decarboxylation may result from interaction between oxygen and a product of the fragmentation process. It has previously been suggested[9] that decarboxylation of pyruvic acid, produced from the Type II decomposition of α-keto-octanoic acid, is responsible for the production of carbon dioxide upon irradiation of α-keto-octanoic acid in both degassed and oxygenated solution.

The ability of 9,10-dicyanoanthracene (DCA), a well-known electron acceptor, to sensitise the photo-oxidative decarboxylation of methyl pyruvate (Table 6.9), in acetonitrile solution, lends support to the proposed electron transfer mechanism outlined in Scheme 6.19. A possible mechanism for the DCA sensitised reaction is outlined in Scheme 6.21.

$$\begin{tikzcd}
\mathrm{DCA} \arrow[r, "h\nu"] & \mathrm{DCA}^{*} \arrow[r, "\mathrm{MeCOCO_2Me}"] & \mathrm{DCA}^{\bar{\cdot}} + (\mathrm{MeCOCO_2Me})^{+\cdot} \arrow[dd] \\
\mathrm{DCA}^{\bar{\cdot}} + {}^{3}\mathrm{O_2} \arrow[r] & \mathrm{DCA} + \mathrm{O_2}^{\bar{\cdot}} & \\
\mathrm{O_2}^{\bar{\cdot}} + (\mathrm{MeCOCO_2Me})^{\dot{+}} \arrow[rr] & & \mathrm{CO_2} + \text{other products}
\end{tikzcd}$$

Scheme 6.21

In Section 6.3 it was proposed that naphthyl-α-keto-carboxylic esters may undergo intramolecular electron transfer. Interaction of such a charge transfer species with oxygen could lead to the generation of superoxide anions (Equation 6.6)



$$\mathrm{R\overset{O^-}{\underset{\cdot}{C}}{-}CO_2CH_2CH_2Np^{+\cdot}} + {}^{3}\mathrm{O_2} \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}{-}CO_2CH_2CH_2Np^{+\cdot}} + \mathrm{O_2}^{\bar{\cdot}} \quad (6.6)$$

which can interact with the ester radical cation to give rise to the observed carbon dioxide production (Table 6.8).

6.4.2 Conclusions

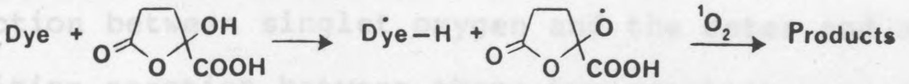
Alkyl pyruvates undergo photo-oxidative decarboxylation in both polar and non-polar solvents, the yields of carbon dioxide being far greater than those obtained in the absence of oxygen. An electron transfer mechanism is proposed in order to account for the decarboxylation of t-butyl pyruvate which is photostable in degassed solution. For esters capable of undergoing Norrish Type II reactions direct electron transfer to ground state oxygen will be in competition with Type II processes for the degradation of these esters. The finding that electron acceptors, e.g. DCA, can sensitise the photo-oxidative decarboxylation of α-keto-carboxylic esters lends credence to the proposed electron transfer mechanism.

6.5 Dye-sensitised photo-oxidation of α-keto-carboxylic acids and esters

Although there are many reports pertaining to the mechanism of the dye-sensitised photo-oxidation of α-keto-carboxylic acids the analagous reactions of α-keto-carboxylic esters have received very little attention.

6.5.1 Introduction

Evidence for the involvement of singlet oxygen in the dye-sensitised photo-oxidation of α-keto-carboxylic acids include (i) the requirement of light, dye and oxygen for decarboxylation, (ii) the retarding effects of added β-carotene[31] (a known quencher of singlet oxygen), (iii) the finding that singlet oxygen generated by non-photochemical means, e.g. microwave discharge, is capable of oxidizing α-keto-carboxylic acids[32] and (iv) observed kinetic solvent isotope effects in D_2O/H_2O[33a,b]. The intermediacy of singlet oxygen in these reactions was first questioned by Davidson[34] who observed that decarboxylation of α-keto-glutaric acid, or its anion, is sensitised by rose bengal and methylene blue even in the absence of oxygen. For the rose bengal sensitised photo-oxidation of α-keto-glutaric acid anion, present as its pyridinium salt, two moles of carbon dioxide were generated for each mole of α-keto-glutarate anion consumed[33b,34]. These results were rationalised on the basis of a reaction pathway involving attack of the excited dye upon the α-keto-carboxylic acid (or its anion). This proposal is in agreement with the reports that the flavoprotein and thiamine sensitised photo-oxidations of α-keto-carboxylic acids involve intermediate adduct formation between the sensitiser and the acid[5,35]. Jefford and co-workers[33b] found that no decarboxylation took place under nitrogen when the dye and α-keto-glutaric acid were immobilised on solid supports, but did occur to some extent under oxygen. A mechanism was proposed[33b] which involved hydrogen abstraction, by the dye, from the lactol tautomer of α-keto-glutaric acid to yield a lactol radical and ultimately oxidation products (Equation 6.7).



(6.7)

Using the technique of laser flash photolysis Davidson and co-workers[36] demonstrated that α-keto-carboxylic acids react with triplet methylene blue more efficiently than with oxygen. In reply to the evidence for the involvement of singlet oxygen it was suggested[36] that β-carotene could have quenched singlet oxygen and/or the excited states of the dye[34], and it was found that kinetic solvent isotope effects upon these reactions in D_2O/H_2O fell within the limits of experimental reproducibility (the largest having a magnitude of 1.65) and consequently, could not be used as evidence for the involvement of singlet oxygen.

Jefford and Cadby[37] demonstrated that superoxide anions, generated from potassium superoxide in dimethylsulphoxide, are capable of oxidizing ρ-hydroxyphenylpyruvic acid. Hamilton[38] has suggested that in the presence of transition metals the spin forbidden direct reaction between ground state α-keto-glutaric acid and triplet oxygen can be made possible by complexation to the metal. The resultant per-succinic acid could then bring about further oxidation of the substrate. Such a mechanism may be important in biological oxidation reactions in which α-keto-glutaric acid acts as a co-factor to mono-oxygenazes[39].

Reports relating to the dye-sensitised photo-oxidation of α-keto-carboxylic esters have been confined to the enol tautomers of phenyl pyruvate ester derivatives[40,41]. Jefford and co-workers[40] have proposed that an ene or free radical reaction between singlet oxygen and the ester and a [2 + 2] addition reaction between these two reactants can account for the observed products from the dye-sensitised photo-oxidation of methyl-ρ-methoxyphenyl pyruvate. Although Kotsuki and co-workers[41] demonstrated that the enol tautomer of the same ester is capable of undergoing [2 + 2] addition with singlet oxygen no intermediates have been isolated and no further evidence for the involvement of singlet oxygen, in the dye-sensitised photo-oxidation of α-keto-carboxylic esters, was presented.

Clearly, the mechanism of the dye-sensitised photo-oxidative decarboxylation of α-keto-carboxylic acids is the subject of controversy and the analagous reactions of their esters have received very little attention. The main point of contention is over the involvement of singlet oxygen in these reactions. One method of determining the rôle of singlet oxygen in dye-sensitised photo-oxidation reactions is to study the effects of a change in oxygen concentration. Singlet oxygen mediated reactions are known to be insensitive to changes in the concentration of oxygen, above a certain 'critical' minimum level[42a,b]. In contrast, reactions which involve radicals, e.g. the dye-sensitised photo-oxidation of amines[42a] show a dependency upon oxygen concentration. Similarly, oxidation reactions occurring via an electron transfer process, e.g. the methylene blue sensitised photo-oxidation of t-stilbene[42b], are subject to an oxygen concentration dependence. Therefore, the effects of changes in oxygen concentration upon the dye-sensitised photo-oxidative decarboxylations of α-oxo-carboxylic acids and their esters were evaluated.

6.5.2 Results and discussion

The results in Table 6.10 illustrate that a known singlet oxygen mediated reaction, i.e. the dye-sensitised photo-oxidation of citronellol, shows little reaction at very low

GAS	OXYGEN CONTENT (%)	RATE OF CONSUMPTION OF CITRONELLOL (Ms^{-1})
Argon	1×10^{-4}	0
Nitrogen (O.F.N.)	1×10^{-3}	0
Air (carbon dioxide-free)	21	4.6×10^{-6}
Oxygen	100	4.6×10^{-6}

TABLE 6.10 RATES OF PHOTO-OXIDATION OF CITRONELLOL (2×10^{-2}M), SENSITISED BY ROSE BENGAL (B.D.H.; 0.02g/25mls), UNDER DIFFERENT GASES (FLUSHED THROUGH AT 10mls/min) IN ACETONITRILE (USING A 2% AQUEOUS POTASSIUM CHROMATE LIGHT FILTER SOLUTION)

oxygen concentrations and the differences in reaction rate between oxygen and air-flushed solutions were found to be negligible. The reactions were carried out under the same conditions as the dye-sensitised photo-oxidations of the α-keto-carboxylic acids and esters so similar results would be expected if these reactions also involve singlet oxygen as the reactive species responsible for the observed oxidative decarboxylation.

6.5.2 (i) α-Keto-carboxylic acids

The effects of changes in oxygen concentration on the yields of carbon dioxide from the rose bengal sensitised photo-oxidation of pyruvic acid and α-keto-glutaric acid are shown in Tables 6.11 and 6.12. These results confirm the previous finding that decarboxylation of α-keto-carboxylic acids occurs even in the absence of oxygen[31,33b,34]. The discrepancies between the low yields obtained in this study and those previously reported under anaerobic conditions may have arisen as a consequence of leakage of air into the nitrogen line used in the earlier study[34].

For both the α-keto-carboxylic acids studied, the yields of carbon dioxide were found to be in the order: air>oxygen> argon>nitrogen. These results can be used to give an insight into the relative importance of each of several possible interactions between the α-keto-carboxylic acid, the triplet dye and oxygen which are outlined in Scheme 6.22.

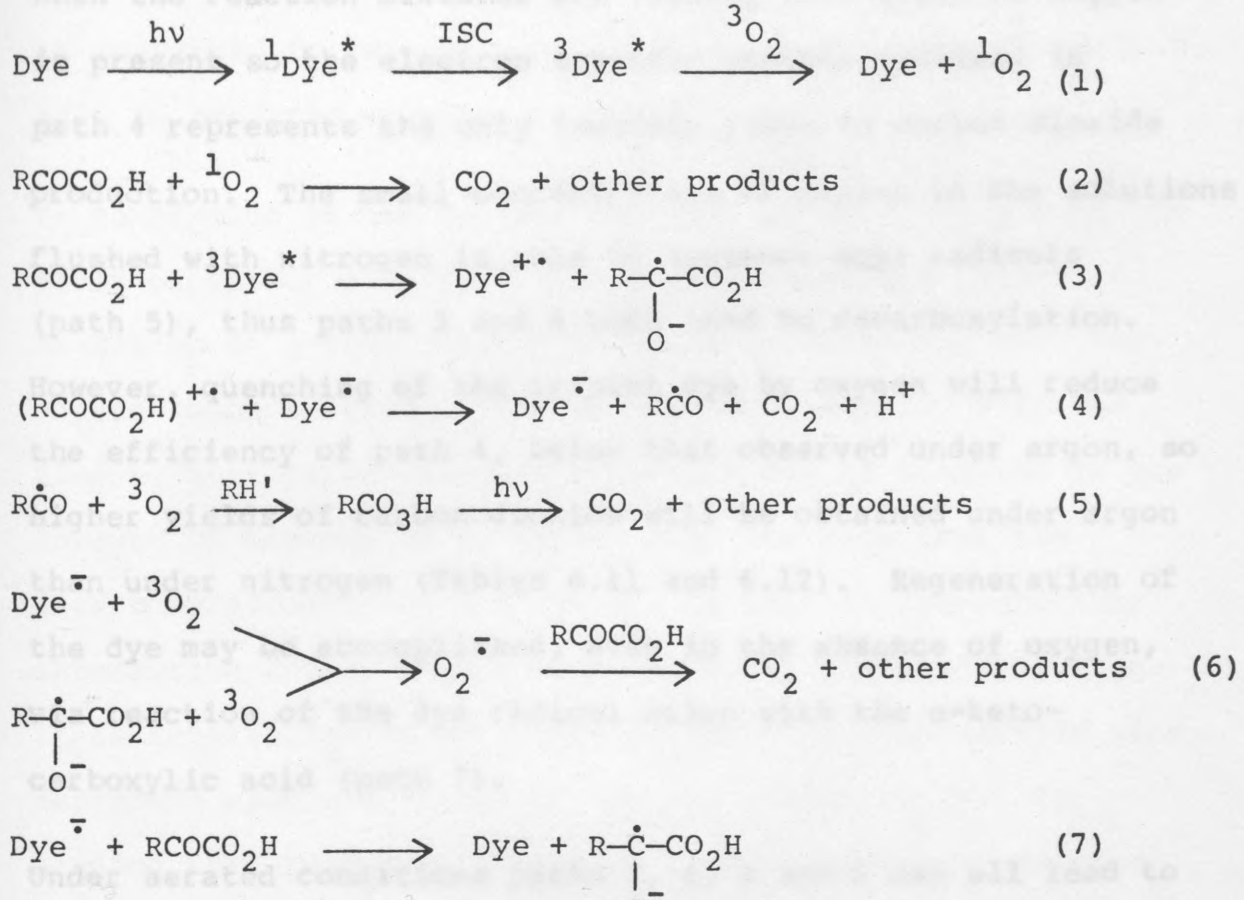
GAS	OXYGEN CONTENT (%)	CARBON DIOXIDE YIELDS (%)			
		ACETONITRILE/PYRIDINE		METHANOL/PYRIDINE	
		6hrs	20hrs	6hrs	20hrs
Argon	1×10^{-4}	12.2	39.6	9.7	28.1
Nitrogen (OFN)	1×10^{-3}	8.1	24.3	7.5	20.0
Nitrogen (commercial)	<5	*a*	*a*	7.1	20.0
Air (carbon dioxide-free)	21	34.5	98.9	12.4	58.7
Oxygen	100	17.7	63.9	6.8	28.5

a - not determined

TABLE 6.11 YIELDS OF CARBON DIOXIDE FROM THE IRRADIATION OF PYRUVIC ACID (2×10^{-2}M), SENSITISED BY ROSE BENGAL (BOH; 0.02g/25mls), UNDER DIFFERENT GASES (FLUSHED THROUGH AT 10mls/min) IN METHANOL/PYRIDINE AND ACETONITRILE/PYRIDINE (4:1 v/v) SOLUTIONS USING A 2% AQUEOUS POTASSIUM CHROMATE LIGHT FILTER SOLUTION, AFTER 6 AND 20 HOURS IRRADIATION

GAS	CARBON DIOXIDE YIELDS (%)					
	ACETONITRILE/PYRIDINE (A)		(A) METHANOL/PYRIDINE		(B)	
	6hrs	20hrs	6hrs	20hrs	6hrs	20hrs
Argon	9.1	37.4	9.8	42.7	11.9	33.0
Nitrogen (OFN)	5.8	22.2	6.2	17.9	10.0	26.2
Nitrogen (commercial)	6.7	29.2	6.4	20.6	8.4	24.3
Air (carbon dioxide-free)	22.1	113.4	20.3	105.9	19.2	75.5
Oxygen	11.7	54.0	11.5	51.3	11.7	45.8

TABLE 6.12 YIELDS OF CARBON DIOXIDE FROM THE IRRADIATION OF α-KETO-GLUTARIC ACID (2×10^{-2}M), SENSITISED BY ROSE BENGAL (0.02g/25mls) (A) - BDH; (B) - EASTMAN-KODAK, UNDER THE CONDITIONS GIVEN IN TABLE 6.11



$$\mathrm{Dye} \xrightarrow{h\nu} {}^{1}\mathrm{Dye}^{*} \xrightarrow{\mathrm{ISC}} {}^{3}\mathrm{Dye}^{*} \xrightarrow{{}^{3}O_2} \mathrm{Dye} + {}^{1}O_2 \qquad (1)$$

$$RCOCO_2H + {}^{1}O_2 \longrightarrow CO_2 + \text{other products} \qquad (2)$$

$$RCOCO_2H + {}^{3}\mathrm{Dye}^{*} \longrightarrow \mathrm{Dye}^{+\cdot} + R\text{—}\underset{\textstyle |\atop \textstyle O^-}{\dot{C}}\text{—}CO_2H \qquad (3)$$

$$(RCOCO_2H)^{+\cdot} + \mathrm{Dye}^{\dot{-}} \longrightarrow \mathrm{Dye} + R\dot{C}O + CO_2 + H^+ \qquad (4)$$

$$R\dot{C}O + {}^{3}O_2 \xrightarrow{RH'} RCO_3H \xrightarrow{h\nu} CO_2 + \text{other products} \qquad (5)$$

$$\left.\begin{array}{l} \mathrm{Dye}^{\dot{-}} + {}^{3}O_2 \\ R\text{—}\underset{\textstyle |\atop \textstyle O^-}{\dot{C}}\text{—}CO_2H + {}^{3}O_2 \end{array}\right\rangle \longrightarrow O_2^{\dot{-}} \xrightarrow{RCOCO_2H} CO_2 + \text{other products} \qquad (6)$$

$$\mathrm{Dye}^{\dot{-}} + RCOCO_2H \longrightarrow \mathrm{Dye} + R\text{—}\underset{\textstyle |\atop \textstyle O^-}{\dot{C}}\text{—}CO_2H \qquad (7)$$

Scheme 6.22

On the basis of the observed effects of oxygen concentration upon the yields of carbon dioxide (Tables 6.11 and 6.12) and previous evidence[26,36] which suggested that singlet oxygen is not involved to a significant extent in the dye-sensitised decarboxylations of α-keto-carboxylic acids paths 1 and 2 may be disregarded. Electron transfer processes (paths 3 and 4) could lead to carbon dioxide production by a mechanism involving superoxide anions (path 6) or as a consequence of the scavenging of acyl radicals (produced via path 4) by oxygen to yield peracids[33b,36] (path 5). The latter may subsequently undergo decarboxylation[13] (path 5). A combination of paths 4 and 5 therefore increases the theoretical maximum yield of carbon dioxide to two moles per mole of α-keto-carboxylic acid consumed[9].

When the reaction mixtures are flushed with argon no oxygen is present so the electron transfer process outlined in path 4 represents the only feasible route to carbon dioxide production. The small concentration of oxygen in the solutions flushed with nitrogen is able to scavenge acyl radicals (path 5), thus paths 3 and 4 both lead to decarboxylation. However, quenching of the triplet dye by oxygen will reduce the efficiency of path 4, below that observed under argon, so higher yields of carbon dioxide will be obtained under argon than under nitrogen (Tables 6.11 and 6.12). Regeneration of the dye may be accomplished, even in the absence of oxygen, via reaction of the dye radical anion with the α-keto-carboxylic acid (path 7).

Under aerated conditions paths 3, 4, 5 and 6 can all lead to decarboxylation. The oxygen concentration will allow efficient scavenging of acyl radicals to produce per-acids, which can undergo decarboxylation[13] to yield a second molar equivalent of carbon dioxide, and a greater yield of superoxide anions (path 6). Consequently, quenching of the triplet dye by oxygen will be unable to counteract the increased yields of carbon dioxide produced via the remaining triplet dye molecules.

Quenching of the triplet dye by oxygen will be most marked under pure oxygen. By analogy, the yield of singlet oxygen from triplet benzophenone has been observed[43] to increase from 50% in air saturated solution to 90% in oxygen saturated benzene solution. The inefficiency in aerated solution was attributed to incomplete oxygen quenching of the triplet benzophenone. The resultant reduction in efficiency of paths 3 and 4 will lead to fewer radicals being available to be scavenged by oxygen, hence a lower yield of carbon dioxide will be produced under oxygen than under air.

In conclusion it can be seen from the above results that the yield of carbon dioxide from the dye-sensitised photo-oxidation of α-keto-carboxylic acids is dependent upon the oxygen concentration. This observation, coupled with the finding that carbon dioxide evolution can be observed in the absence of oxygen, is in accord with the view that the decarboxylation reactions involve an initial dye-substrate interaction rather than a singlet oxygen mediated reaction. It is interesting to note that yields of carbon dioxide were dependent upon the source of the dye (Table 6.12). The finding that rose bengal samples from a variety of sources have been found to have different photophysical properties[13] could account for the discrepancy in carbon dioxide yields from BDH and Eastman-Kodak rose bengal samples. These findings demonstrate that caution must be taken when results obtained using dyes from different sources are being compared.

6.5.2 (ii) α-Keto-carboxylic esters

The results in Table 6.13 illustrate that a wide range of α-keto-carboxylic esters undergo rose bengal and methylene blue sensitised photo-oxidation. These esters, unlike those previously studied[40,41], predominantly exist in their keto form rather than as enol tautomers. A range of dyes behaved as sensitisers for the photo-oxidation of methyl pyruvate as shown in Table 6.14. The effects of changes in oxygen con-

α-KETO-CARBOXYLIC ESTER	IRRADIATION TIME (HRS.)	YIELD OF CARBON DIOXIDE (%)	
		METHYLENE BLUE	ROSE BENGAL
Methyl pyruvate	20	39	54
Isopropyl pyruvate	18	15.5	23
n-Butyl pyruvate	18	30	34
t-Butyl pyruvate	18	27	29
n-Hexyl pyruvate	18	21	34
Benzyl pyruvate	18	24.5	26
Ethyl benzoyl formate	18	14	14
2-(1-Naphthyl)ethyl pyruvate	18	28	51
2-(2-Naphthyl)ethyl pyruvate	18	29	45
2-(2-Naphthyl)ethyl-α-keto-octanoate	18	47	43

TABLE 6.13 YIELDS OF CARBON DIOXIDE FROM THE DYE (BDH; 0.02g/25mls) SENSITISED PHOTO-OXIDATION OF α-KETO-CARBOXYLIC ESTERS (10^{-2}M) IN ACETONITRILE/PYRIDINE (4:1 v/v) SOLUTION USING A 2% AQUEOUS POTASSIUM CHROMATE LIGHT FILTER SOLUTION

SENSITISER	SENSITISER CONCENTRATION	LIGHT FILTER (AQUEOUS SOLUTION)	YIELD OF CARBON DIOXIDE (%)
Methylene blue	0.02g/25mls	2% K_2CrO_4	59.3
Rhodamine B	0.02g/50mls	saturated $NaNO_3$	45
Erythrosin B	0.02g/50mls	saturated $NaNO_3$	70.3
Tetraphenylporphyrin	OD = 0.8 @ 514nm	saturated $NaNO_3$	28

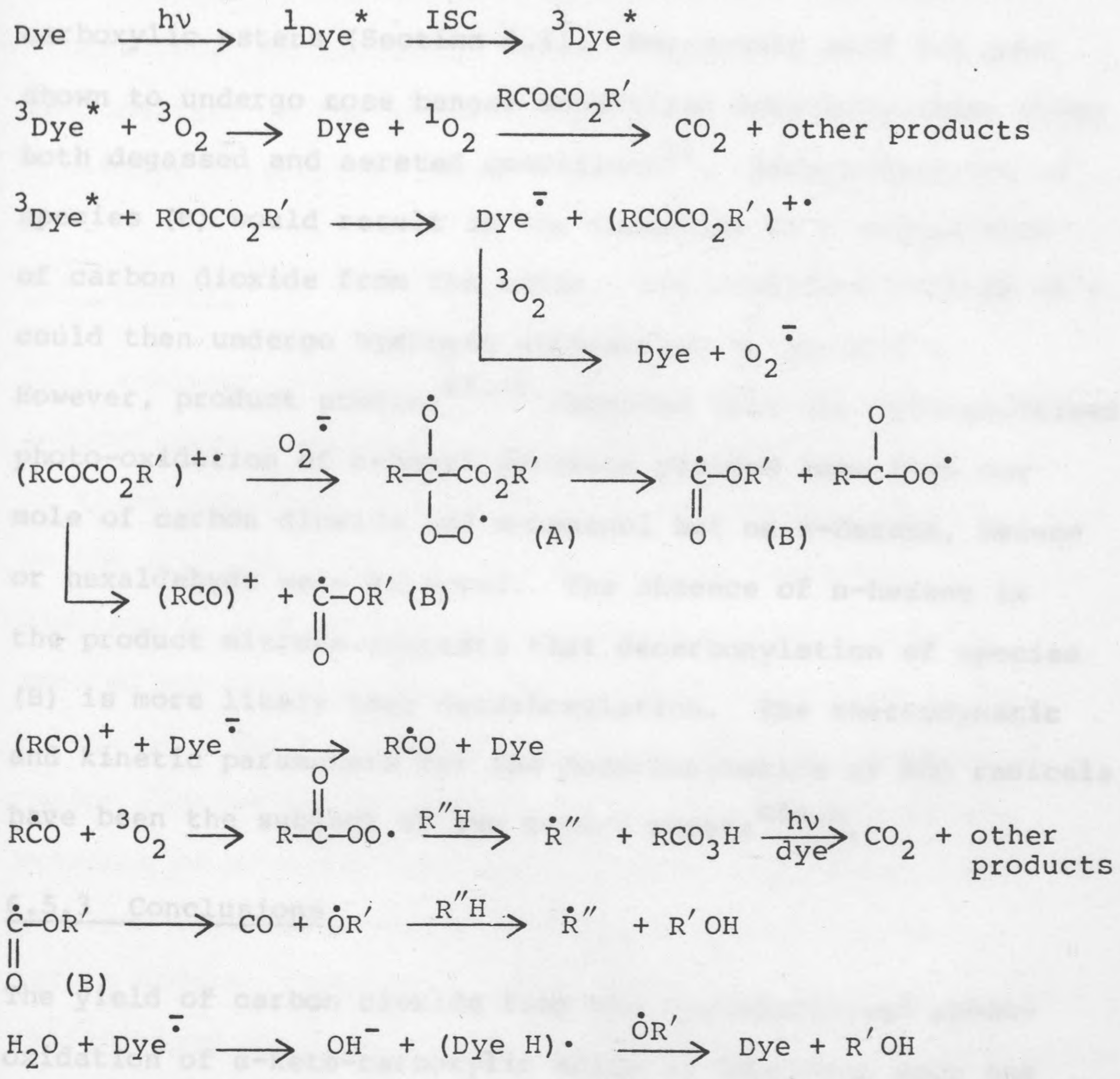
TABLE 6.14 YIELDS OF CARBON DIOXIDE FROM THE DYE-SENSITISED PHOTO-OXIDATION OF METHYL PYRUVATE (10^{-2}M) IN ACETONITRILE/PYRIDINE (4:1 v/v) SOLUTION FOR 18 HOURS

centration upon the rose bengal sensitised decarboxylation of methyl pyruvate are shown in Table 6.15 and are of interest in ascertaining the mechanism of this reaction.

As the same trend in carbon dioxide yields produced under a range of gases, i.e. air>oxygen>argon>nitrogen was obtained for methyl pyruvate and α-keto-carboxylic acids (Section 6.5.2 (i)) it is considered improbable that singlet oxygen is involved in the major pathway leading to decarboxylation. On the basis of the results in Table 6.15 and the observation that α-keto-carboxylic esters are capable of undergoing electron transfer reactions (Section 6.3) the following mechanism (Scheme 6.23) is proposed to account for the observed carbon dioxide production under dye sensitised photo-oxidation conditions.

GAS	YIELD OF CARBON DIOXIDE (%)
Argon	17.4
Nitrogen (OFN)	12.0
Nitrogen (commercial)	11.4
Air (carbon dioxide-free)	42.5
Oxygen	27.1

TABLE 6.15 YIELDS OF CARBON DIOXIDE FROM THE PHOTO-OXIDATION OF METHYL PYRUVATE (2 x 10^{-2}M), SENSITISED BY ROSE BENGAL (BDH; 0.02g/25mls), IN ACETONITRILE/PYRIDINE (4:1 v/v) SOLUTION FOR 18 HOURS UNDER THE CONDITIONS GIVEN IN TABLE 6.11



$$\text{Dye} \xrightarrow{h\nu} {}^{1}\text{Dye}^{*} \xrightarrow{\text{ISC}} {}^{3}\text{Dye}^{*}$$

$${}^{3}\text{Dye}^{*} + {}^{3}O_2 \longrightarrow \text{Dye} + {}^{1}O_2 \xrightarrow{\text{RCOCO}_2\text{R}'} CO_2 + \text{other products}$$

$${}^{3}\text{Dye}^{*} + \text{RCOCO}_2\text{R}' \longrightarrow \text{Dye}^{\bar{\cdot}} + (\text{RCOCO}_2\text{R}')^{+\cdot}$$

$$\text{Dye}^{\bar{\cdot}} \xrightarrow{{}^{3}O_2} \text{Dye} + O_2^{\bar{\cdot}}$$

$$(\text{RCOCO}_2\text{R}')^{+\cdot} \xrightarrow{O_2^{\bar{\cdot}}} \text{R–}\underset{\text{O–O}^{\cdot}}{\overset{\text{O}}{\text{C}}}\text{–CO}_2\text{R}' \ (\text{A}) \longrightarrow \underset{\text{O}}{\overset{\cdot}{\text{C}}}\text{–OR}' + \text{R–}\overset{\text{O}}{\text{C}}\text{–OO}^{\cdot} \ (\text{B})$$

$$(\text{RCOCO}_2\text{R}')^{+\cdot} \longrightarrow (\text{RCO})^{+} + \underset{\text{O}}{\overset{\cdot}{\text{C}}}\text{–OR}' \ (\text{B})$$

$$(\text{RCO})^{+} + \text{Dye}^{\bar{\cdot}} \longrightarrow \text{R}\dot{\text{C}}\text{O} + \text{Dye}$$

$$\text{R}\dot{\text{C}}\text{O} + {}^{3}O_2 \longrightarrow \text{R–}\overset{\text{O}}{\text{C}}\text{–OO}\cdot \xrightarrow{\text{R}''\text{H}} \dot{\text{R}}'' + \text{RCO}_3\text{H} \xrightarrow[\text{dye}]{h\nu} CO_2 + \text{other products}$$

$$\underset{\text{O}}{\overset{\cdot}{\text{C}}}\text{–OR}' \ (\text{B}) \longrightarrow \text{CO} + \dot{\text{O}}\text{R}' \xrightarrow{\text{R}''\text{H}} \dot{\text{R}}'' + \text{R}'\text{OH}$$

$$H_2O + \text{Dye}^{\bar{\cdot}} \longrightarrow OH^{-} + (\text{Dye H})\cdot \xrightarrow{\dot{\text{O}}\text{R}'} \text{Dye} + \text{R}'\text{OH}$$

Scheme 6.23

The high yield of carbon dioxide obtained in the absence of oxygen can only be accounted for by the presence of small quantities of water which enable the dye to be regenerated. A species similar to (A) in Scheme 2 has been proposed as an intermediate in the direct photo-oxidation of α-keto-carboxylic acids (Section 6.2) and their esters (Section 6.3). Such an intermediate has also been suggested for the direct photo-oxidation of non-conjugated ketones (e.g. menthone)[29], and as a possible intermediate in the analagous reactions of 1,4-dicarbonyl compounds[30]. The formation of per-acids has been demonstrated for the direct photo-oxidation of α-keto-carboxylic esters (Section 6.4). Per-acetic acid has been shown to undergo rose bengal sensitised decarboxylation under both degassed and aerated conditions[13]. Decarboxylation of species (B) would result in the formation of a second mole of carbon dioxide from the ester. The resultant radical (R') could then undergo hydrogen abstraction to yield $R'H$. However, product studies[13,44] revealed that the dye-sensitised photo-oxidation of n-hexyl pyruvate yielded less than one mole of carbon dioxide and n-hexanol but no n-hexane, hexene or hexaldehyde were detected. The absence of n-hexane in the product mixture suggests that decarbonylation of species (B) is more likely than decarboxylation. The thermodynamic and kinetic parameters for the decarbonylation of $R\dot{C}O$ radicals have been the subject of two recent papers[45a,b].

6.5.3 Conclusions

The yield of carbon dioxide from the dye-sensitised photo-oxidation of α-keto-carboxylic acids is dependent upon the oxygen concentration. This observation, coupled with the finding that carbon dioxide evolution can be observed in the absence of oxygen, is in accord with the view that the decarboxylation reactions involve an initial dye-acid interaction.[34] Although the results disfavour the involvement of singlet oxygen as the primary oxidizing species reaction of the acid with singlet oxygen may represent a minor pathway for the sensitised decarboxylation of α-keto-carboxylic acids.

Like their parent acids, α-keto-carboxylic esters undergo dye-sensitised photo-oxidation to yield carbon dioxide and the extent of decarboxylation is dependent upon the oxygen concentration. Consequently, the observed results can be rationalised on the basis of a mechanism involving an initial dye-ester interaction rather than a singlet oxygen mechanism.

6.6 Summary

Both α-keto-carboxylic acids and their esters undergo photo-induced decarboxylation in degassed solution. The ability of these compounds to undergo electron transfer reactions led to the proposal that the decarboxylation reactions occur via bimolecular electron transfer processes between triplet excited and ground state α-keto-carboxylic acid or ester molecules. The finding that electron acceptors can sensitise carbon dioxide production and yields are enhanced in the presence of aromatic hydrocarbons lends credence to the proposed electron transfer mechanism. α-Keto-carboxylic esters undergo photo-oxidative decarboxylation which can be rationalised on the basis of electron transfer processes which give rise to the production of superoxide anions. Yields of carbon dioxide from α-keto-carboxylic esters are greater in oxygenated than in degassed solution.

Carbon dioxide can be generated as a consequence of dye sensitised photo-oxidation of a wide range of α-keto-carboxylic esters. Dye sensitised decarboxylation of α-keto-carboxylic acids and their esters was found to be affected by changes in the oxygen concentration. This phenomenon could be explained by a mechanism involving an initial dye-acid interaction. Although singlet oxygen is not the primary species responsible for oxidation, its involvement in a minor pathway for decarboxylation of α-keto-carboxylic acids and esters cannot be ruled out.

6.7 Experimental

Details of equipment, determination of Stern-Volmer constants and sources of the chemicals are contained in Chapter 11. The experimental procedures outlined below were used to obtain the results presented in this chapter.

6.7.1 Direct photo-oxidation reactions

Photolysis tubes containing the acid or ester solutions (25 mls) were flushed with a stream of dry, carbon dioxide-free, argon or oxygen (as appropriate) for 45 minutes, stoppered and rotated within a circular array of fluorescent lamps (having a maximum emission at 350 nm). Following irradiation the solutions were flushed for 2 hours with argon or oxygen and the exit gas passed through a saturated aqueous solution of barium hydroxide. The precipitated barium carbonate was weighed and the percentage yield of carbon dioxide calculated on the basis of one mole of carbon dioxide being generated per mole of α-keto-carboxylic acid or ester present prior to irradiation.

6.7.2 Dye-sensitised photo-oxidation reactions

Photolysis tubes containing citronellol, acid or ester solutions (25 mls) were continuously flushed (~10 mls/min) with the appropriate gas (dry and carbon dioxide-free) for 45 minutes prior to irradiation, during irradiation and for 2 hours after irradiation. Irradiations were carried out within a circular array of Chryselco fluorescent daylight lamps with each of the five gases simultaneously to ensure that the rate of flushing was the same for all the gases. The rate of loss of citronellol was followed by glc analysis using a Perkin Elmer Sigma 3 chromatograph and 10% SE 30 column and the solution was flushed for thirty minutes, after each sample had been taken for analysis, before further irradiation. The exit gases from the acid and ester solutions, during and after irradiation were passed through a saturated aqueous solution of barium hydroxide. The precipitated barium carbonate was weighed and the percentage yield of carbon dioxide calculated on the basis of one mole of carbon dioxide being generated per mole of acid or ester present before irradiation commenced.

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CHAPTER 7

LIMITATIONS UPON THE USE OF KINETIC SOLVENT ISOTOPE EFFECTS TO DETERMINE THE RÔLE OF SINGLET OXYGEN IN PHOTO-OXIDATION REACTIONS

CHAPTER 7

LIMITATIONS UPON THE USE OF KINETIC SOLVENT ISOTOPE EFFECTS TO DETERMINE THE RÔLE OF SINGLET OXYGEN IN PHOTO-OXIDATION REACTIONS

7.1 Introduction

As oultined in Chapter 5 (Section 5.3.4(ii)) the lifetime of singlet oxygen in solution is markedly dependent upon the nature and isotopic composition of the solvent. The lifetime of singlet oxygen is often considerably longer in a deuterated solvent than in its non-deuterated counterpart (see Table 5.2). As the replacement of solvent hydrogen atoms by deuterium only causes a minor perturbation to the properties of the solvent the observation of a solvent isotope effect upon the rate of a photo-oxidation reaction (as given by Equation 7.1, see Appendix 5.6) is often used as evidence for the involvement

$$\mathrm{RATE} = \frac{Ia\ \phi_T\ k_r\ [A]}{k_d + (k_r + k_q)\ [A]} \qquad \text{Equation 7.1}$$

where Ia is the intensity of light absorbed by the sensitiser (S)

ϕ_T is the quantum yield of triplet production from the sensitiser (S)

k_d is the unimolecular decay constant for singlet oxygen

k_r is the rate constant for reaction of singlet oxygen with the substrate (A)

k_q is the rate constant for physical quenching of singlet oxygen by the substrate (A)

of singlet oxygen. This test which was pioneered by Merkel and Kearns[1a,b] is based on the assumption that the photophysical properties of the potential sensitiser of singlet oxygen and the rate constants of the system, other than k_d (the unimolecular decay constant for singlet oxygen) are unaffected by the isotopic composition of the solvent. This is an assumption which has not, in general, been put to the test.

Provided k_d is the only factor affected by a change from a deuterated to a non-deuterated solvent the observed kinetic solvent isotope effect is given by Equation 7.2. For kinetic

$$\frac{\mathrm{RATE}_D}{\mathrm{RATE}_H} = \frac{k_d + (k_r + k_q)\,[A]}{k_d' + (k_r + k_q)\,[A]} \qquad (7.2)$$

where k_d, k_d' are the unimolecular decay constants for singlet oxygen in the non-deuterated and deuterated solvent respectively.

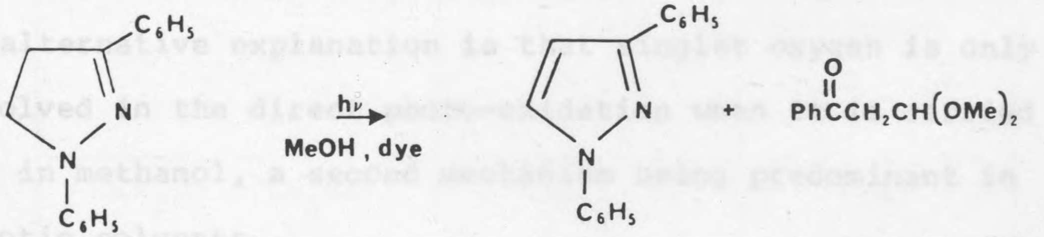
solvent isotope effects to be maximal the reaction with singlet oxygen must involve a diffusional process and the concentration of the substrate should be kept as low as possible in order that $k_d >> (k_r + k_q)\,[A]$.

7.2 The influence of photophysical properties on the magnitude of kinetic solvent isotope effects

The interpretation of kinetic solvent isotope effects upon photo-oxidation reactions is based on the assumption that the photophysical properties of the potential sensitiser of singlet oxygen are independent of the isotopic composition of the solvent. As stated earlier this is an assumption which has not been widely tested.

7.2.1 Direct photo-oxidation reactions

An example of the use of kinetic solvent isotope effects for determining the mechanism of a photo-oxidation reaction is the oxidation of 1,3-diphenyl-2-pyrazoline (DPP). This compound and its derivatives are widely used as fluorescent whitening agents for textiles, plastics and paper[2]. Little is known about their photochemistry and their usefulness as whiteners is limited by their poor stability to light. The finding by Evans and co-workers that the direct[3] and the Eosin Y sensitised[4] reactions exhibited solvent isotope effects in CD_3OD and CH_3OH (of 9.5 and 13.8 respectively) led to the proposal that both reactions involved singlet oxygen. The major product is the corresponding 1,3-diphenyl-pyrazole but in methanol the dye sensitised reaction also afforded β,β-dimethoxypropiophenone (Scheme 7.1). In the latter reaction the formation of the pyrazole was inhibited in the presence of the singlet oxygen quencher β-carotene, whereas formation of the secondary product was unaffected. This second product has been suggested[4] to result from direct electron transfer from the DPP to the triplet excited dye which leads to the generation of the dye radical anion and DPP radical cation.



Scheme 7.1

Results are now presented which demonstrate that photophysical properties can be subject to solvent isotope effects and make kinetic solvent isotope effects upon photo-oxidation reactions, in which this phenomenon occurs, impossible to interpret.

(i) Results and discussion

The dye-sensitised photo-oxidation of DPP exhibits kinetic solvent isotope effects in a wide range of solvent systems (Table 7.1) leaving little doubt that these are singlet oxygen mediated reactions. In contrast to the dye-sensitised reactions the self-sensitised photo-oxidation of DPP only exhibits substantial kinetic solvent isotope effects in protic solvents (Table 7.3). Such behaviour is only consistent with the intermediacy of singlet oxygen if the oxidation reaction occurs within the solvent cage, in which the singlet oxygen was generated, in aprotic but not protic solvents. As acetonitrile is less viscous (~0.35 cp^5) than the other solvents used (~0.6 cp^5) this explanation would seem unlikely. An alternative explanation is that singlet oxygen is only involved in the direct photo-oxidation when it is carried out in methanol, a second mechanism being predominant in aprotic solvents.

Based on earlier observations of solvent isotope effects upon the photophysical properties of intramolecular exciplex forming systems, e.g. α-naphthylaklylamines (see Chapter 4), the possibility arose that the kinetic solvent isotope effects observed in protic solvents (Table 7.1) may be due to the affects of the latter upon the photophysical properties of the DPP. The fluorescence lifetime and quantum yield of triplet production, were found to increase when methanol-d$_1$ was used in place of methanol as the solvent, whereas no differences were observed when acetonitrile-d$_3$ was used in place of acetonitrile. These results were explained on the

	SOLVENT ISOTOPE EFFECT	
	SELF-SENSITISED	DYE–SENSITISED
C_6D_6 / C_6H_6	1.1	14.2[a]
CD_3CN / CH_3CN	1.5	3.8[b]
$CDCl_3$ / $CHCl_3$	1.2	---
CH_3OD / CH_3OH	2.9	4.0[b] (3.9)[c]
CD_3OD / CH_3OH	6.5	13.9[b] (13.2)[c]

a - tetraphenylporphyrin (2×10^{-5}M)
b - methylene blue (1×10^{-5}M)
c - eosin Y (1×10^{-5}M)

TABLE 7.1 SOLVENT ISOTOPE EFFECTS UPON THE RATES OF THE DIRECT AND DYE-SENSITISED PHOTO-OXIDATION OF 1,3-DIPHENYL-2- PYRAZOLINE (3.2×10^{-5}M) IN A RANGE OF SOLVENT SYSTEMS

	SOLVENT ISOTOPE EFFECT	
	ϕ_f^D / ϕ_f^H	τ_f^D / τ_f^H[a]
CH_3OD / CH_3OH	2.1	2.43
CD_3OD / CH_3OH	3.9	2.30

a - calculated using lifetimes of the longer lived component of the fluorescence decay curve

TABLE 7.2 SOLVENT ISOTOPE EFFECTS UPON THE FLUORESCENCE QUANTUM YIELD (ϕ_f) AND LIFETIME (τ_f) OF 1,3-DIPHENYL-2-PYRAZOLINE

1,3,5-TRIPHENYL-2-PYRAZOLINE		SOLVENT ISOTOPE EFFECT	
R_1	R_3	ϕ_f^D/ϕ_f^H	τ_f^D/τ_f^H [a]
H	H	1.31	1.47
NH_2	H	1.71	1.91
H	NH_2	1.46	1.82
CO_2H	H	1.32	*b*
NO_2	H	1.06	*b*
CN	H	1.13	*b*
H	OH	1.64	*b*
H	OEt	1.57	*b*

a - calculated using lifetimes of the longer lived component of the fluorescence decay curve

b - not determined

TABLE 7.3 SOLVENT ISOTOPE EFFECTS UPON THE FLUORESCENCE QUANTUM YIELDS (ϕ_f) AND LIFETIMES (τ_f) OF SUBSTITUTED 1,3,5-TRIPHENYL-2-PYRAZOLINES (FIGURE 7.4) IN CH_3OD/CH_3OH

	SOLVENT ISOTOPE EFFECT	
	ϕ_f^D/ϕ_f^H	ϕ_T^D/ϕ_T^H
Indole	1.22	1.38
N-methylindole	1.17	1.18
Np-$(CH_2)_2$-NEt_2	1.31[a]	1.31
Np-$(CH_2)_3$-NEt_2	3.0[a]	1.29
Np-$(CH_2)_3$-NMePh	1.69[a]	1.73
Np-$(CH_2)_4$-NMePh	1.50[a]	1.92

Np = 1-naphthyl-

a - exciplex fluorescence

TABLE 7.4 SOLVENT ISOTOPE EFFECTS UPON THE QUANTUM YIELDS OF FLUORESCENCE (ϕ_f) AND TRIPLET PRODUCTION (ϕ_T) FOR INDOLE,[9a] N-METHYLINDOLE[9a] AND SOME α-NAPHTHYLALKYLAMINES[8] IN CH_3OD/CH_3OH

basis of hydrogen bonding to the amine group increasing its ionisation potential and consequently disfavouring exciplex (Figure 7.1) formation, and protonation being a non-radiative

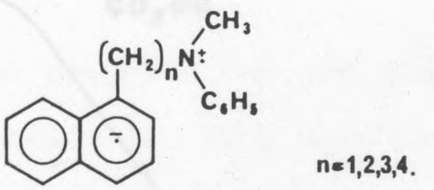


Figure 7.1

decay pathway for the resultant exciplex. As the energetics of hydrogen bonding and deuterium bonding are different, the latter being less efficient, the fluorescence quantum yield and lifetime of the exciplex will be greater in CH_3OD than in CH_3OH. Essentially, methanol behaves as a quencher of both the exciplex and the route to exciplex formation.

The considerable degree of charge transfer character[6] exhibited by the lowest excited singlet state of DPP (Figure 7.2) may

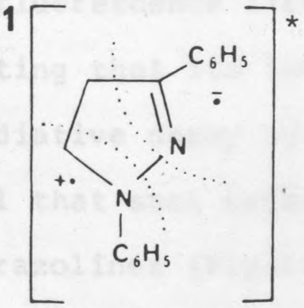


Figure 7.2

enable it to undergo protonation as a non-radiative decay route in a similar manner to the exciplexes formed by α-naphthylalkylamines. In order to evaluate the solvent isotope effects upon the fluorescence of DPP the quantum yields and lifetime of fluorescence were determined in deuterated solvents and their non-deuterated counterparts. No solvent isotope effects were observed upon the quantum yield of fluorescence of DPP in C_6D_6/C_6H_6 or CD_3CN/CH_3CN in contrast to the protic solvents where the observed effects were substantial (Figure 7.3). Solvent isotope effects were also observed upon the fluorescence lifetime of DPP in CH_3OD/CH_3OH (Table 7.2) suggesting that its lowest excited singlet state can undergo non-radiative decay by protonation. The results in Table 7.3 reveal that such behaviour is a general phenomenon for substituted pyrazolines (Figure 7.4). The decay of the fluorescence of these compounds was generally non-exponential

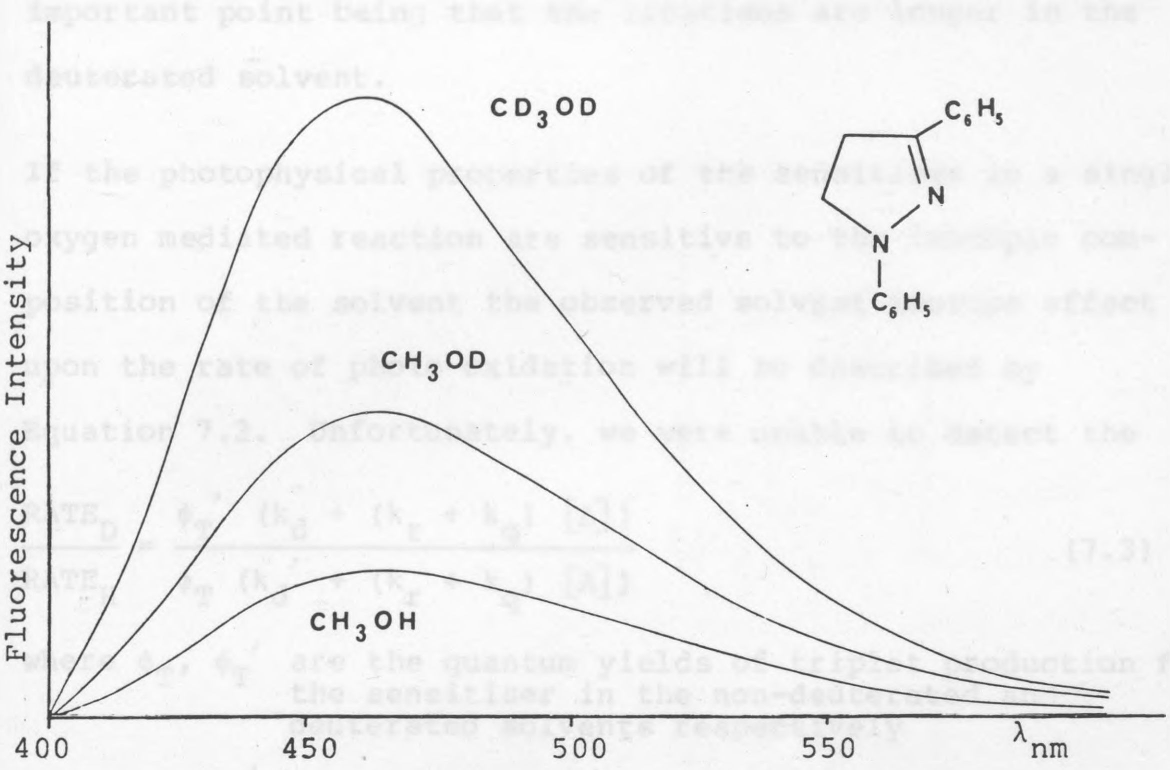


Figure 7.3 <u>Fluorescence spectra of 1,3-diphenyl-2-pyrazoline in CH_3OH, CH_3OD and CD_3OD at 20°C</u>

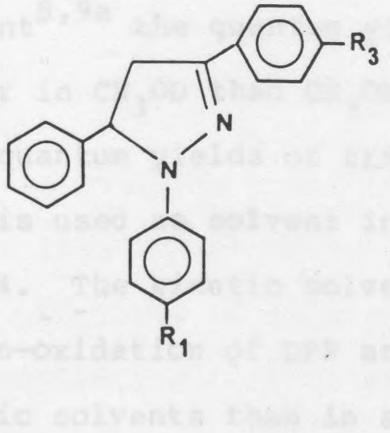


Figure 7.4

(see Section 7.5.2) so the lifetimes have only been used for comparison purposes rather than as absolute lifetimes, the important point being that the lifetimes are longer in the deuterated solvent.

If the photophysical properties of the sensitiser in a singlet oxygen mediated reaction are sensitive to the isotopic composition of the solvent the observed solvent isotope effect upon the rate of photo-oxidation will be described by Equation 7.3. Unfortunately, we were unable to detect the

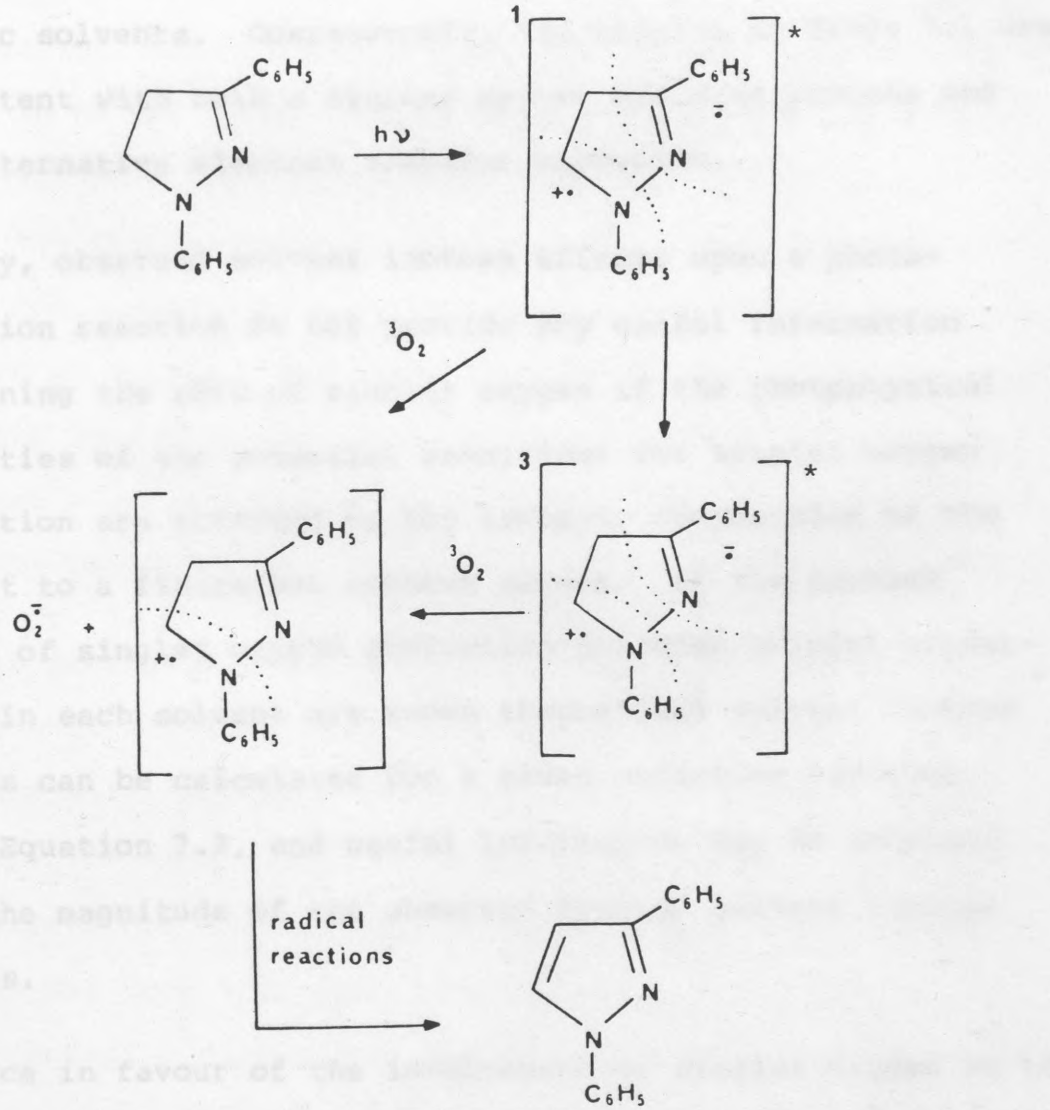
$$\frac{\mathrm{RATE}_D}{\mathrm{RATE}_H} = \frac{\phi_T{}' \; (k_d + (k_r + k_q)\;[A])}{\phi_T \; (k_d{}' + (k_r + k_q)\;[A])} \qquad (7.3)$$

where ϕ_T, $\phi_T{}'$ are the quantum yields of triplet production for the sensitiser in the non-deuterated and deuterated solvents respectively

k_d, $k_d{}'$ are the unimolecular decay constants for singlet oxygen in the non-deuterated and deuterated solvents respectively.

triplet state of DPP by the technique of laser flash photolysis. The triplet yield of DPP is known[7] to be very small and upon direct excitation it cannot be detected by esr spectroscopy. No phosphorescence can be observed from DPP at 77K in polar solvent but the triplet can be detected at low temperature by energy transfer excitation[7]. However, on the basis of precedent[8,9a] the quantum yield of triplets is expected to be higher in CH_3OD than CH_3OH. Some representative increases in quantum yields of triplet production observed when CH_3OD is used as solvent instead of CH_3OH are included in Table 7.4. The kinetic solvent isotope effects upon the direct photo-oxidation of DPP are therefore predicted to be larger in protic solvents than in aprotic solvents if singlet oxygen participates in these reactions. The results in Table 7.1 are therefore consistent with the involvement of singlet oxygen in the self-sensitised photo-oxidations of DPP.

However, an alternative oxidation mechanism (Scheme 7.2) can



Scheme 7.2

also be considered as a possible route to the production of pyrazoles upon direct irradiation of pyrazoline compounds in oxygenated solution. The rate of such an oxidation mechanism will depend on the quantum yield of singlet and triplet production from the pyrazoline so in aprotic solvents should not be affected by the isotopic composition of the solvent. In contrast to the aprotic solvents the isotopic composition of protic solvents may have a marked affect upon the quantum yields of production of the excited singlet and triplet states of the pyrazoline, so the oxidation reaction may exhibit a kinetic solvent isotope effect in protic but not aprotic solvents. Consequently, the results in Table 7.1 are consistent with both a singlet oxygen mediated process and the alternative electron transfer mechanism.

Clearly, observed solvent isotope effects upon a photo-oxidation reaction do not provide any useful information concerning the rôle of singlet oxygen if the photophysical properties of the potential sensitiser for singlet oxygen production are affected by the isotopic composition of the solvent to a finite but unknown extent. If the quantum yields of singlet oxygen production (or even triplet production) in each solvent are known theoretical solvent isotope affects can be calculated for a given oxidation reaction using Equation 7.3, and useful information may be obtained from the magnitude of the observed kinetic solvent isotope effects.

Evidence in favour of the involvement of singlet oxygen in the direct photo-oxidation of DPP includes the reported[3] retarding effects, in benzene, of added 1,4-diazobicyclo[2.2.2.]octane (DABCO) and triethylamine which are known quenchers of singlet oxygen. Although quenching of the direct reaction by DABCO[3] appears to indicate that singlet oxygen is involved, DABCO was found to be ineffective in quenching the eosin Y and methylene blue sensitised photo-oxidation of DPP[4]. The quenching of the direct reaction is particularly remarkable because the concentration of DABCO (3.5×10^{-4}M) in the direct reaction was ten times lower than in the dye-sensitised reaction, where singlet oxygen is known to be the species responsible for reaction. The direct photo-oxidation of 1,3,5-triphenyl-2-pyrazoline, which exhibits a kinetic solvent isotope effect of 2.2 in CH_3OD/CH_3OH, was not quenched[9b] by the addition of DABCO (3.5×10^{-4}M). The latter does not significantly quench the fluorescence of 1,3,5-triphenyl-2-pyrazoline at such a low concentration but fluorescence quenching is observed at higher DABCO concentrations. Therefore, observed quenching of the direct photo-oxidation of DPP by DABCO may have been a consequence of quenching of the excited states of DPP by DABCO.

Although increases in the relative rates of the direct photo-oxidation of DPP in a range of solvents (see Section 7.2.1) correlate with increases in the lifetime of singlet oxygen, i.e. $CHCl_3$ >> MeCN ~ C_6H_6 > MeOH no such clear correlation was observed for the dye-sensitised reactions. If the correlation was more than coincidental it would indicate the involvement of a diffusional process of singlet oxygen which is inconsistent with the observation of negligible kinetic solvent isotope effects upon the direct photo-oxidation in aprotic solvents. The latter can only be rationalised on the basis of a singlet oxygen mediated process if the oxidation is a cage reaction rather than a diffusional process. A cage reaction involving singlet oxygen would be expected to be insensitive to the addition of DABCO at low concentrations provided the latter does not quench the excited states of the sensitiser. The observation that the kinetic solvent isotope effect in CD_3CN/CH_3CN is slightly higher than those in the other aprotic solvent systems (Table 7.1) is also consistent with a cage reaction involving singlet oxygen. This is because acetonitrile has a lower viscosity than the other solvents, so the probability of singlet oxygen escaping from the solvent cage, in which it was generated, before it can be chemically trapped is greatest when acetonitrile is used as the solvent. As the singlet-triplet splitting of DPP is estimated[7] to be ~7300 cm^{-1} singlet oxygen production as a result of oxygen quenching of the excited singlet state of DPP is forbidden on energetic grounds. Therefore, singlet oxygen can only be generated from DPP by oxygen quenching of its excited triplet state.

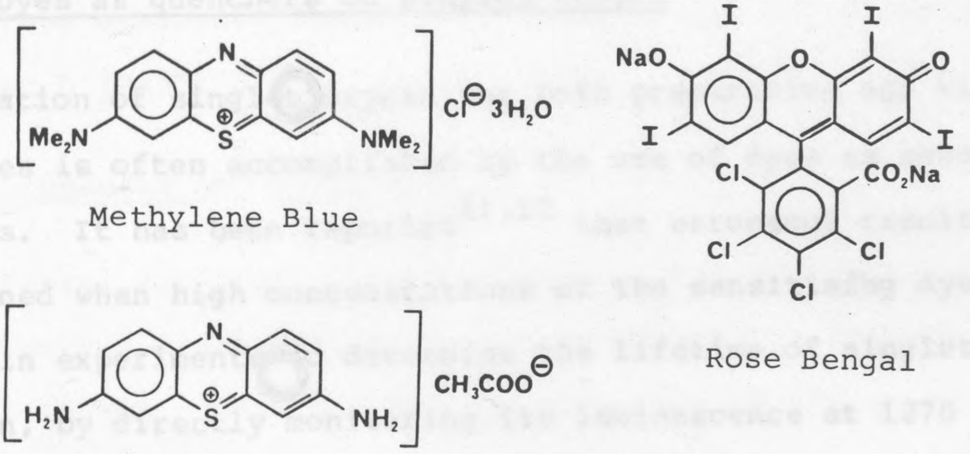
(ii) Conclusions

No firm conclusions can be drawn regarding the mechanism of the direct photo-oxidation of DPP, but it is clear that the observed kinetic solvent isotope effects in protic solvents may have given a totally wrong impression (i.e. indicating a diffusional process involving singlet oxygen) regarding the rôle of singlet oxygen in these reactions. In order to elucidate the mechanism which is operative in the direct photo-oxidation of DPP it will be necessary to measure both the quantum yield of singlet oxygen production from DPP, in both deuterated and non-deuterated solvents, and the effect of added DPP upon the lifetime of singlet oxygen generated by independent methods.

7.2.2 Sensitised photo-oxidation reactions

The implications of the above findings are particularly important for kinetic studies of biological systems because evidence for the involvement of singlet oxygen sometimes hinges on observed kinetic solvent isotope effects in D_2O/H_2O. In many biological systems the potential sensitisers of singlet oxygen contain species, e.g. amino groups, which are capable of undergoing hydrogen bonding with protic solvents.

Since several dyes which are commonly used as sensitisers of singlet oxygen, e.g. methylene blue, are aromatic amines the possibility that they can hydrogen bond to protic solvents must not be overlooked. Although it has been reported[10] that both the fluorescence lifetime and quantum yield for tris(2,2′-bipyridyl)ruthenium (II) ions ($[Ru(bipy)_3]^{2+}$) increase by a factor of two on changing from H_2O to D_2O, as the solvent, no data is available concerning solvent isotope effects upon its quantum yield of triplets. Recent work by Davidson and Goodwin[9a] has indicated that solvent isotope effects upon the quantum yields of triplet production for the widely used dyes, rose bengal and methylene blue, in MeOD/MeOH are minimal. However, significant solvent isotope effects were observed upon the quantum yields of triplet production from thionine in MeOD/MeOH and D_2O/H_2O (1.1 and 1.96 respectively)[9a]. The structures of these dyes are illustrated in Figure 7.5.



Methylene Blue

Rose Bengal

Thionin

Figure 7.5

7.2.3 Summary

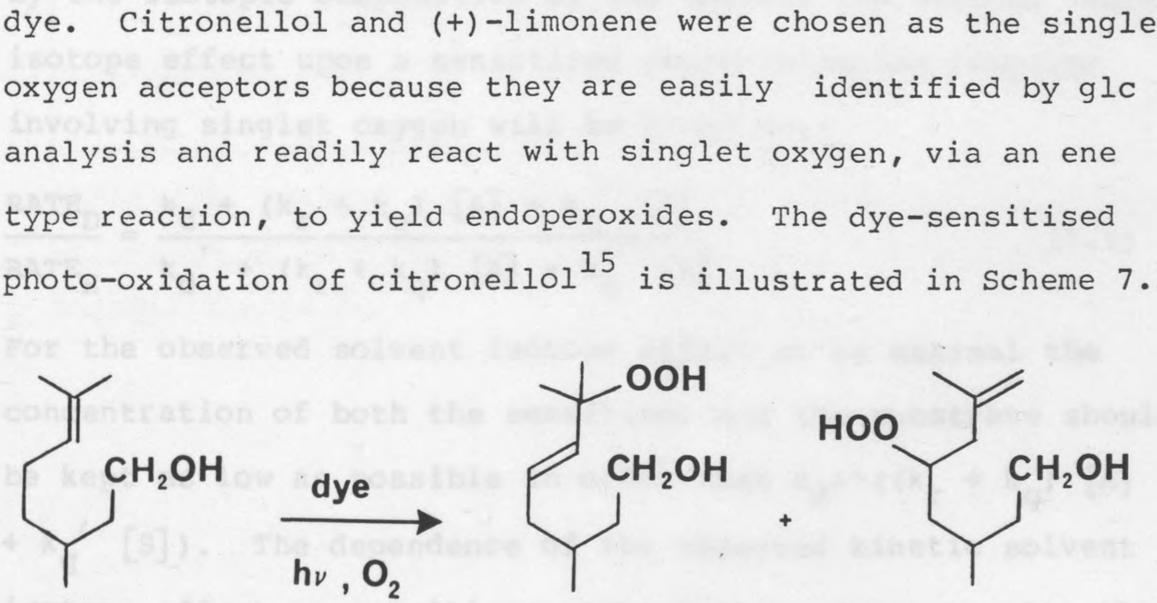
Before interpreting observed solvent isotope effects upon the rate of photo-oxidation reactions it is necessary to determine whether the quantum yield of triplet production for the potential sensitiser of singlet oxygen is dependent upon the isotopic composition of the solvent. If the photophysical properties do exhibit a solvent isotope effect Equation 7.3 rather than Equation 7.1 describes the observed kinetic solvent isotope effects upon the photo-oxidation reaction. If the photophysical parameters are not known, but large kinetic solvent isotope effects are observed in both CD_3OD/CH_3OH and C_6D_6/C_6H_6 solvent systems, singlet oxygen is probably involved because both the viscosity and the change in the lifetime of singlet oxygen are similar for these solvent systems.

The assumption that the isotopic composition of protic solvents does not affect photophysical properties should not be applied to compounds which have the potential to take part in hydrogen bonding or undergo protonation in their ground or excited states.

7.3 Dyes as quenchers of singlet oxygen

Generation of singlet oxygen for both preparative and kinetic studies is often accomplished by the use of dyes as sensitisers. It has been reported[11,12] that erroneous results are obtained when high concentrations of the sensitising dye are used in experiments to determine the lifetime of singlet oxygen, by directly monitoring its luminescence at 1270 nm (see Chapter 5, Section 5.4.3 (ii)). This has been attributed, at least in part, to the simultaneous generation, by electron transfer from the excited sensitiser, of a small amount of the superoxide anion[13a,b] ($O_2^{\overline{\cdot}}$) which is a potent quencher of singlet oxygen[14a,b]. To avoid this problem reproducible estimates for the lifetime of singlet oxygen are obtained by extrapolating to zero dye concentration[11,12].

An investigation was therefore carried out in order to determine whether the observed kinetic solvent isotope effects upon singlet oxygen mediated photo-oxidation reactions are affected by the nature and concentration of the sensitising dye. Citronellol and (+)-limonene were chosen as the singlet oxygen acceptors because they are easily identified by glc analysis and readily react with singlet oxygen, via an ene type reaction, to yield endoperoxides. The dye-sensitised photo-oxidation of citronellol[15] is illustrated in Scheme 7.3



Scheme 7.3

while the analagous reaction of (+)-limonene is outlined in Chapter 5 (Table 5.1).

7.3.1 Results and discussion

From Tables 7.5 and 7.6 it can be seen that the magnitude of the observed kinetic solvent isotope effects is dependent upon both the nature and the concentration of the sensitiser.

The decrease in the observed solvent isotope effects with increase in dye concentration can be explained if the sensitising dyes are behaving as quenchers of singlet oxygen. Under such circumstances the rate of a sensitised photo-oxidation reaction will be given by Equation 7.4[16].

$$\text{RATE} = \frac{\text{Ia}\ \phi_T\ k_r\ [A]}{(k_d + (k_r + k_q)\ [A] + k_q'\ [S])} \tag{7.4}$$

where k_q' = the rate constant for quenching of singlet oxygen by the sensitiser (S)

Provided k_d is the only term in Equation 7.4 to be affected by the isotopic composition of the solvent the kinetic solvent isotope effect upon a sensitised photo-oxidation reaction involving singlet oxygen will be given by:-

$$\frac{\text{RATE}_D}{\text{RATE}_H} = \frac{k_d + (k_r + k_q)\ [A] + k_q'\ [S]}{k_d' + (k_r + k_q)\ [A] + k_q'\ [S]} \tag{7.5}$$

For the observed solvent isotope effect to be maximal the concentration of both the sensitiser and the substrate should be kept as low as possible in order that $k_d \gg ((k_r + k_q)\ [A] + k_q'\ [S])$. The dependence of the observed kinetic solvent isotope effect on sensitiser concentration suggests that the magnitude of $\left(k_q'\ [S]\right)$ at high dye concentrations is too large

SENSITISER	SENSITISER CONCENTRATION (M)	SOLVENT ISOTOPE EFFECT
Rose Bengal	7.86×10^{-4}	2.18
"	1.0×10^{-5}	3.2
Methylene Blue	2.14×10^{-3}	1.79
"	1.0×10^{-5}	3.68
Thionine	2.78×10^{-3}	2.12
"	5.0×10^{-5}	6.08
Tris-ruthenium(11)-(2,2'-bipyridyl)-chloride, hexahydrate	1.0×10^{-3}	2.75
	1.0×10^{-4}	5.32

TABLE 7.5 SOLVENT ISOTOPE EFFECTS UPON THE RATE OF PHOTO-OXIDATION OF (+)-LIMONENE (5×10^{-3}M) IN CH_3CN/D_2O AND CH_3CN/H_2O (1:1 v/v)

SENSITISER	SENSITISER CONCENTRATION (M)	SOLVENT ISOTOPE EFFECT
Methylene Blue	2.14×10^{-3}	1.59
"	1.0×10^{-5}	2.4
Thionine	2.78×10^{-3}	1.45
"	5.0×10^{-5}	2.5

TABLE 7.6 SOLVENT ISOTOPE EFFECTS UPON THE RATE OF PHOTO-OXIDATION OF CITRONELLOL (5×10^{-3}M) IN CH_3CN/D_2O AND CH_3CN/H_2O (1:1 v/v)

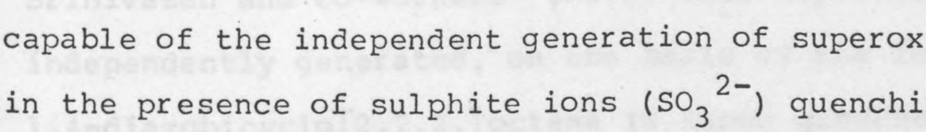
for the above inequality to hold in CD_3CN/D_2O (1:1 v/v). For solvents in which the lifetime $(1/k_d)$ of singlet oxygen is relatively long (e.g. in chloroform $(1/k_d) = 265\ \mu s^{11}$) the term $\left((k_r + k_q)\ [A] + k_q{}'\ [S]\right)$ may well dominate k_d and/or $k_d{}'$. Hence, the quenching reaction will have a more dominant affect upon the rate of photo-oxidation in the deuterated solvent. It was indeed observed that the increase in the rate of oxidation as a consequence of increasing the dye concentration (and thereby increasing the proportion of incident light absorbed) was more marked in the non-deuterated solvents than their deuterated counterparts (Section 7.5.4).

It is hardly surprising that if dyes quench singlet oxygen the observed solvent isotope effects upon photo-oxidation reactions are dependent upon the nature of the sensitising dye. However, the observed solvent isotope effects will also be modified if the photophysical properties of the dye are sensitive to the isotopic composition of the solvent. Under such circumstances it can be seen from Equation 7.4 that the observed solvent isotope effects will be determined by Equation 7.6 rather than Equation 7.5.

$$\frac{RATE_D}{RATE_H} = \frac{\phi_T{}'\ (k_d + (k_r + k_q)\ [A] + k_q{}'\ [S])}{\phi_T\ (k_d{}' + (k_r + k_q)\ [A] + k_q{}'\ [S])} \qquad (7.6)$$

The effects of solvent deuteration upon the photophysical properties of sensitisers, e.g. thionine in D_2O/H_2O, and the consequences as regards the utility of observed kinetic solvent isotope effects in the determination of the rôle of singlet oxygen in photo-oxidation reactions have been dealt with in Section 7.2.2. However, the sensitivity of the photophysical parameters of $[Ru(bipy)_3]^{2+}$ and thionin to solvent deuteration cannot explain the dependency of the observed solvent isotope effects upon the concentration of these dyes.

Quenching of singlet oxygen by the dyes is unlikely to be an energy transfer process because the triplet states of the sensitisers are higher in energy than singlet oxygen. As all the sensitisers in this study are potential electron donors the quenching may be due to electron transfer processes. Many compounds, e.g. azide ions[17], quench singlet oxygen by an electron transfer mechanism and the observation[18a] that "oil-soluble" chlorophyll quenches singlet oxygen can also be rationalised in these terms. A combination of energy transfer and electron transfer mechanisms have been proposed[18b] in order to explain the efficiency with which azomethine dyes quench singlet oxygen. Quenching is believed to occur via an exciplex intermediate, stabilised by both energy transfer and charge transfer contributions, as outlined in Scheme 7.4.



$$\begin{tikzcd} {}^1O_2 + Q \arrow[r] & {}^1(O_2^{\delta-} \cdots Q^{\delta+})^* \arrow[r] \arrow[d] & {}^3O_2 + Q \\ & {}^3O_2 + {}^3Q^* & \end{tikzcd}$$

Scheme 7.4

Since rose bengal and $[Ru(bpy)_3]^{2+}$ have been shown[19] to be capable of the independent generation of superoxide anions in the presence of sulphite ions (SO_3^{2-}) quenching of the singlet oxygen may be due to its interaction with superoxide anions. However, this would require that the ratio of superoxide to singlet oxygen production from the dyes increases with increasing dye concentration, if it is to be consistent with the results in Table 7.5 and 7.6. This will be the case[20] when high laser power levels are used to excite the dyes as in studies of the luminescence of singlet oxygen (as a result of photo-ejection of electrons[21] and interactions between ground state and triplet excited sensitiser molecules[22]) but seems unlikely under normal irradiation conditions. Ogilby and Foote[20] have recently reported rate constants (obtained using high laser powers) for the quenching of singlet oxygen by dyes which are significantly larger than those reported under less intense irradiation conditions. It is relevant to note that no solvent isotope effects were observed[20] upon the rate constants for the quenching of singlet oxygen by mesoporphyrin IX dimethyl ester or thionine in a range of solvent systems.

If the interaction between the ground state dye and singlet oxygen is an electron transfer process it may lead to the generation of superoxide anions which can in turn quench more singlet oxygen. The question then arises as to whether the reported generation of superoxide anions by rose bengal and $[Ru(bipy)_3]^{2+}$ is due to quenching of singlet oxygen, by the dye, within the solvent cage in which it was generated. This provides an alternative explanation to the one proposed by Srinivasan and co-workers[19], i.e. that superoxide anions are independently generated, on the basis of the inability of 1,4-diazabicyclo[2.2.2.]octane (a known quencher of singlet oxygen) to quench the formation of the superoxide anion. DABCO would not be expected to have a marked quenching effect upon a non-diffusional cage reaction between the dye and singlet oxygen so this process is consistent with the observations of Srinivasan and co-workers[19].

7.3.2 Conclusions

For kinetic investigations of dye-sensitised photo-oxidation reactions, involving singlet oxygen, it is essential to keep the dye concentration as low as possible in order to minimise quenching of the singlet oxygen by the dye. As a consequence dyes with high extinction coefficients in the visible region will be of particular use.

7.4 Interpretation of observed kinetic solvent isotope effects

Equation 7.6 describes the solvent isotope effect upon the rate of a photo-oxidation reaction involving singlet oxygen. This equation can only be abbreviated to the more simple Equation 7.2 under circumstances where the photophysical properties of the sensitiser are unaffected by the isotopic composition of the solvent and the sensitiser does not quench singlet oxygen. For self-sensitised photo-oxidation reactions quenching of singlet oxygen by the sensitiser is already accommodated in Equation 7.2. By carrying out kinetic analyses on the first few percent of reactions the affect of any quenching of singlet oxygen by the oxidation products can be minimised.

The advent of direct techniques for the determination of the lifetime of singlet oxygen and the quantum yields of its production from sensitisers is of great importance for interpreting observed kinetic solvent isotope effects. Use of such techniques can provide a knowledge of all the parameters in Equation 7.6 which will enable realistic predictions of kinetic solvent isotope effects upon a photo-oxidation reaction, if it involves singlet oxygen, to be made. Although, the use of direct techniques for identifying singlet oxygen and determining its reactivity towards a wide range of substrates may eventually supercede kinetic solvent isotope effects as a test for the involvement of singlet oxygen in photo-oxidation reactions they do have drawbacks at present (e.g. the use of high laser powers can result in electron ejection and multiphoton processes so the results have to be extrapolated to zero laser power). Until equipment for detecting the luminescence of singlet oxygen is widely available interpretation of kinetic solvent isotope effects will continue to have a part to play in determining the rôle of singlet oxygen in photo-oxidation reactions.

7.5 Experimental

This section deals with experimental procedures used only for the reactions outlined in this chapter. Details of the methods used to determine quantum yields of fluorescence, triplet production and fluorescence lifetimes, the equipment and sources of the chemicals are provided in Chapter 11.

7.5.1 Solvent isotope effects upon the photo-oxidation of pyrazolines

For the direct reactions solutions of the pyrazoline (3.2 x 10^{-5}M) were made up, in the appropriate solvent, in 1 cm^2 quartz cuvettes. The solutions were flushed with oxygen (dry and carbon dioxide-free) and stoppered prior to being irradiated, with stirring, within a circular array of 16 Sylvania black light lamps of maximal output at 350 nm. The rate of disappearance of the pyrazoline was determined by monitoring the decrease in its UV absorption spectrum with time using a Perkin Elmer UV spectrophotometer. Solutions in the corresponding deuterated solvents were made up as described above and irradiated under similar conditions. The results can be seen in Table 7.7 and some are illustrated in Figures 7.6 and 7.7.

Dye-sensitised photo-oxidations were carried out as above (with the dyes being added to the pyrazoline solution prior to oxygenation) using 8 Chryselco daylight fluorescent lamps and a 2% aqueous solution of potassium chromate as a light filter solution. The results are detailed in Table 7.8 and some are illustrated in Figure 7.8.

7.5.2 Fluorescence lifetimes of the pyrazolines

Fluorescence lifetimes were determined according to the procedure outlined in Chapter 11 and are included in Table 7.9. The fluorescence decay curves are, in most cases, best fit by a dual exponential function rather than a singlet exponential one (Table 7.9). The appearance of the plots (Figures 7.9-7.11) would suggest that the dual exponentiality is not an artefact, but its origin is not obvious. The short decay times (τ_1) are not expected to be accurate and errors in τ_2 are probably in the region of ±10%. These lifetimes do not fit the double exponential function well as determined by the reduced chi square Durbin-Watson parameter[23], weighted residuals and autocorrelation functions. The lifetimes are therefore used for comparison pruposes only rather than as absolute lifetimes. Solvent isotope effects upon the longer

SOLVENT	RATE (Ms^{-1})	SOLVENT	RATE (Ms^{-1})
C_6D_6	2.967×10^{-8}	C_6H_6	2.754×10^{-8}
CD_3CN	5.644×10^{-8}	CH_3CN	3.459×10^{-8}
$CDCl_3$	7.196×10^{-7}	$CHCl_3$	5.863×10^{-7}
CH_3OD	5.726×10^{-8}	CH_3OH	1.976×10^{-8}
"	$(2.565 \times 10^{-8})^{a}$	"	$(1.161 \times 10^{-8})^{a}$
CD_3OD	1.279×10^{-7}		

a - 1,3,5-triphenyl-2-pyrazoline

TABLE 7.7 RATES OF DIRECT PHOTO-OXIDATION OF 1,3-DIPHENYL-2-PYRAZOLINE (3.2×10^{-5}M) IN A RANGE OF SOLVENTS

DYE	DYE CONCEN-TRATION (M)	SOLVENT	RATE (Ms^{-1})
Methylene Blue	1×10^{-5}	CD_3CN	8.762×10^{-8}
"	"	CH_3CN	2.333×10^{-8}
"	"	CD_3OD	1.29×10^{-6}
"	"	CH_3OD	3.731×10^{-7}
"	"	CH_3OH	9.301×10^{-8}
Eosin Y	1×10^{-5}	CD_3OD	1.666×10^{-7}
"	"	CH_3OD	4.924×10^{-8}
"	"	CH_3OH	1.267×10^{-8}
Tetraphenylporphyrin	2×10^{-5}	C_6D_6	1.634×10^{-8}
"	"	C_6H_6	1.152×10^{-9}

TABLE 7.8 RATES OF THE DYE-SENSITISED PHOTO-OXIDATION OF 1,3-DIPHENYL-2-PYRAZOLINE (3.2×10^{-5}M) IN A RANGE OF SOLVENTS

PYRAZOLINE	SOLVENT	τ_1(ns)	τ_2(ns)	χ^2	τ_F(ns)	χ^2
DPP	CD_3OD	3.39	3.39	2.0	3.39	1.9
"	CH_3OD	1.53	3.57	1.2	2.6	11.5
"	CH_3OH	2.33	1.47	1.6	1.7	1.9
TPP; R_1=R_3=H	CH_3OD	4.4	4.88	1.6	4.7	8.7
" "	CH_3OH	0.24	3.40	1.3	3.2	14.0
TPP; R_1=NH_2, R_3=H	CH_3OD	0.55	2.67	2.0	2.48	18.0
"	CH_3OH	0.76	2.36	2.7	1.3	74.0
TPP; R_1=H, R_3=NH_2	CH_3OD	2.04	10.03	1.9	7.34	34.0
"	CH_3OH	0.70	7.01	5.3	4.02	300.0

TABLE 7.9 FLUORESCENCE LIFETIMES OF 1,3-DIPHENYL-2-PYRAZOLINE (DPP) AND 1,3,5-TRIPHENYL-2-PYRAZOLINES (TPP; SEE FIGURE 7.4) OBTAINED USING A DOUBLE EXPONENTIAL FITTING FUNCTION (τ_1 AND τ_2) AND A SINGLE EXPONENTIAL FITTING FUNCTION (τ_F) AND THE APPROPRIATE DURBIN-WATSON PARAMETER (χ^2) IN CD_3OD, CH_3OD AND CH_3OH

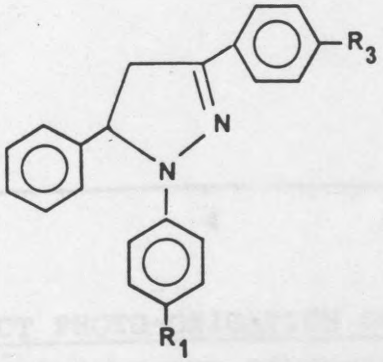


FIGURE 7.4

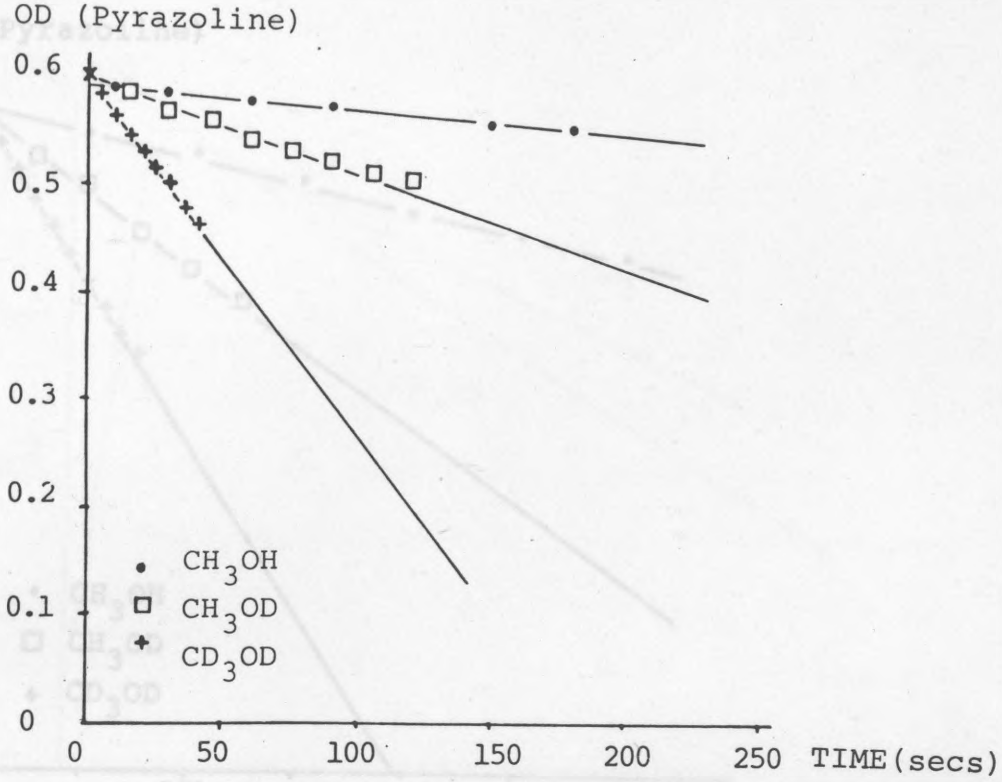


FIGURE 7.6 DIRECT PHOTO-OXIDATION OF 1,3-DIPHENYL-2-PYRAZOLINE IN METHANOL AND DEUTERATED METHANOL SOLUTIONS

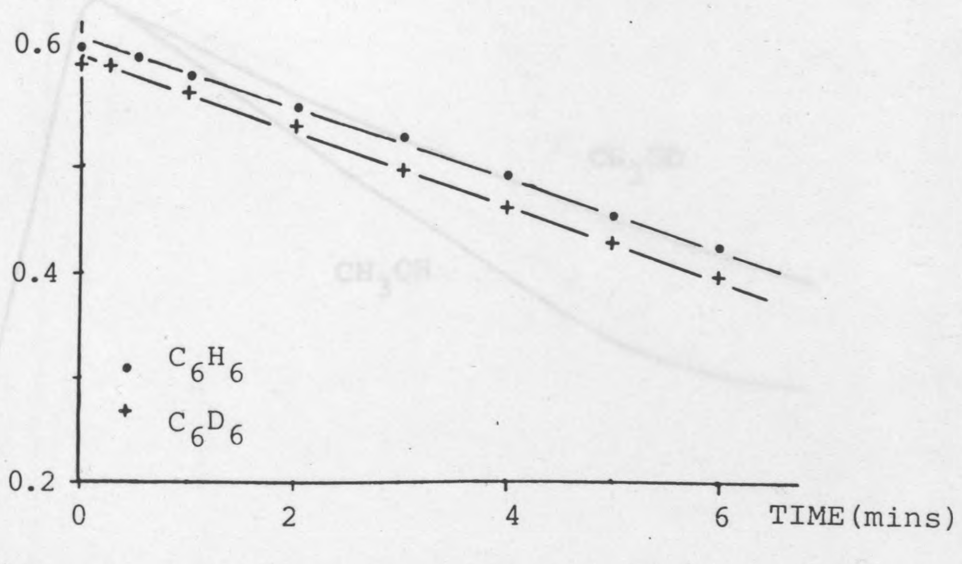


FIGURE 7.7 DIRECT PHOTO-OXIDATION OF 1,3-DIPHENYL-2-PYRAZOLINE IN BENZENE AND DEUTERATED BENZENE SOLUTIONS

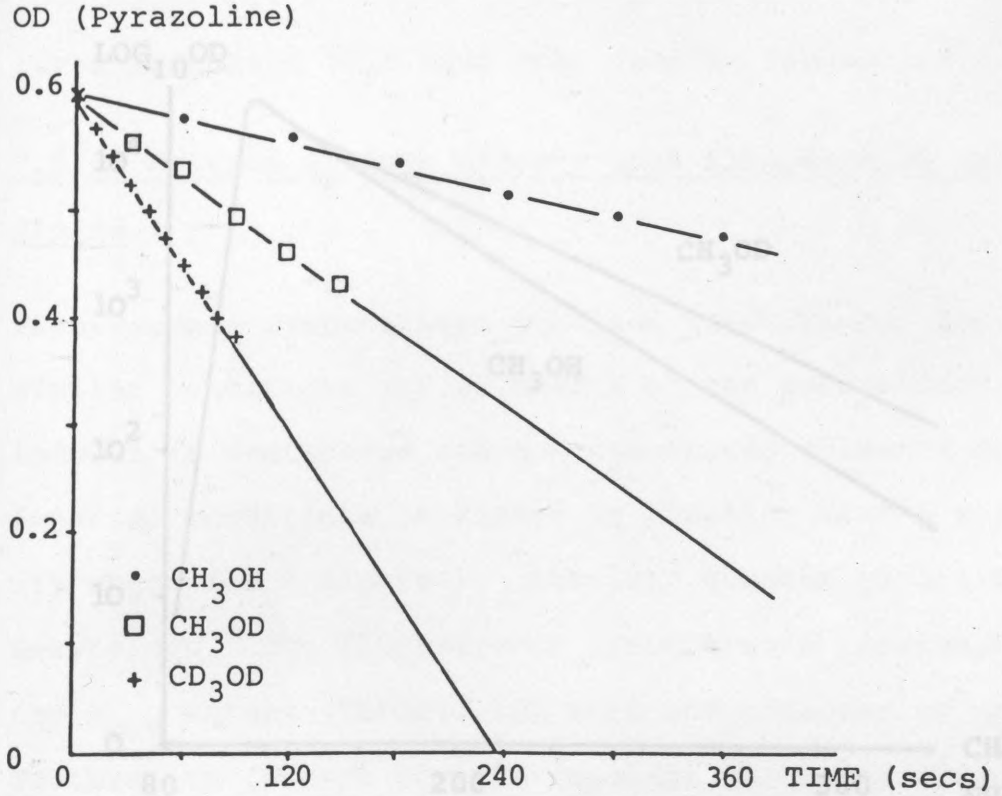


FIGURE 7.8 EOSIN Y SENSITISED PHOTO-OXIDATION OF 1,3-DIPHENYL-2-PYRAZOLINE IN METHANOL AND DEUTERATED METHANOL SOLUTIONS

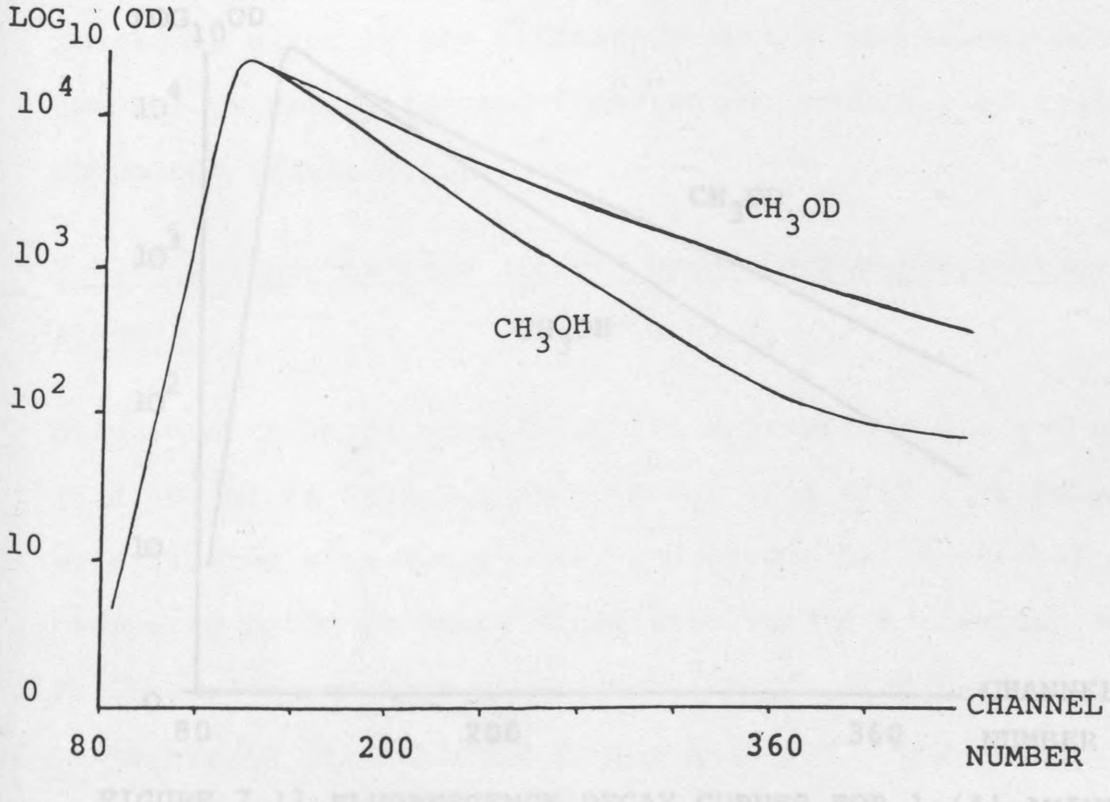


FIGURE 7.9 FLUORESCENCE DECAY CURVES FOR 1,3-DIPHENYL-2-PYRAZOLINE IN METHANOL(CH_3OH) AND DEUTERATED METHANOL SOLUTIONS

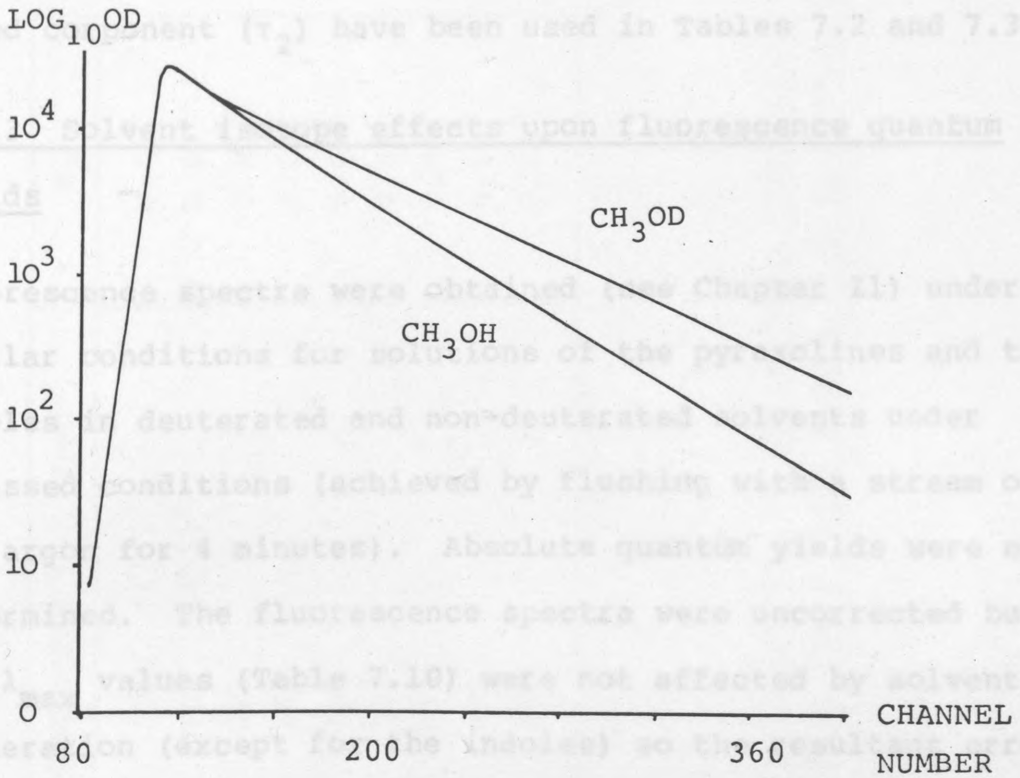


FIGURE 7.10 FLUORESCENCE DECAY CURVES FOR 1,3,5-TRIPHENYL-2-PYRAZOLINE IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

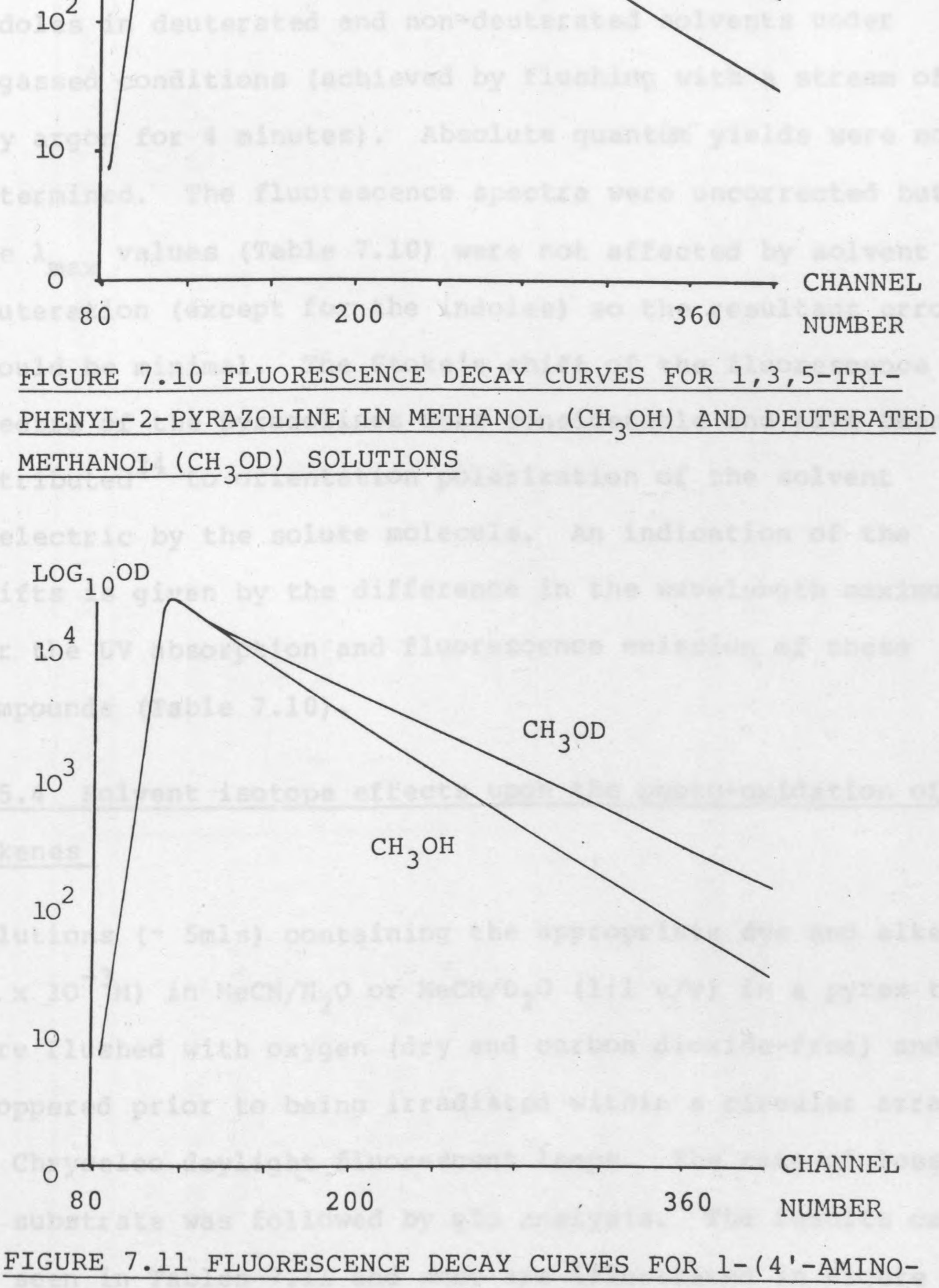


FIGURE 7.11 FLUORESCENCE DECAY CURVES FOR 1-(4'-AMINOPHENYL)-3,5-DIPHENYL-2-PYRAZOLINE IN METHANOL (CH_3OH) AND DEUTERATED METHANOL (CH_3OD) SOLUTIONS

lived component (τ_2) have been used in Tables 7.2 and 7.3.

7.5.3 Solvent isotope effects upon fluorescence quantum yields

Fluorescence spectra were obtained (see Chapter 11) under similar conditions for solutions of the pyrazolines and the indoles in deuterated and non-deuterated solvents under degassed conditions (achieved by flushing with a stream of dry argon for 4 minutes). Absolute quantum yields were not determined. The fluorescence spectra were uncorrected but the λ_{max} values (Table 7.10) were not affected by solvent deuteration (except for the indoles) so the resultant errors should be minimal. The Stoke's shift of the fluorescence spectra of the pyrazolines were considerable and have been attributed[24] to orientation polarization of the solvent dielectric by the solute molecule. An indication of the shifts is given by the difference in the wavelength maximum for the UV absorption and fluorescence emission of these compounds (Table 7.10).

7.5.4 Solvent isotope effects upon the photo-oxidation of alkenes

Solutions (~ 5mls) containing the appropriate dye and alkene (5×10^{-3}M) in $MeCN/H_2O$ or $MeCN/D_2O$ (1:1 v/v) in a pyrex tube were flushed with oxygen (dry and carbon dioxide-free) and stoppered prior to being irradiated within a circular array of Chryselco daylight fluorescent lamps. The rate of loss of substrate was followed by glc analysis. The results can be seen in Tables 7.11 and some are illustrated in Figure 7.12.

	UV λ_{max} (nm)	FLUORESCENCE λ_{max} (nm)	ϕ_f
DPP	352	463 $(475)^a$	0.23^a
TPP; R_1=H_1 R_3=H	355	463 $(473)^a$	0.46^a
TPP; R_1=NH_2, R_3=H	377	525	$<0.05^b$
TPP; R_1=H, R_3=NH_2	354	460	0.13^b
TPP; R_1=CO_2H, R_3=H	366	455	0.41^c
TPP; R_1=NO_2, R_3=H	418	532	$<0.05^c$
TPP; R_1=CN, R_3=H	358	424	0.90^b
TPP; R_1=H, R_3=OH	353	458	0.14^c
TPP; R_1=H, R_3=OEt	354	460	0.21^c

a - reference 24

b - reference 25

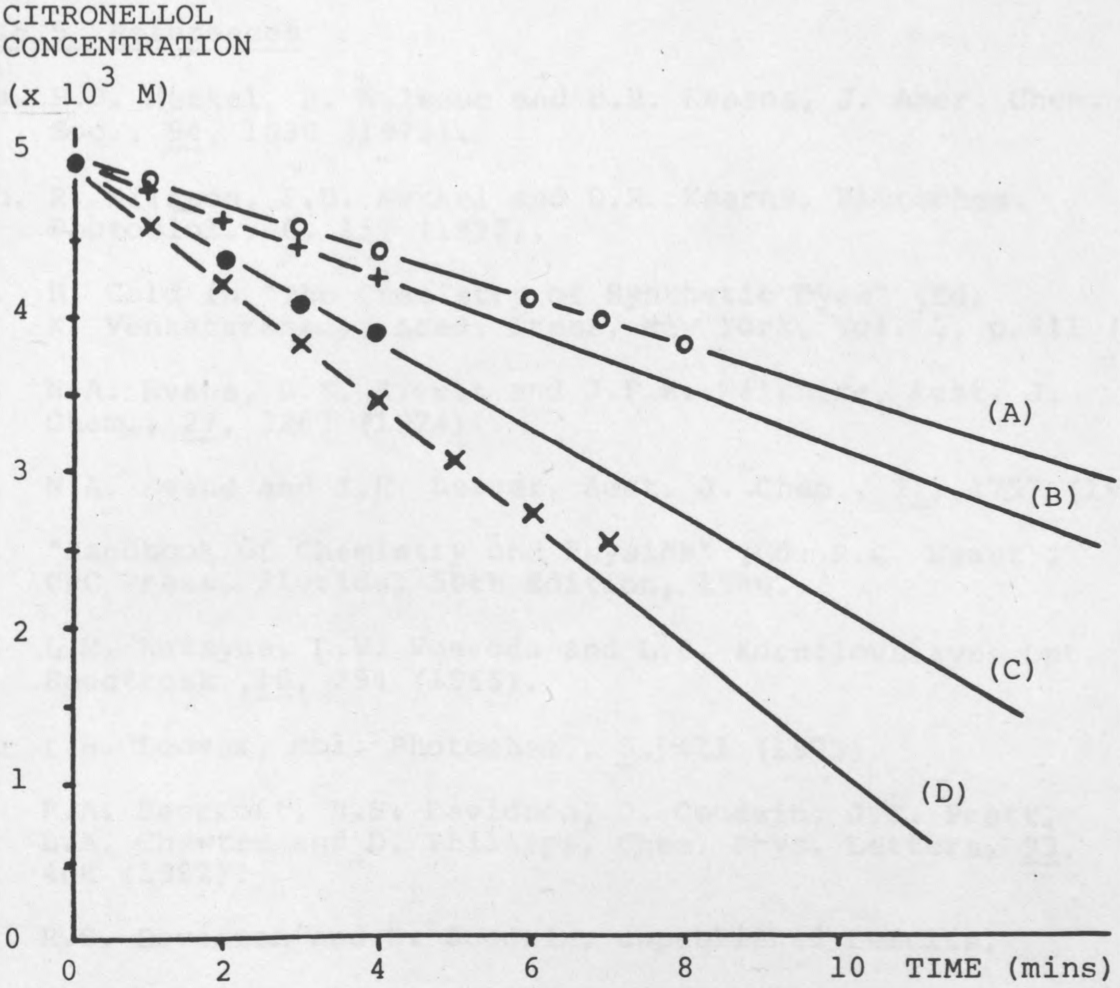
c - reference 26

TABLE 7.10 λ_{max} VALUES FOR THE UV ABSORPTION AND FLUORESCENCE SPECTRA OF SUBSTITUTED PYRAZOLINES ⌈1,3-DIPHENYL-2-PYRAZOLINE (DPP), 1,3,5-TRIPHENYL-2-PYRAZOLINE (TPP) - SEE FIGURE 7.4⌉ IN METHANOL

DYE	DYE CONCENTRATION (M)	RATE (Ms^{-1})			
		(+)-LIMONENE		CITRONELLOL	
		MeCN/D_2O	MeCN/H_2O	MeCN/D_2O	MeCN/H_2O
Rose Bengal	7.86×10^{-4}	1.39×10^{-6}	3.03×10^{-6}		
"	1×10^{-5}	9.9×10^{-7}	3.2×10^{-6}		
"	"	1.19×10^{-6}	3.82×10^{-6}		
Methylene Blue	2.14×10^{-3}	1.22×10^{-6}	2.19×10^{-6}	1.72×10^{-6}	2.73×10^{-6}
"	1×10^{-5}	5.95×10^{-7}	2.19×10^{-6}	5.41×10^{-6}	1.3×10^{-5}
Thionin	2.78×10^{-3}	7.35×10^{-7}	1.56×10^{-6}	3.33×10^{-6}	4.84×10^{-6}
"	5×10^{-5}	3.47×10^{-7}	2.11×10^{-6}	2.64×10^{-6}	6.61×10^{-6}
$Ru(bipy)_3Cl_3.6H_2O^a$	$1 \times 10^{-3}M$	1.26×10^{-6}	3.47×10^{-6}		
"	$1 \times 10^{-4}M$	4.12×10^{-7}	2.19×10^{-6}		

a - saturated sodium nitrate aqueous light filter solution

TABLE 7.11 RATES OF THE DYE-SENSITISED PHOTO-OXIDATION OF ALKENES ($5 \times 10^{-3}M$) IN MeCN/D_2O AND MeCN/H_2O (1:1 v/v) (2% K_2CrO_4 AQUEOUS LIGHT FILTER SOLUTION)



where (A) = CH_3CN/H_2O; thionin - 5.0×10^{-5}M,

(B) = CH_3CN/H_2O, thionin - 2.78×10^{-3}M,

(C) = CH_3CN/D_2O, thionin - 2.78×10^{-3}M,

and (D) = CH_3CN/D_2O, thionin - 5.0×10^{-5}M.

FIGURE 7.12 THIONIN SENSITISED PHOTO-OXIDATION OF CITRONELLOL IN CH_3CN/D_2O AND CH_3CN/H_2O (1:1 v/v) SOLVENT MIXTURES

7.5.5 References

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CHAPTER 8

THE GENERATION OF SINGLET OXYGEN FROM EXCITED SINGLET STATES

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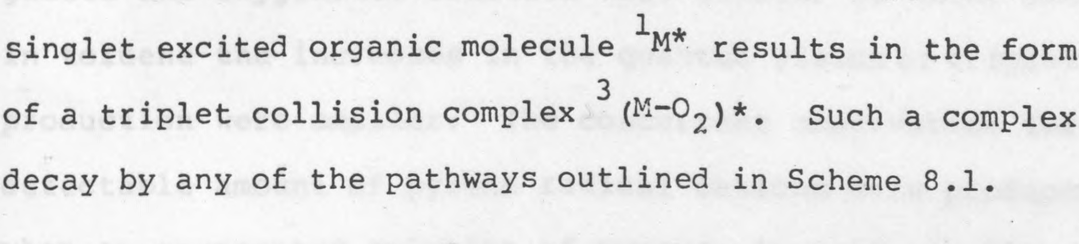
THE GENERATION OF SINGLET OXYGEN FROM EXCITED SINGLET STATES

8.1 Introduction

It is well known that oxygen quenches the fluorescence of many organic molecules with diffusion-controlled rate constants, although the exact mechanism of quenching remains controversial. Interaction of ground state oxygen with a singlet excited organic molecule $^{1}M^{*}$ results in the formation of a triplet collision complex $^{3}(M{-}O_2)^{*}$. Such a complex may decay by any of the pathways outlined in Scheme 8.1.



Scheme 8.1

Path a requires that all the excitation energy is dissipated by the complex so is considered unlikely[1]. Path b is regarded to be more probable and represents oxygen-enhanced intersystem crossing. Although path c is spin-allowed[2] it is forbidden on energetic grounds unless the singlet-triplet splitting of the organic molecule exceeds the excitation energy of singlet oxygen which is 7880 cm^{-1} (94.5 kJ mol^{-1}). Rate constants for oxygen quenching of aromatic compounds have been shown to be diffusion controlled regardless of the magnitude of the energy gap between their lowest excited singlet and triplet states[3]. This phenomenon can be explained if there is some charge-transfer interaction in the intermediate $^3(M\text{-}O_2)^*$ complex[3,4,5]. Potashnik and co-workers[5] have reported that in toluene the decrease in the quantum yield of fluorescence of a wide range of aromatic hydrocarbons, observed when oxygen is introduced into the solutions, is equal to the resultant increase in the quantum yield of triplet production. But in acetonitrile although the difference between the quantum yields of fluorescence in degassed and oxygenated solution were similar to those observed in toluene the increases in the quantum yields of triplet production were smaller. The concurrent observation that a detectable amount of pyrene radical cations were produced when an oxygenated solution of pyrene, in acetonitrile, was irradiated indicates that in polar solvents path d can be a feasible route for oxygen quenching of the excited singlet states of aromatic hydrocarbons.

8.2 Oxygen quenching of the excited states of aromatic hydrocarbons

8.2.1 Background

Scheme 8.2 illustrates the four most important processes involved in the quenching of the excited states of polycyclic aromatic hydrocarbons (ArH), with singlet-triplet energy gaps in excess of 7880 cm^{-1}, by ground state oxygen. Considerable debate has centred on the ability of process 1 to compete with oxygen enhanced inter-system crossing (process 2). The rate constants for oxygen quenching of the excited triplet states of aromatic hydrocarbons are often an order of magnitude lower[6] than for their singlet excited states, but may be

$$ArH_{S_1} + {}^3O_2 \xrightarrow{k_1} ArH_{T_1} + {}^1O_2 \qquad (1)$$

$$ArH_{S_1} + {}^3O_2 \xrightarrow{k_2} ArH_{T_1} + {}^3O_2 \qquad (2)$$

$$ArH_{T_1} + {}^3O_2 \xrightarrow{k_3} ArH_{S_0} + {}^1O_2 \qquad (3)$$

$$ArH_{T_1} + {}^3O_2 \xrightarrow{k_4} ArH_{S_0} + {}^3O_2 \qquad (4)$$

Scheme 8.2

increased if the intermediate $(M\text{-}O_2)^*$ complex exhibits some charge-transfer character[7,8,9]. However, the quenching of excited triplet states is usually more efficient than the quenching of the corresponding excited singlet states because the former are longer lived species. The generation of singlet oxygen as a result of the quenching of triplet excited aromatic hydrocarbons by ground state oxygen (process 3) is usually 10^2-10^3 times faster than oxygen enhanced inter-system crossing[10] (process 4). It must not be forgotten that oxygen quenching of both singlet and triplet excited states are potentially reversible processes[10,11].

As the sum of the quantum yields of fluorescence and triplet production is close to unity (within experimental error) for all aromatic hydrocarbons internal conversion from their singlet excited states can be considered to be a very minor process.[12] The quantum yield of singlet oxygen production as a result of oxygen quenching of the excited states of aromatic hydrocarbons is therefore given by equation 8.1[13] (Appendix 8.1). For highly fluorescent (i.e. $\phi_f \sim 1$) aromatic hydrocarbons,

$$\phi_{^1O_2} = \frac{\alpha \phi_T + (\alpha + \beta)\ K\ [^3O_2]}{(1 + K[^3O_2])} \qquad (8.1)$$

where $\alpha = k_3/(k_3 + k_4)$

$\beta = k_1/(k_1 + k_2)$

ϕ_T = the quantum yield of triplets in degassed solution

K = the Stern-Volmer constant for oxygen quenching of ArH_{S_1}

e.g. rubrene, the limiting quantum yield of singlet oxygen production will approach a value of 2 if processes 1 and 3 are the only routes by which the excited states of the aromatic hydrocarbon are quenched by ground state oxygen (i.e. $\alpha=\beta=1$). Under such circumstances quenching of the excited singlet state would produce one equivalent of singlet oxygen and oxygen quenching of the resultant triplet excited state would produce a second equivalent of singlet oxygen. Information relating to the quantum yield of singlet oxygen production from aromatic hydrocarbons can be obtained either by monitoring their self-sensitised photo-oxidation, to yield endoperoxides (see Chapter 5, Section 5.3.7 (i)a), or by using them as sensitisers for the photo-oxidation of highly reactive singlet oxygen acceptors, e.g. 1,3-diphenylisobenzofuran[14].

As early as 1939 Bowen and Williams[15] reported that the sum of the quantum yields of fluorescence and photo-peroxidation of rubrene at relatively high concentration exceed unity. Later Livingston and Rao[16] concluded that the "interaction of the fluorescent state with oxygen is the principal step (in photooxidation) in strongly fluorescent solutions (whereas) for weakly fluorescent solutions the triplet state plays the dominant role".

However, in the 1960's Stevens and Algar[17a,b] claimed that singlet oxygen was produced solely by oxygen quenching of the triplet excited state of the aromatic hydrocarbon, which is the yield-limiting process at very low oxygen concentrations. These conclusions were based on the observed effects of changes in oxygen concentration upon the quantum yields of autoperoxidation of a range of aromatic hydrocarbons, e.g. 9,10-dimethyl-1,2-benzanthracene. Subsequently, Stevens and Ors[18] determined values of α and β, for a range of aromatic hydrocarbons, which indicated that process 1 was important for the highly fluorescent compounds rubrene and 9,10-dimethylanthracene (i.e. $(\alpha + \beta) \simeq 2$) but not for weakly fluorescent compounds, e.g. tetracene. These results are therefore in complete agreement with the earlier work of Bowen[15] and Livingston[16].

More recent work[13,19,a,b,20] has indicated that for a wide range of aromatic hydrocarbons with singlet-triplet splitting energies in excess of 7880cm^{-1} the parameter $(\alpha + \beta)$ has values between 1.35 and 1.54. However, the limiting quantum of singlet oxygen production from oxygen quenching of the excited states of 9,10-dicyanoanthracene has been reported[21] to be approximately two in acetonitrile solution. All these later results were determined from experiments where the aromatic hydrocarbon was used as a sensitiser for the photo-oxidation of a reactive singlet oxygen acceptor and are included, along with the earlier results, in Table 8.1.

The value of α has been generally accepted as being close to unity on the basis of theoretical work by Porter and co-workers[6] and observations that the yield of singlet oxygen from the quenching of triplet excited aromatic hydrocarbons by ground state oxygen is close to 100%[5,13,18]. However, Gorman and co-workers[23] have reported that the efficiency of process 3 can be significantly less than unity and attributed this to the involvement of process 4. They concluded that the factors which enhance intersystem crossing from the singlet state probably influence the mode of decay of the $(M - O_2)^*$ complex between the triplet excited state and oxygen because the value of α decreases as the quantum yield of triplet production (in degassed solution) increases. Even so, for highly fluorescent complexes; $\beta \approx (\alpha + \beta - 1)$ and it can be seen from the results in Table 8.1 that $\beta \approx 0.5$ for a wide range of aromatic hydrocarbons. Several possibilities have been considered in order to explain why β has a value ≈ 0.5. The most obvious explanation is that process 1 and process 2 have comparable rate constants, but a laser flash photolysis study of the mechanism of oxygen quenching of the excited states of rubrene indicated that process 2 is not involved[24a] in this particular case. Stevens[13] has suggested that the low values of β could be due to re-encounter of the products of process 1 to form the same products as process 2 (Equation 8.2). A third possibility is that oxygen enhanced

$$ArH_{T_1} + {}^1O_2 \longrightarrow ArH_{T_1} + {}^3O_2 \qquad (8.2)$$

AROMATIC HYDROCARBON	β^{a}	$(\alpha + \beta)$	$\phi_{^1O_2}$
9,10-dimethyl-1,2-benzanthracene		1.0 ± 0.2^{b}	
rubrene	$\geqslant 0.54$	1.9 ± 0.4^{b}	$1.46 - 1.47^{c}$
		1.4 ± 0.2^{d}	1.75 ± 0.08^{e}
tetracene		1.2 ± 0.2^{b}	
1,2-benzanthracene			1.4 ± 0.06^{e}
chrysene			1.2 ± 0.08^{e}
perylene	$\geqslant 0.65$		
pyrene		1.54 ± 0.22^{f}	1.85 ± 0.05^{e}
			1.45 ± 0.15^{f}
1,3-diphenylisobenzofuran		1.46 ± 0.13^{d}	
anthracene		1.46^{d}	
9-methylanthracene	$\geqslant 0.19$		
9,10-dimethylanthracene	$\geqslant 0.41$	2.0 ± 0.4^{b}	
		1.35 ± 0.11^{d}	
9-phenylanthracene	$\geqslant 0.42$		
9,10-diphenylanthracene	$\geqslant 0.48$		
9,10-dicyanoanthracene			2.04 ± 0.11^{g}
coronene		$\geqslant 0.95^{d}$	0.90 ± 0.05^{e}

a - reference 19b; photo-oxidation of an acceptor in air saturated n-hexane

b - reference 18; direct photo-oxidation in oxygen saturated benzene

c - reference 19a; photo-oxidation of an acceptor in oxygen saturated benzene and n-hexane respectively

d - reference 13; photo-oxidation of an acceptor in oxygen saturated benzene

e - reference 22b; singlet oxygen luminescence in air saturated benzene

f - reference 20; photo-oxidation of an acceptor in oxygen saturated benzene

g - reference 21; photo-oxidation of an acceptor in oxygen saturated benzene

TABLE 8.1 REPORTED DATA PERTAINING TO THE LIMITING QUANTUM YIELDS OF SINGLET OXYGEN PRODUCTION ($\phi_{^1O_2}$) FROM AROMATIC HYDROCARBONS WITH SINGLET-TRIPLET ENERGY GAPS (ΔE) IN EXCESS OF 7,880 CM^{-1} AND CORONENE (ΔE = 4,500 CM^{-1})

internal conversion from the singlet excited aromatic hydrocarbon is a significant process, as has been reported to be the case for 9,10-diphenylanthracene[24b].

The inherent errors in the indirect techniques used to determine the above results precludes too much discussion regarding the discrepancy between the observed and maximum value of β. In self-sensitised photo-oxidation reactions the substrate concentration must be kept low[18] in order to minimise competing processes, such as dimerisation, e.g. of anthracene and excimer formation, e.g. by pyrene. Consequently, only a small proportion of the singlet oxygen generated will be trapped by the substrate and extrapolation from these very low concentrations of substrate to infinite concentration, in order to determine limiting quantum yields will obviously produce errors. Any singlet oxygen generated in the presence of a ground state substrate, ie by process 3, will experience an apparently abnormally high concentration of substrate and the distribution of the latter with respect to singlet oxygen will not be the normal random distribution when low concentrations of substrate are employed. These difficulties may be alleviated by utilising the aromatic hydrocarbon as a sensitiser for the photo-oxidation of a reactive singlet oxygen acceptor. Care must be taken to ensure that the acceptor is neither a quencher of singlet oxygen nor of the excited states of the sensitiser.

Gurinovich and Salokhiddinov[22a,b] have recently used a direct technique, monitoring the luminescence of singlet oxygen at 1270 nm, to determine the quantum yield of singlet oxygen production from aromatic hydrocarbons relative to Pd-mesoporphyrin 1X-dimethyl ether ($\phi_{^1O_2} \simeq 1$). Their results (Table 8.1) indicate that process 1 is efficient for these compounds and the values obtained for rubrene and pyrene approach the theoretical limiting value. It therefore remains to be seen whether values of ~0.5 for β, determined by indirect techniques, are real or merely a reflection of the experimental conditions. By analogy with the above situation, values determined for the lifetime of singlet oxygen, in solution, using direct techniques are generally longer than those obtained by indirect methods (see Chapter 5, Section 5.3.4 (i)).

The above results (Table 8.1), obtained by direct and indirect methods, indicate that the production of singlet oxygen as a result of the quenching of the excited singlet states of aromatic hydrocarbons, with sufficient singlet-triplet energy gaps, by ground state oxygen is a widespread phenomenon. Consequently, in order to carry out a kinetic analysis of a photo-oxidation reaction, it is necessary to know whether the singlet excited state of the sensitiser can give rise to singlet oxygen production. It would be advantageous to be able to readily determine which excited states of a sensitiser can give rise to singlet oxygen production, under given reaction conditions, even when insufficient data is available concerning their singlet-triplet splitting energies. The advantages of monitoring singlet oxygen luminescence for this purpose become negligible if one does not have access to the required, and expensive, equipment.

A useful technique for determining the rôle of singlet oxygen in photo-oxidation reactions relies upon the fact that the lifetime of singlet oxygen ($1/k_d$) is considerably longer in deuterated solvents than in their non-deuterated counterparts (see Chapter 5, Section 5.3.4). Provided the photophysical properties of the sensitiser and the rate constants of the system other than k_d are unaffected by a change from a non-deuterated solvent to its deuterated analogue the kinetic solvent isotope effect upon a self-sensitised singlet oxygen mediated reaction will be given by Equation 8.3 (see Chapter 5, Appendix 5.1). The observation of a solvent isotope effect upon the rate of a photo-oxidation reaction, under such circumstances, is often used as evidence for the involvement of singlet oxygen. In order for the observed solvent isotope effect to be maximal the concentration of substrate must be kept as low as possible and the reaction with singlet oxygen must involve a diffusional process in order that $k_d >> (k_r + k_q)\ [A]$. The solvent isotope effects upon the rates of the direct photo-oxidation of several aromatic hydrocarbons were therefore determined in a range of solvents and their deuterated counterparts.

$$\frac{\text{RATE}_D}{\text{RATE}_H} = \frac{k_d + (k_r + k_q)\ [A]}{k_d' + (k_r + k_q)\ [A]} \qquad (8.3)$$

where k_d, k_d' = the unimolecular decay constants for singlet oxygen in the non-deuterated and the deuterated solvent respectively;

k_r = the rate constant for reaction of the substrate (A) with singlet oxygen;

k_q = the rate constant for physical quenching of singlet oxygen by the substrate (A).

8.2.2 Results and Discussion

It can be seen from Table 8.2 that some quite high solvent isotope effects were observed upon the rates of the direct photo-oxidation of anthracene compounds, especially when benzene was used as the solvent.

	$\frac{MeOD}{MeOH}$	$\frac{CDCl_3}{CHCl_3}$	$\frac{CH_3CN}{CD_3CN}$	$\frac{C_6D_6}{C_6H_6}$
Anthracene	1	1.9	6.8	4.3
9-Methylanthracene	1.4	3.4	6.4	15.4
9,10-Dimethylanthracene	2.7	3.5	3.9	10.3
9,10-Diphenylanthracene	1.8	5.0	8.2	13.4

TABLE 8.2 SOLVENT ISOTOPE EFFECTS UPON THE RATE OF SELF-SENSITISED PHOTO-OXIDATION OF ANTHRACENE DERIVATIVES (3.2×10^{-5} M)

Addition of singlet oxygen to ground state aromatic hydrocarbons occurs by an allowed[25] ($_{\pi}4_s + {}_{\pi}2_s$) cycloaddition reaction to yield endoperoxides (see Chapter 5, Section 5.3.7 (i) c)which in the case of the anthracene compounds used in this study will be 9,10-endoperoxides. Solvent effects upon concerted cycloaddition reactions tend to be very small because the transition states closely resemble the reactants and little, if any, charge is developed. Similarly, the observation of negligible solvent isotope effects upon the quantum yield of fluorescence for 9,10-dimethylanthracene (1.0 in CH_3OD/CH_3OH, 1.0 in CD_3OD/CH_3OH and 1.1 in C_6D_6/C_6H_6) indicates that its photophysical properties are not markedly affected by solvent deuteration. Consequently, a change from a non-deuterated solvent to its deuterated counterpart will not be expected to have a marked affect upon either k_r or the photophysical properties of the aromatic hydrocarbons. The observed solvent isotope effects upon the rates of the direct photo-oxidation of anthracenes are therefore attributed to solvent isotope effects upon the lifetime of singlet oxygen.

It can be seen from Scheme 8.3 that singlet oxygen produced

$$ArH_{T_1} + {}^3O_2 \xrightarrow{k_3} ArH_{S_O} + {}^1O_2 \qquad (3)$$

$$ArH_{S_O} + {}^1O_2 \xrightarrow{k_r} ArHO_2 \qquad (5)$$

Scheme 8.3

via process 3 is generated at a site available for reaction (process 5). Therefore, if the aromatic hydrocarbon has a high rate constant for reaction with singlet oxygen the latter may be chemically trapped before it can escape from the solvent cage in which it was generated. If the predominant sequence of events is process 3 followed by process 5 the relative magnitudes of the solvent isotope effects for each substrate would be expected to reflect the relative reactivities (Table 8.3) of the substrate towards singlet oxygen, i.e. the photo-oxidation of the most reactive substrate would exhibit the lowest solvent isotope effect. Therefore, the observed solvent isotope effects should follow the trend:- anthracene->9,10-diphenylanthracene>9-methylanthracene>9,10-dimethylanthracene, if process 3 is the only route to singlet oxygen production from the excited states of these compounds.

	ANTHRACENE	9-METHYLANTHRACENE	9,10-DIMETHYLANTHRACENE	9,10-DIPHENYLANTHRACENE
ϕ_f	0.26[a]	0.51[b]	0.90[a]	0.89[b]
$K\ [^3O_2]$	1.14[c]	2.33[d]	3.1[c]	2.21[e]
ϕ_T	0.74[a]	0.48[b]	0.03[a]	0.12[b]
$k_r{}^e\ (s^{-1})$	2.2×10^5	2.65×10^6	2.3×10^7	1.3×10^6
$\phi^S_{^1O_2}$	0.53	0.7	0.76	0.69
$\phi^T_{^1O_2}$	0.88	0.84	0.76	0.72
$\phi^S_{^1O_2}/\phi^T_{^1O_2}$	0.60	0.83	1.0	0.96
Ia (rel)	3667	3142	2788	4195
ϕ_{ox} (rel)	1	12.8	100	6.5
ϕ_{ox}	2.18×10^{-4}	2.80×10^{-3}	2.18×10^{-2}	1.42×10^{-3}
$(\alpha + \beta)$	1.37	1.47	1.36	1.65

a - reference 13; *b* - reference 27, liquid paraffin solution; c - reference 13;

d - reference 19b; *e* - reference 28.

ϕ_f = the quantum yield of fluorescence in degassed solution

k = the Stern-Volmer constant for fluorescence quenching by oxygen

ϕ_T = the quantum yield of triplet production in degassed solution

k_r = "average" rate constant for reaction with singlet oxygen from the β values in reference 28 assuming $k_d = 3.45 \times 10^4 s^{-1}$

$\phi^S_{^1O_2}$ = limiting quantum yield of singlet oxygen production from ArH_{S_1}

$\phi^T_{^1O_2}$ = limiting quantum yield of singlet oxygen production from ArH_{T_1}

Ia (rel) = relative intensity of light absorbed

ϕ_{ox} (rel) = quantum yield of oxidation relative to anthracene (ϕ_{ox} (rel) = 1)

ϕ_{ox} = absolute quantum yields of oxidation

TABLE 8.3 PARAMETERS RELATING TO THE DIRECT PHOTO-OXIDATION OF ANTHRACENES (3.2×10^{-5}M) IN OXYGENATED BENZENE SOLUTION

In contrast with the above situation singlet oxygen generated by process 1 cannot give rise to endoperoxide formation by process 6 (Scheme 8.4) because the $({}_{\pi}4_s + {}_{\pi}2_s)$ cycloaddition of singlet oxygen to triplet excited aromatic hydrocarbons is

$$\mathrm{ArH}_{S_1} + {}^3\mathrm{O}_2 \xrightarrow{k_1} \mathrm{ArH}_{T_1} + {}^1\mathrm{O}_2 \qquad (1)$$

$$\mathrm{ArH}_{T_1} + {}^1\mathrm{O}_2 \not\longrightarrow \mathrm{ArHO}_2$$

Scheme 8.4

symmetry forbidden[25,26]. In the absence of a suitable acceptor the singlet oxygen will be free to diffuse into the bulk solvent and subsequently undergo reaction with an acceptor molecule, unless it is first quenched to its ground state within the solvent cage or in the bulk solvent. Consequently, a change from a non-deuterated solvent to its deuterated analogue will have a greater affect upon the lifetime of singlet oxygen if it is generated by process 1 rather than by process 3.

The observed solvent isotope effects in CD_3OD/CH_3OH upon the direct and the methylene blue sensitised photo-oxidation of 9,10-dimethylanthracene are 13.8 and 12.2 respectively. The fact that those results are comparable indicates that, like the dye-sensitised reaction, the direct photo-oxidation involves singlet oxygen taking part in a diffusional process. The observation of large solvent isotope effects (Table 8.2) upon the rates of the direct photo-oxidation reactions of substituted anthracenes, in benzene solution, are therefore attributed to the participation of process 1 in the generation of singlet oxygen by these compounds. The finding that the kinetic solvent isotope effects upon the direct photo-oxidation of anthracene are generally the lowest in each solvent (Table 8.2), even though it has the smallest rate constant for reaction with singlet oxygen (Table 8.3), provides a further indication that process 3 is not the only route to singlet oxygen production from anthracene compounds.

In order to explain the variation in the observed solvent isotope effects upon the direct photo-oxidation of anthracene and its derivatives in benzene solution (Table 8.2) it is necessary to consider their photophysical properties. The maximum ratio of the quantum yields of singlet oxygen production from singlet and triplet excited states ($\phi_{^1O_2}^{S}/\phi_{^1O_2}^{T}$) in oxygenated benzene solution can be calculated using Equations 8.4 and 8.5 (see Appendix 8.1) by giving α and β values of unity, and using the appropriate data in Table 8.3.

$$\phi_{^1O_2}^{S} = \frac{\beta K [^3O_2]}{(1 + K [^3O_2])} \qquad (8.4)$$

$$\phi_{^1O_2}^{T} = \frac{\alpha\phi_T + \alpha K [^3O_2]}{(1 + K [^3O_2])} \qquad (8.5)$$

The results (Table 8.3) indicate that the contribution by process 1 to the limiting quantum yield of singlet oxygen production is almost as important as the contribution from process 3, for the substituted anthracenes, but much less important for anthracene. This is a consequence of the relatively high quantum yield of triplet production from anthracene and its relatively low fluorescence quantum yield. As β probably has a value less than unity anthracene represents a case where the majority of the singlet oxygen is generated by process 3. The solvent isotope effects upon the lifetime of singlet oxygen have been predicted to be larger when it is generated by process 1 rather than by process 3 on the basis of the earlier discussion. Therefore, if process 1 effectively competes with process 2 the observed kinetic solvent isotope effects should increase as the proportion of singlet oxygen generated by process 1 (i.e. $\phi_{1_{O_2}}^{S}/\phi_{1_{O_2}}^{T}$) increases (Table 8.3), i.e. 9,10-dimethylanthracene,9,10-diphenylanthracene>~9-methylanthracene>>anthracene.

It can be seen from Table 8.2 that the latter trend, modified by the relative reactivities of the anthracenes towards singlet oxygen, is the dominant one in all the solvent systems except CD_3CN/CH_3CN. Acetonitrile differs from the other solvents in being considerably less viscous, the viscosities being 0.35 cp and ~0.6 cp respectively, so singlet oxygen generated by process 3 will have the greatest opportunity to escape from rather than reacting (with the ground state aromatic hydrocarbon) within the solvent cage in which it was generated when acetonitrile is used as the solvent. This explains why the dominant trend of increasing kinetic solvent isotope effects upon the direct photo-oxidation reactions in acetonitrile solution is the same as the trend of decreasing rate constants for the reaction of each substrate with singlet oxygen. As the dominant trend in acetonitrile solution is modified by the relative magnitudes of the ratio $\phi_{1_{O_2}}^{S}/\phi_{1_{O_2}}^{T}$ the solvent isotope effects upon the lifetime of singlet oxygen must be slightly higher when it is generated by process 3 rather than process 1 even in this solvent. If the degree of charge-transfer character in the intermediate complex between the singlet excited aromatic hydrocarbon and ground state oxygen is enhanced in acetonitrile solution[5] process 1 will be a less important process for oxygen quenching of the singlet excited aromatic hydrocarbon in this solvent than in the other solvents. All the results in Table 8.2 are therefore consistent with the involvement of process 1 in the generation of singlet oxygen by anthracene compounds.

Although the observed solvent isotope effects upon the direct photo-oxidation of anthracenes are consistent with the involvement of process 1 in the generation of singlet oxygen by these compounds they give no indication of the magnitude of the β values for these compounds. In order to ascertain the β values the quantum yields of direct photo-oxidation of the anthracene compounds were determined. This was achieved by measuring the relative amount of incident light absorbed by each compound (S) in benzene solution and using Equation 8.6

$$\phi_{ox}(\text{rel}) = \frac{\text{rate of photo-oxidation of S}}{\text{rate of photo-oxidation of A}} \times \frac{\text{Ia (A)}}{\text{Ia (S)}} \qquad (8.6)$$

to obtain quantum yields of direct photo-oxidation relative to anthracene (A). In order to place these relative quantum yields on an absolute basis the quantum yield of direct photo-oxidation of anthracene was determined by comparing the rate of this reaction with the rate of dimerisation (under degassed conditions) for which the quantum yield, in benzene solution, has been reported[29]. As a consequence of the low concentration (3.2×10^{-5} M) of anthracene compounds utilised in these direct photo-oxidation reactions dimerisation is expected to be relatively inefficient in oxygenated benzene and consequently will not have a significant affect upon the magnitude of the observed solvent isotope effects upon the direct photo-oxidation reactions. Values for the parameter $(\alpha + \beta)$ were then calculated from the quantum yields for direct photo-oxidation (ϕ_{ox}) using Equation 8.7 (see Appendix 8.1), assuming that $\alpha = 1$ (Table 8.3).

$$\phi_{ox} = \frac{k_r\,[ArH]}{(k_d + (k_r + k_q)\,[ArH])} \times \frac{(\alpha\phi_T + (\alpha + \beta)\,K[{}^3O_2])}{(1 + K[{}^3O_2])} \qquad (8.7)$$

The results are consistent with reported values, obtained by indirect techniques, for a wide range of aromatic hydrocarbons (Table 8.1), i.e. $(\alpha + \beta) \sim 1.5$, and confirm that process 1 is an important route to singlet oxygen production from anthracene compounds. As a cautionary note it should be pointed out that the discrepancy in the reported values of k_r[28] (the rate constant for reaction with singlet oxygen) for anthracene and 9,10-dimethylanthracene is vast (i.e. $6.0 \times 10^4 - 7.3 \times 10^5$ and $1.72 \times 10^7 - 1.15 \times 10^8 M^{-1}s^{-1}$ respectively using β values and $k_d = 3.45 \times 10^4 s^{-1}$). Consequently, the calculated values of $(\alpha + \beta)$ for these compounds are based on average values of k_r which may well be inaccurate. Other drawbacks to using indirect techniques, as outlined earlier, apply to the method in which these $(\alpha + \beta)$ values were evaluated.

8.2.3 Conclusions

The observation of large solvent isotope effects upon the direct photo-oxidation reactions of highly fluorescent aromatic hydrocarbons provides a readily determined indication that process 1 is an important route to singlet oxygen production. However, the results of such a test give no indication of the relative efficiency of process 1 with respect to process 2 so can only be used qualitatively. Benzene would appear to be the most preferable solvent to use in such tests because the magnitude of the solvent isotope effects upon diffusional processes involving singlet oxygen are so large in C_6D_6/C_6H_6. Another advantage of benzene over protic solvents, e.g. CD_3OD/CH_3OH is that there can be no danger of the former hydrogen bonding to the substrate, resulting in a change of the substrate's photophysical properties when O-H is replaced by O-D. It must be stressed that observed kinetic solvent isotope effects can be totally misleading (see Chapter 7) if the photophysical properties of the sensitiser are different in the deuterated and non-deuterated analogues of the same solvent.

Obviously, this technique will not provide useful information if the aromatic hydrocarbon has a high quantum yield of triplet production relative to its quantum yield of fluorescence (both in degassed solution) e.g. as illustrated by anthracene. Similarly, it can only be used for compounds which are reactive towards singlet oxygen because sensitised photo-oxidation reactions involve a diffusional process of singlet oxygen by definition.

These results highlight the utility of kinetic solvent isotope effects for determining the rôle of singlet oxygen in photo-oxidation reactions and reveal that even self-sensitised photo-oxidation can exhibit substantial kinetic solvent isotope effects. The application of solvent isotope effects to determining whether or not excited singlet states can give rise to singlet oxygen production underlines the fact that large solvent isotope effects are only observed upon photo-oxidation reactions if the reaction with singlet oxygen involves a diffusional process.

8.2.4 Experimental

This section deals with experimental procedures which have been used specifically for the substrates dealt with in this chapter. Details of equipment and the sources of the chemicals used can be found in Chapter 11.

a) Solvent isotope effects

Solutions of the aromatic hydrocarbons (3.2×10^{-5} M) in the non-deuterated solvents, in 1 cm^2 quartz cuvettes, were flushed with a stream of oxygen (dry and carbon dioxide free) for three minutes prior to being irradiated within a circular array of 16 Sylvania black-light lamps with maximal output at 350 nm. The loss of substrate was followed by monitoring the decrease in its UV absorption, using a Cecil linear readout spectrometer, at a wavelength close to its absorption maximum, with time. The solutions of the aromatic hydrocarbons in the deuterated solvents were made up to the same optical density, at the monitoring wavelength, as the solution in the corresponding non-deuterated solvent at t = 0. The irradiations were then carried out as described above. The measured rates of direct photo-oxidation are shown in Table 8.4 and some are illustrated in Figures 8.1 - 8.3.

Solvent isotope effects upon the methylene blue (1×10^{-5} M) sensitised photo-oxidation (Figure 8.4) of 9,10-dimethyl-

	RATE OF PHOTO-OXIDATION (Ms^{-1})			
SOLVENT	ANTHRACENE	9-METHYLANTHRACENE	9,10-DIMETHYLANTHRACENE	9,10-DIPHENYLANTHRACENE
CH_3OH	3.41×10^{-9}	1.84×10^{-9}	4.89×10^{-8} 8.00×10^{-8}[a]	2.33×10^{-9} 1.94×10^{-9}[b]
CH_3OD	3.04×10^{-9}	2.51×10^{-9}	1.18×10^{-7} 2.31×10^{-7}[a]	3.73×10^{-9} 3.90×10^{-9}[b]
$CHCl_3$	5.42×10^{-8}	2.17×10^{-7}	4.89×10^{-7} 1.18×10^{-6}[a]	4.21×10^{-8} 4.36×10^{-8}[b] 9.60×10^{-8}[a]
$CDCl_3$	1.01×10^{-7}	7.35×10^{-7}	1.65×10^{-6} 4.26×10^{-6}[a]	2.37×10^{-7} 2.13×10^{-7}[b] 4.43×10^{-7}[a]
CH_3CN	1.01×10^{-8}	1.14×10^{-7}	2.93×10^{-7} 6.53×10^{-7}[a]	3.10×10^{-8} 5.13×10^{-8}[a]
CD_3CN	6.91×10^{-8}	7.32×10^{-7}	1.27×10^{-6} 2.30×10^{-6}[a]	2.37×10^{-7} 4.48×10^{-7}[a]
C_6H_6	2.53×10^{-9}[c] 3.43×10^{-9}[d]	2.73×10^{-8}[c] 3.88×10^{-8}[d]	1.81×10^{-7}[c] 1.24×10^{-7}[b] 2.78×10^{-7}[d]	6.00×10^{-9} 2.54×10^{-8}[d]
C_6D_6	1.08×10^{-8}[c]	4.20×10^{-7}[c]	1.88×10^{-6}[c] 1.28×10^{-6}[b]	7.45×10^{-8} 3.66×10^{-7}[c]

a - new lamps

b - repeat run

c - the intensity of the incident light was the same for all these reactions

d - new lamps and new starters - these rates are the only ones where all four compounds received the same amount of incident light

TABLE 8.4 RATES OF THE DIRECT PHOTO-OXIDATION REACTIONS OF ANTHRACENE DERIVATIVES (5×10^{-3}M) IN A RANGE OF SOLVENTS

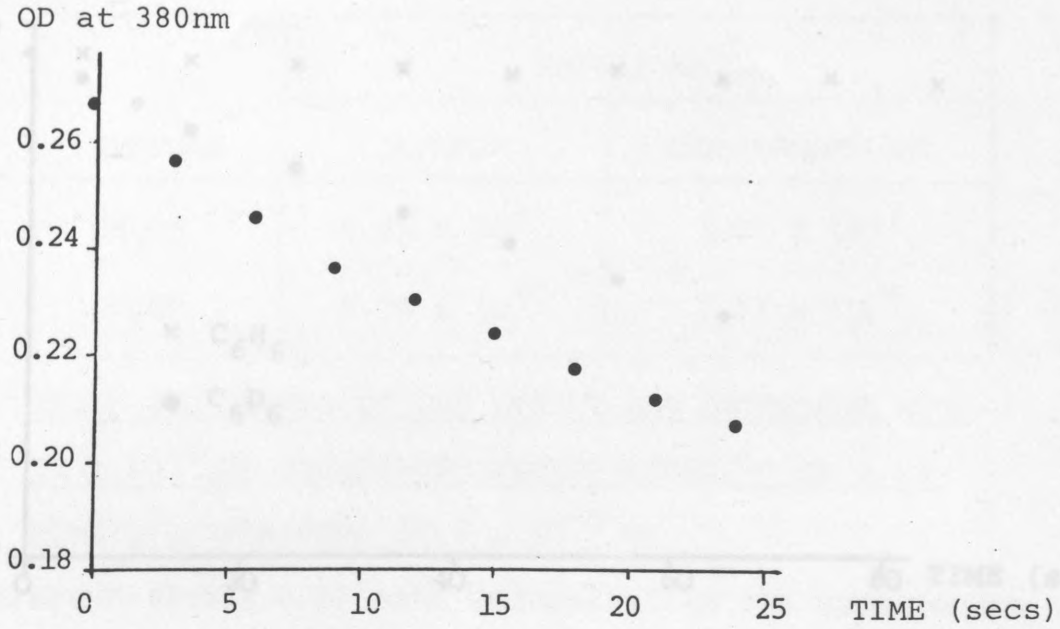


FIGURE 8.1 DIRECT PHOTO-OXIDATION OF 9,10-DIMETHYL-ANTHRACENE IN METHANOL SOLUTION

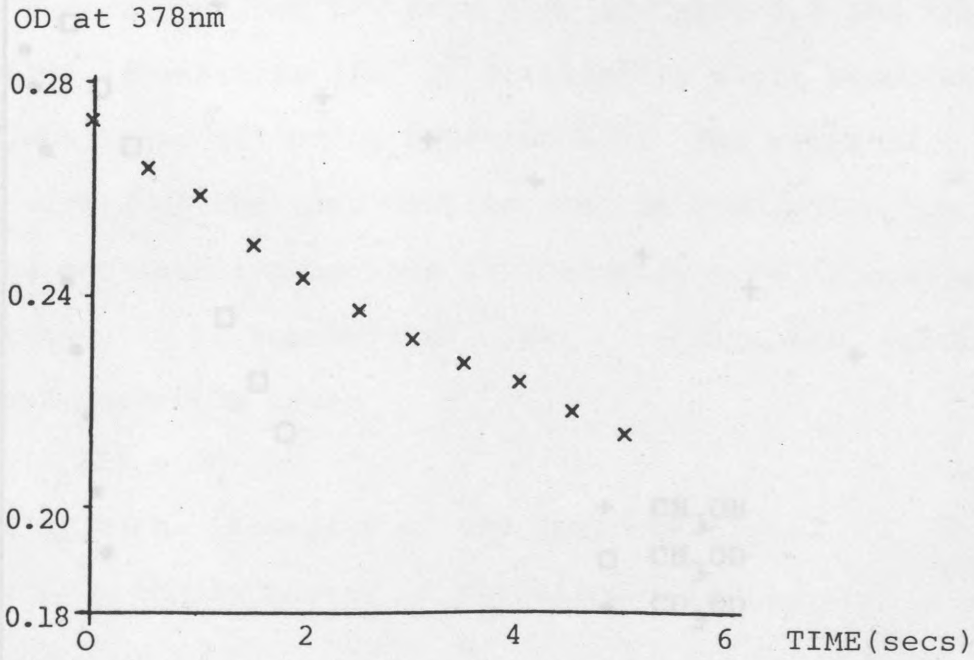


FIGURE 8.2 DIRECT PHOTO-OXIDATION OF 9,10-DIMETHYL-ANTHRACENE IN DEUTERATED METHANOL (CH_3OD) SOLUTION

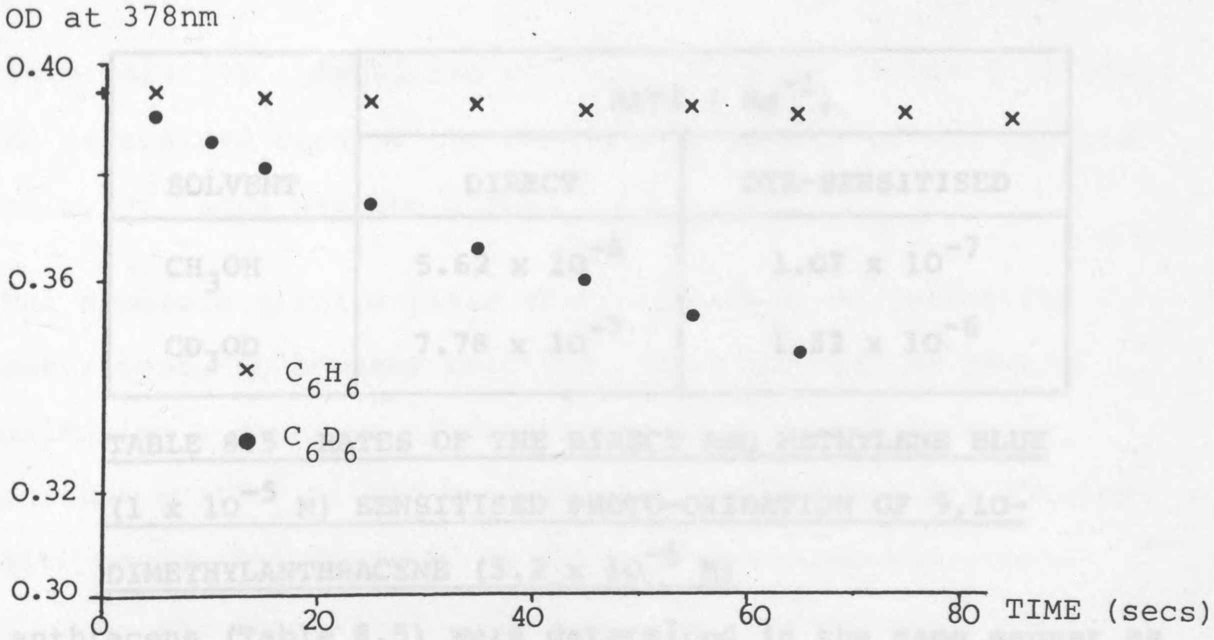


FIGURE 8.3 DIRECT PHOTO-OXIDATION OF 9,10-DIPHENYLANTHRACENE IN BENZENE AND DEUTERATED BENZENE SOLUTIONS

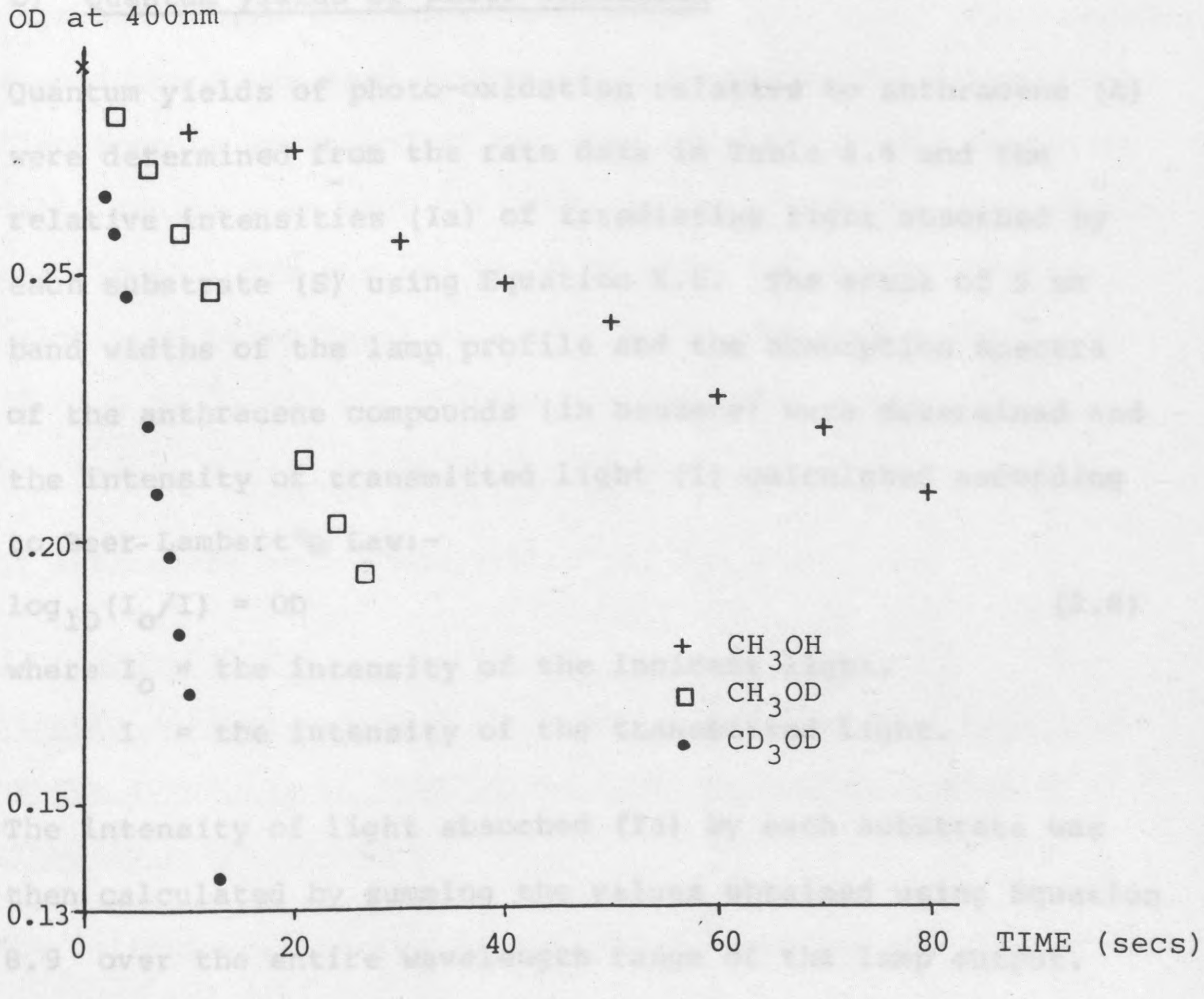


FIGURE 8.4 METHYLENE BLUE SENSITISED PHOTO-OXIDATION OF 9,10-DIMETHYLANTHRACENE IN METHANOL AND DEUTERATED METHANOL SOLUTIONS

SOLVENT	RATE (Ms^{-1})	
	DIRECT	DYE-SENSITISED
CH_3OH	5.62×10^{-8}	1.07×10^{-7}
CD_3OD	7.78×10^{-7}	1.32×10^{-6}

TABLE 8.5 RATES OF THE DIRECT AND METHYLENE BLUE (1×10^{-5} M) SENSITISED PHOTO-OXIDATION OF 9,10-DIMETHYLANTHRACENE (3.2×10^{-5} M)

anthracene (Table 8.5) were determined in the same manner as the direct reactions, using daylight lamps and a 2% aqueous potassium chromate light filter solution.

b) Quantum yields of photo-oxidation

Quantum yields of photo-oxidation relative to anthracene (A) were determined from the rate data in Table 8.4 and the relative intensities (Ia) of irradiating light absorbed by each substrate (S) using Equation 8.6. The areas of 5 nm band widths of the lamp profile and the absorption spectra of the anthracene compounds (in benzene) were determined and the intensity of transmitted light (I) calculated according to Beer-Lambert Law:-

$$\log_{10}(I_o/I) = OD \qquad (8.8)$$

where I_o = the intensity of the incident light,

I = the intensity of the transmitted light.

The intensity of light absorbed (Ia) by each substrate was then calculated by summing the values obtained using Equation 8.9 over the entire wavelength range of the lamp output.

$$Ia = I_o - I \qquad (8.9)$$

Only relative intensities of light absorbed (Table 8.3) could be determined because the absolute intensity of the circular array of lamps was not known.

The absolute quantum yield of direct photo-oxidation for anthracene, in benzene solution, was evaluated by photo-oxidizing a solution of anthracene (3.2×10^{-5} M) while another portion of the same solution, which was not flushed with oxygen but degassed by three freeze-pump-thaw-shake cycles, was irradiated under the same conditions as the oxygenated solution. The rate of disappearance of anthracene (5.95×10^{-9} Ms^{-1} in degassed solution and 4.87×10^{-9} M^{-1} in oxygenated solution) was determined by monitoring the decrease in its fluorescence intensity with time. Fluorescence spectroscopy was used instead of UV spectroscopy because the fluorescence spectrometer has been adapted to hold degassing cells (which were used for both the oxidation and dimerisation reactions). The quantum yield of photo-oxidation was then calculated using Equation 8.10 and the reported value[29] (2.67×10^{-4}) for the quantum yield of dimerisation (ϕ_{dim})

$$\phi_{ox} = \phi_{dim} \times \frac{\text{rate of photo-oxidation}}{\text{rate of dimerisation}} \qquad (8.10)$$

of anthracene at a concentration of 3.2×10^{-5} M.

8.2.5 Appendix 8.1

Kinetic analysis of singlet oxygen production as a result of oxygen quenching of singlet and triplet excited states of aromatic hydrocarbons

The following processes must be considered for the production and decay of singlet and triplet excited states of aromatic hydrocarbons irradiated in oxygenated solution:-

$$ArH \xrightarrow{Ia} ArH_{S_1}$$

$$ArH_{S_1} \xrightarrow{k_{ISC}} ArH_{T_1}$$

$$ArH_{S_1} \xrightarrow{k_F} ArH_{S_O} + h\nu$$

$$ArH_{S_1} \xrightarrow{k_{IC}} ArH$$

$$ArH_{S_1} + {}^3O_2 \xrightarrow{k_1} ArH_{T_1} + {}^1O_2$$

$$ArH_{S_1} + {}^3O_2 \xrightarrow{k_2} ArH_{T_1} + {}^3O_2$$

$$ArH_{T_1} + {}^3O_2 \xrightarrow{k_3} ArH + {}^1O_2$$

$$ArH_{T_1} + {}^3O_2 \xrightarrow{k_4} ArH + {}^3O_2$$

$$ArH_{T_1} \xrightarrow{k_7} ArH$$

Scheme 8.5

The rate of production of singlet oxygen is given by Equation 8.11

$$d[{}^1O_2]/dt = k_1\,[ArH_{S_1}]\,[{}^3O_2] + k_3\,[ArH_{T_1}]\,[{}^3O_2] \qquad (8.11)$$

Using the steady-state approximation for ArH_{S_1}:-

$$[ArH_{S_1}] = Ia \,/\, \left((k_{ISC} + k_F + k_{IC}) + (k_1 + k_2)\,[{}^3O_2]\right) \qquad (8.12)$$

Defining the Stern-Volmer constant (K) for the quenching of the aromatic hydrocarbon by ground state oxygen as:-

$$K = (k_1 + k_2) \,/\, (k_{ISC} + k_F + k_{IC}) \qquad (8.13)$$

and combining Equations 8.11 and 8.12 Equation 8.14 is obtained.

$$[ArH_{S_1}] = \frac{Ia\;K\;[{}^3O_2]}{(k_1 + k_2)(1 + K\,[{}^3O_2])} = \frac{Ia\;\alpha\;K\;[{}^3O_2]}{(1 + K\,[{}^3O_2])} \qquad (8.14)$$

Using the steady-state approximation for ArH_{T_1} :-

$$[ArH_{T_1}] = [ArH_{S_1}]\ (k_{ISC} + (k_1 + k_2)[^3O_2])/(k_3 + k_4)[^3O_2] \quad (8.15)$$

and substituting Equation 8.14 into Equation 8.15:-

$$[ArH_{T_1}] = \frac{Ia\ (k_{ISC} + (k_1 + k_2)\ [^3O_2]}{(k_1 + k_2)(1 + K[^3O_2])(k_3 + k_4)[^3O_2]} \quad (8.16)$$

Substituting Equations 8.14 and 8.16 into Equation 8.11, using $\beta = k_1/(k_1 + k_2)$, $\alpha = k_3/(k_3 + k_4)$ and defining the quantum yield of triplets (ϕ_T) as $k_{ISC}/(k_{ISC} + k_F + k_{IC})$ the rate of production of singlet oxygen is given by:-

$$d[^1O_2]/dt = Ia\ \alpha\ \phi_T + Ia\ (\alpha + \beta)\ K\ [^3O_2]/(1 + K[^3O_2]) \quad (8.17)$$

Defining the quantum yield of singlet oxygen production ($\phi_{^1O_2}$) as:-

$$\phi_{^1O_2} = (\ d[^1O_2]\ /\ dt)\ /\ Ia \quad (8.18)$$

and substituting Equation 8.18 into Equation 8.17 the following equation is derived for the quantum yield of singlet oxygen production as a result of oxygen quenching of the excited states of an aromatic hydrocarbon with a singlet-triplet energy gap in excess of 7880 cm^{-1}.

$$\phi_{^1O_2} = (\alpha\ \phi_T + (\alpha + \beta)\ K\ [^3O_2])\ /\ (1 + K\ [^3O_2]) \quad (8.1)$$

Once produced the singlet oxygen can undergo either of the following processes:-

$$^1O_2 + ArH \xrightarrow{k_r} ArHO_2$$

$$^1O_2 + ArH \xrightarrow{k_q} {}^3O_2 + ArH$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2$$

Scheme 8.6

The rate of direct photo-oxidation of the aromatic hydrocarbon is given by:-

$$- d[ArH] \,/\, dt = k_r \, [ArH] \, [{}^1O_2] \qquad (8.19)$$

Using the steady state approximation for singlet oxygen:-

$$d[{}^1O_2] \,/\, dt = [{}^1O_2] \, (k_d + k_r \, [ArH] \,) \qquad (8.20)$$

Substituting Equation 8.17 into Equation 8.20 gives:-

$$[{}^1O_2] = \frac{Ia \, (\alpha \, \phi_T + (\alpha + \beta) \, K \, [{}^3O_2] \,)}{(1 + K \, [{}^3O_2]) \, (k_d + (k_r + k_q) \, [ArH])} \qquad (8.21)$$

Substituting Equation 8.21 into Equation 8.19 gives:-

$$\frac{-d[ArH]}{dt} = \frac{Ia \, k_r \, [ArH]}{(k_d + (k_r + k_q)[ArH])} + \frac{(\alpha\phi_T + (\alpha + \beta) \, K \, [{}^3O_2])}{(1 + K \, [{}^3O_2] \,)} \qquad (8.22)$$

The quantum yield of photo-oxidation (ϕ_{ox}), assuming that all the aromatic hydrocarbon consumed has given rise to oxidation products, can be defined as:-

$$\phi_{ox} = (- d[ArH] \,/\, dt) \,/\, Ia \qquad (8.23)$$

Equation 8.7 (obtained by substituting Equation 8.22 into Equation 8.23) describes the quantum yield of direct photo-oxidation of an aromatic hydrocarbon with a singlet-triplet splitting energy in excess of 7880 cm^{-1}.

$$\phi_{ox} = \frac{k_r \, [ArH]}{(k_d + (k_r + k_q) \, [ArH])} \times \frac{(\alpha \, \phi_T + (\alpha + \beta) \, K \, [{}^3O_2])}{(1 + K \, [{}^3O_2])} \qquad (8.7)$$

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CHAPTER 9

EXCIMERS AND EXCIPLEXES AS SENSITISERS OF SINGLET OXYGEN

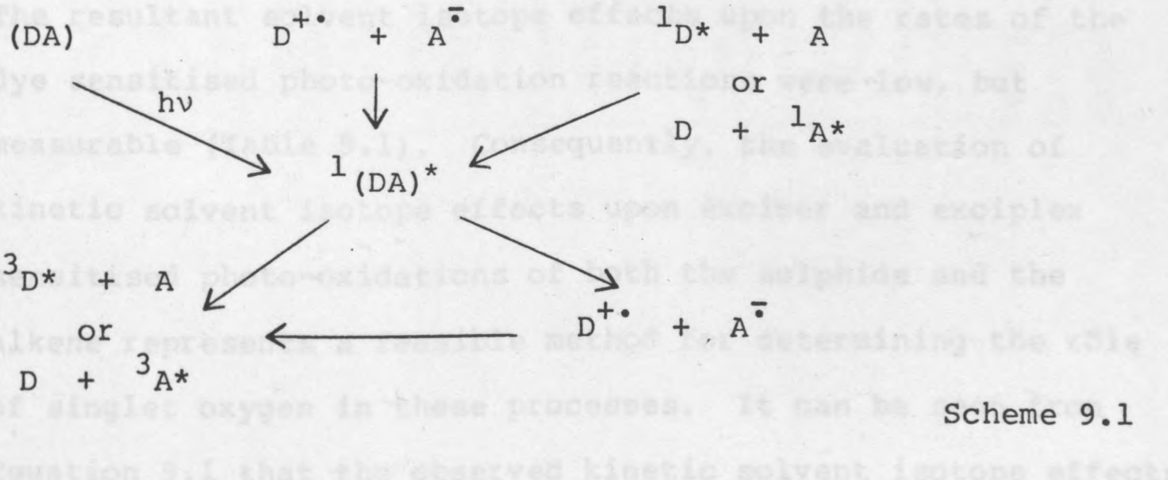
CHAPTER 9

EXCIMERS AND EXCIPLEXES AS SENSITISERS OF SINGLET OXYGEN

9.1 Introduction

Photo-oxidation reactions of aromatic compounds, sensitised by electron acceptors (e.g. 9,10-dicyanoanthracene[1,2]), have in some cases yielded products consistent with the involvement of both singlet oxygen and superoxide anions[3a,b]. Recently, Foote and co-workers[4] have reported that 9,10-dicyanoanthracene can give rise to singlet oxygen production as a result of oxygen quenching of both its singlet and triplet excited states. However, little attention has been paid to the fact that electron transfer reactions of excited singlet states and recombination of radical ions may yield triplets, which can give rise to singlet oxygen production[5].

The ability of both non-relaxed and equilibrium excited complexes, $^1(DA)^*$, to decay to yield reactive species such as triplet states of organic compounds and radical ions, and their interconversions (see Chapter 2) are outlined in Scheme 9.1. It can be seen from Scheme 9.1 that excited



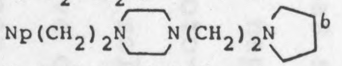
Scheme 9.1

complexes are potential sensitisers of both electron transfer photo-oxidation and singlet oxygen mediated reactions, the singlet oxygen being generated by oxygen quenching of excited triplet states. The utility of excited complexes as sensitisers of photo-oxidation reactions depends upon the efficiency with which the generation of triplet states and/or radical ions compete with other non-radiative and radiative decay pathways.

To investigate the ability of excited complexes to sensitise photo-oxidation reactions a range of excimer and exciplex forming systems have been utilised as sensitisers for the photo-oxidation of di-(t-butyl)sulphide and citronellol. Both these compounds are reactive towards singlet oxygen (see Section 5.3.7) and the rate of their consumption is readily determined by glc analysis.

9.2 Results and discussion

In order to determine the magnitude of the kinetic solvent isotope effects upon known singlet oxygen mediated reactions of di-(t-butyl)sulphide and citronellol, their rose bengal sensitised photo-oxidations were studied in CD_3CN and CH_3CN. The resultant solvent isotope effects upon the rates of the dye sensitised photo-oxidation reactions were low, but measurable (Table 9.1). Consequently, the evaluation of kinetic solvent isotope effects upon excimer and exciplex sensitised photo-oxidations of both the sulphide and the alkene represents a feasible method for determining the rôle of singlet oxygen in these processes. It can be seen from Equation 9.1 that the observed kinetic solvent isotope effects

SENSITISER SYSTEM	DI-(t-BUTYL)SULPHIDE RATE (Ms^{-1})	 SIE	CITRONELLOL RATE (Ms^{-1})	 SIE
Rose bengal (1×10^{-5}M)^a	3.22×10^{-7}	3.8	3.41×10^{-6}	2.1
Naphthalene^b	5.68×10^{-7}	4.1	1.47×10^{-6}	2.0
Np(CH$_2$)$_2$NMePh^b	5.31×10^{-7}	2.9	1.14×10^{-6}	1.0
NpCH$_2$OCH$_2$Np^b	8.86×10^{-7}	3.2	2.45×10^{-6}	1.7
	7.8×10^{-7}	*d*	1.34×10^{-6}	1.0
1-Naphthaldehyde	1.59×10^{-6}	4.2	4.83×10^{-6}	3.5
Pyrene monomer^b	1.28×10^{-6}	4.2	3.04×10^{-6}	*d*
Pyrene excimer	1.48×10^{-6}	2.4	5.63×10^{-6}	*d*
Pyrene^c/triphenylamine (7.5×10^{-2}M)	3.6×10^{-7}	1.3	1.9×10^{-6}	*d*
Pyrene^c/1,4-dicyanobenzene (1×10^{-2}M)	3.82×10^{-6}	2.6	*d*	*d*
Naphthalene (2.5×10^{-2}M)/1-cyano-naphthalene (2.5×10^{-2}M)	3.75×10^{-7}	2.2	*d*	*d*
1-Cyanonaphthalene^b	2.86×10^{-6}	3.2	*d*	*d*
Phenanthrene (1.5×10^{-2}M)/9-cyano-phenanthrene (3×10^{-2}M)	3.44×10^{-6}	2.0	5.29×10^{-6}	*d*
None (λ_{ex} 254nm)	1.75×10^{-6}	1.0	*d*	*d*

a - daylight lamps, *b* - OD 0.7 @ 300nm, *c* - OD 0.42 @ 350nm, *d* - not determined, Np - 1-naphthyl.

TABLE 9.1 RATES OF, AND KINETIC SOLVENT ISOTOPE EFFECTS (SIE) UPON, THE PHOTO-OXIDATION OF DI-(t-BUTYL)SULPHIDE AND CITRONELLOL (BOTH 5×10^{-3}M) USING A RANGE OF SENSITISERS IN OXYGENATED ACETONITRILE SOLUTION (λ_{ex} 300 or 350nm)

$$\frac{\mathrm{RATE}_D}{\mathrm{RATE}_H} = \frac{k_d + (k_r + k_q)\,[A] + k_q'\,[S]}{k_d' + (k_r + k_q)\,[A] + k_q'\,[S]} \qquad (9.1)$$

where k_d and k_d' are the unimolecular decay constants for singlet oxygen in the non-deuterated and deuterated solvents respectively;

k_r is the rate constant for reaction of singlet oxygen with the substrate (A);

k_q and k_q' are the rate constants for the physical quenching of singlet oxygen by the substrate (A) and sensitiser (S) respectively.

will only be maximal if $k_d >> [(k_r + k_q)\,[A] + k_q'\,[S]]$. Consequently, if large kinetic solvent isotope effects are to be observed the oxidation must involve a diffusional process of singlet oxygen and the concentration of both the substrate and the sensitiser should be kept to a minimum. To determine whether triplet production from excimers and exciplexes would lead to photo-oxidation, in the presence of oxygen, it was necessary to evaluate the utility of the parent aromatic hydrocarbons as sensitisers. The results in Table 9.1 indicate that both naphthalene and pyrene are effective sensitisers for the photo-oxidation of the sulphide and the alkene and the kinetic solvent isotope effects upon these reactions are indicative of the involvement of a diffusional process of singlet oxygen.

It can be seen from Table 9.1 that many excited complex forming systems sensitised the photo-oxidation of both the sulphide and the alkene. Kinetic solvent isotope effects which suggest the involvement of singlet oxygen in a diffusional process were obtained in several cases.

Excimers owe most of their stability to exciton resonance rather than coulombic interactions so are more likely to decay to yield triplet states than to generate radical ions. Di-(1-naphthylmethyl)ether, which exhibits intramolecular excimer formation (ϕ_f monomer = 0.015, ϕ_f excimer = 0.03, ϕ_T excimer = 0.11[6]), sensitises the photo-oxidation of both the sulphide and the alkene. As would be expected these reactions exhibit substantial kinetic solvent isotope effects which are consistent with a mechanism involving singlet oxygen.

The photo-oxidation of di-(t-butyl)sulphide exhibits a much lower kinetic solvent isotope effect when pyrene excimer is used instead of pyrene monomer as the sensitiser. The quantum yields of singlet oxygen production by pyrene monomer and excimer have been reported[7] to be 1.4 and 0.4 respectively, in air-saturated benzene solution. Photo-oxidations sensitised by pyrene excimer would therefore be expected to involve singlet oxygen and exhibit substantial kinetic solvent isotope effects. The low value of the observed kinetic solvent isotope effect when pyrene excimer was used as the sensitiser is attributed to quenching of the singlet oxygen by pyrene in its ground or excited triplet state. The latter has been reported[8] to quench singlet oxygen via a pyrene-oxygen complex which exhibits some charge transfer character. In order for the monomer fluorescence of pyrene to be minimal compared to excimer fluorescence high concentrations of pyrene are required and consequently quenching of singlet oxygen will be substantially greater in the excimer system. Several explanations have been proposed[7] in order to account for the much lower quantum yield of singlet oxygen production from pyrene excimer than from pyrene monomer. Firstly, oxygen quenching of both the singlet and triplet states of pyrene can lead to the generation of singlet oxygen (see Chapter 8). However, the singlet-triplet splitting of pyrene excimer is estimated to be insufficient, i.e. $< 7880\text{cm}^{-1}$, for oxygen quenching of the singlet excimer to lead to the generation of singlet oxygen. Secondly, oxygen quenching of the excimer (to yield the triplet excimer) is less efficient[7] than oxygen quenching of singlet excited pyrene monomer. The triplet state of pyrene excimer is believed to be dissociative so singlet oxygen production results from oxygen quenching of triplet pyrene monomer formed as a consequence of the decay of the excimer. Scheme 9.2 illustrates the pathways leading to singlet oxygen production from pyrene monomer and pyrene excimer.

$$\text{pyrene}_{S_1} + {}^3O_2 \longrightarrow \text{pyrene}_{T_1} + {}^1O_2$$

$$\text{pyrene}_{T_1} + {}^3O_2 \longrightarrow \text{pyrene}_{S_O} + {}^1O_2$$

$$^1(\text{pyrene excimer}) + {}^3O_2 \longrightarrow \text{pyrene}_{T_1} + \text{pyrene}_{S_O} + {}^3O_2$$

$$^1(\text{Pyrene excimer}) \longrightarrow \text{pyrene}_{T_1} + \text{pyrene}_{S_O}$$

Scheme 9.2

In contrast to excimers, exciplexes and excited charge-transfer complexes are mainly stabilised by coulombic interactions. As a consequence decay to yield radical ions will be in competition with triplet production from exciplexes and excited charge-transfer complexes. Even though a polar solvent like acetonitrile would be expected to favour the generation of discrete radical ions from excited complexes, the results in Table 9.1 indicate that for many excited complexes triplet production is not a negligible process, even in polar solvents. In aprotic solvents the isotopic composition of the solvent is not expected to affect the rate of an electron transfer process (see Chapter 4). The quenching of singlet oxygen by any superoxide anions[9], generated as a consequence of the generation of radical ions from the excited complexes, will reduce the magnitude of the observed kinetic solvent isotope effects upon the resultant photo-oxidation processes.

$$^{1}(DA)^{*} \longrightarrow D^{+\cdot} + A^{\bar{\cdot}}$$

$$D^{+\cdot} + S \longrightarrow S^{+\cdot}$$

$$A^{\bar{\cdot}} + {}^{3}O_2 \longrightarrow O_2^{\bar{\cdot}} + A$$

$$S^{+\cdot} + O_2^{\bar{\cdot}} \longrightarrow \text{oxidation products}$$

Scheme 9.3

It has been previously observed[10] that the fluorescence of many polycyclic hydrocarbons is quenched by electron donors and acceptors. This was established for the following systems: pyrene/triphenylamine, pyrene/1,4-dicyanobenzene, naphthalene/1-cyanonaphthalene and phenanthrene/9-cyanophenanthrene. Concentrations of the quenchers were chosen in order for the fluorescence quenching to be > 90%. Obviously, fluorescence from the exciplexes was not observed when acetonitrile was used as the solvent because non-radiative decay effectively competes with radiative decay in such a polar solvent. Interestingly, it was found that although naphthalene/1,4-dicyanobenzene has been reported[10] to be an exciplex forming system fluorescence quenching was accompanied by the appearance of emission from 1,4-dicyanobenzene. At concentrations where fluorescence quenching was substantial a fair proportion of the incident light (λ_{ex} 322nm) was being absorbed directly by the 1,4-dicyanobenzene. A similar problem was encountered for the 1,4-dimethoxybenzene/1,4-dicyanobenzene system.

As stated earlier, any superoxide anions generated as a consequence of oxygen quenching of radical ions, will quench singlet oxygen[9] and lead to a reduction in the magnitude of the observed solvent isotope effects. Therefore, the fact that the kinetic solvent isotope effects obtained upon the photo-oxidations sensitised by exciplex forming systems are lower than those obtained using the parent aromatic hydrocarbons (Table 9.1) indicates that, for these systems, triplet production is in competition with decay to yield radical ions. The ability of pyrene/1,4-dicyanobenzene exciplex to undergo ionic dissociation in acetonitrile has recently been investigated[11] by picosecond laser flash photolysis and transient photoconductivity experiments. It was found that ionic dissociation can occur from both the non-relaxed and equilibrium exciplex.

Relatively low kinetic solvent isotope effects are observed (Table 9.1) when intramolecular and intermolecular exciplex forming systems which contain amine groups are used as sensitisers for the photo-oxidation of the sulphide and the alkene. As amines are known to quench singlet oxygen (see Section 5.3.5) this may account for the low kinetic solvent isotope effects. In the case of pyrene/triphenylamine, laser flash photolysis studies revealed that the quantum yield of production of pyrene triplet increases ten-fold (Figure 9.1) in the presence of triphenylamine (pyrene and the amine were used at the concentrations given in Table 9.1). Consequently, quenching of singlet oxygen by triphenylamine (which is present at a relatively high concentration; 7.5×10^{-2}M) must be, at least partly, responsible for the low kinetic solvent isotope effects observed upon photo-oxidations sensitised by pyrene/triphenylamine. It can be seen from Figure 9.1 that the presence of triphenylamine considerably reduces the lifetime of triplet pyrene. This is consistent with the results reported in Chapter 3 which provided evidence that amines and sulphides are capable of quenching the triplet states of many aromatic hydrocarbons. Under the conditions used for photo-oxidation reactions the amine will be in competition with oxygen for quenching of the triplet excited pyrene.

The mechanisms of the reactions which utilised the α-naphthylalkylamines illustrated in Figure 9.2, which are intramolecular exciplex forming systems with high triplet yields (see Chapter 4 and reference 12), as sensitisers were found to be complicated by competing radical reactions of the sensitisers. These caused the oxidation reactions to exhibit induction periods which were prolonged in the presence of radical inhibitors, e.g. tinuvin 770. Hindered piperidines, such as tinuvin 770, have attracted widespread interest as

$Np(CH_2)_2NMePh$ and

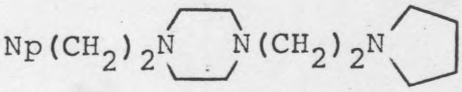


Figure 9.2

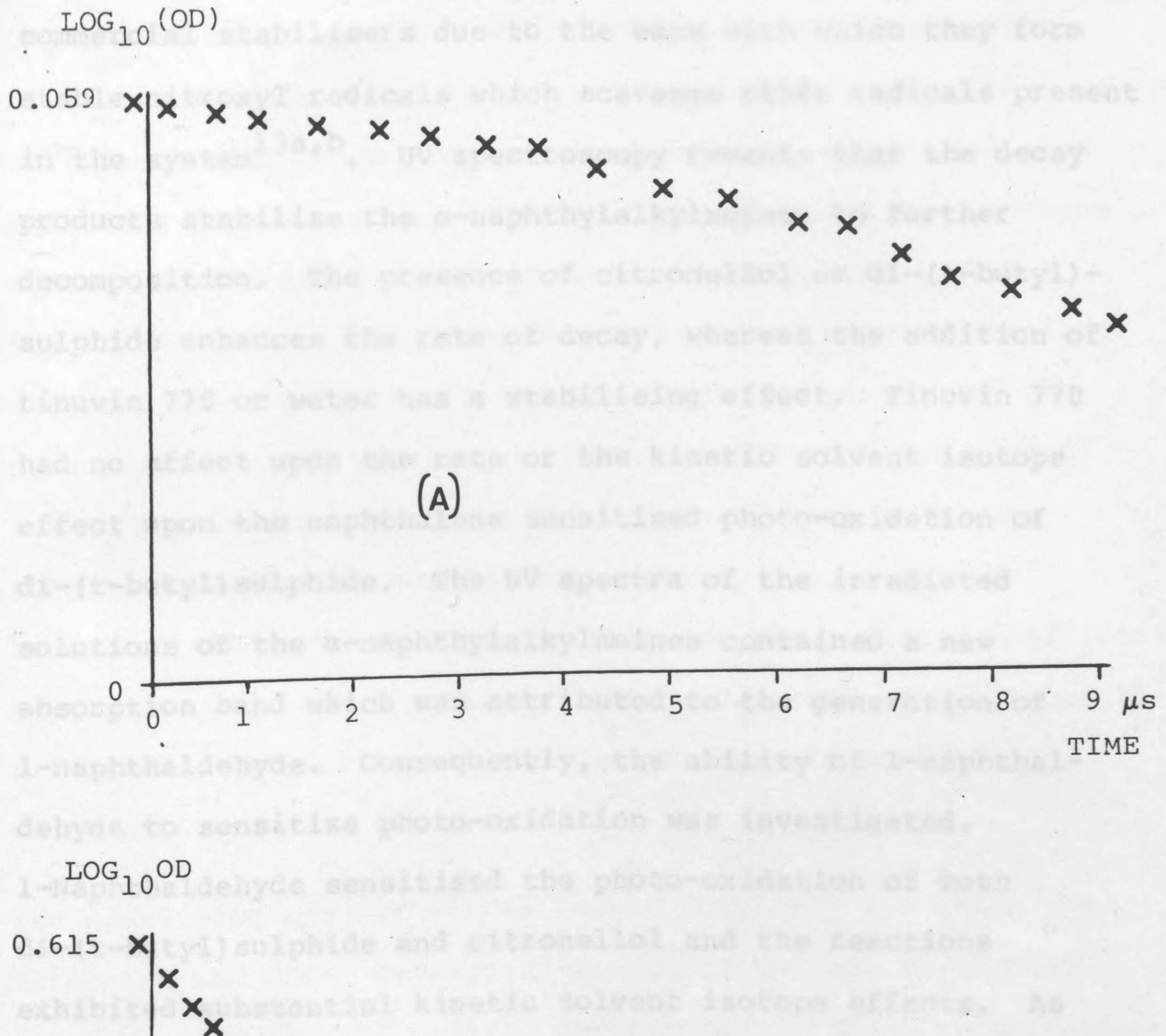


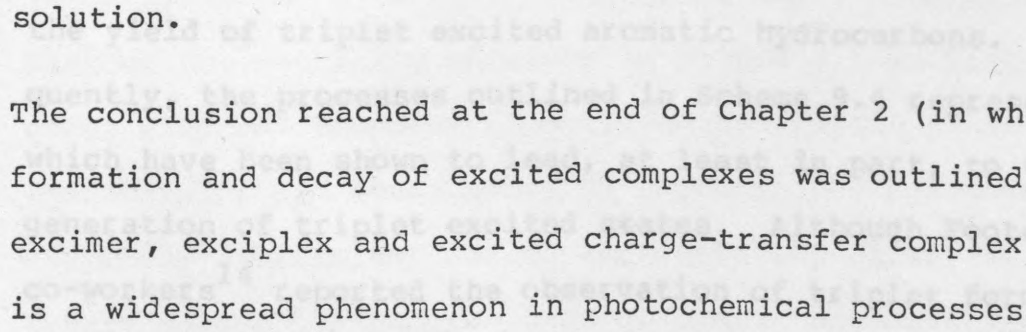
FIGURE 9.1 DECAY OF PYRENE TRIPLET-TRIPLET ABSORPTION IN THE ABSENCE (A) AND PRESENCE (B) OF TRIPHENYLAMINE ($7.5\ 10^{-2}$ M) IN DEGASSED ACETONITRILE SOLUTION

commercial stabilisers due to the ease with which they form stable nitroxyl radicals which scavenge other radicals present in the system[13a,b]. UV spectroscopy reveals that the decay products stabilise the α-naphthylalkylamines to further decomposition. The presence of citronellol or di-(t-butyl)-sulphide enhances the rate of decay, whereas the addition of tinuvin 770 or water has a stabilising effect. Tinuvin 770 had no affect upon the rate or the kinetic solvent isotope effect upon the naphthalene sensitised photo-oxidation of di-(t-butyl)sulphide. The UV spectra of the irradiated solutions of the α-naphthylalkylamines contained a new absorption band which was attributed to the generation of 1-naphthaldehyde. Consequently, the ability of 1-naphthaldehyde to sensitise photo-oxidation was investigated.

1-Naphthaldehyde sensitised the photo-oxidation of both di-(t-butyl)sulphide and citronellol and the reactions exhibited substantial kinetic solvent isotope effects. As di-(t-butyl)sulphide does not contain any α-hydrogen atoms hydrogen abstraction by the excited 1-naphthaldehyde, to yield species of the type $R\text{-}\dot{C}H\text{-}S\text{-}R'$, is avoided. Consequently, the consumption of the sulphide should be entirely due to oxidation reactions with no competing radical processes. The photo-oxidations sensitised by α-naphthylalkylamines are therefore proposed to occur as a consequence of the generation of 1-naphthaldehyde, the low kinetic solvent isotope effects being attributed to quenching of singlet oxygen by the amine moiety. No problems due to decomposition were encountered with the intermolecular systems.

These experiments have established the feasibility of using intra- and intermolecular excited complexes as sensitisers of singlet oxygen, even in polar solvents. However, the efficiency with which they sensitise singlet oxygen mediated reactions does not always justify their use, e.g. naphthalene versus naphthalene/1-cyanonaphthalene (Table 9.1). Only a few of the rates of reaction can be compared because the light absorbed by each system is not the same. Comparison of the pyrene monomer and exciplex systems reveals that the pyrene/1,4-dicyanobenzene system is the only one which is a more effective sensitiser than pyrene monomer, i.e. a similar amount of the incident light is absorbed when either sensitiser system is used, but the rate of photo-oxidation of di-(t-butyl)-sulphide is greater when 1,4-dicyanobenzene is present in solution.

The conclusion reached at the end of Chapter 2 (in which the formation and decay of excited complexes was outlined) that excimer, exciplex and excited charge-transfer complex formation is a widespread phenomenon in photochemical processes is the key to the importance of the findings described above. The potential for intermediate excited complex formation in sensitised electron-transfer photo-oxidation reactions is considerable. Scheme 9.4 illustrates two possible excited



Scheme 9.4

complex intermediates which can undergo decay to yield excited triplet states, oxygen quenching of which may lead to the generation of singlet oxygen. The efficiency with which triplets are formed will depend upon the extent to which the excited complex decays by other non-radiative and radiative processes. Evidence for triplet production as the result of oxygen quenching of a sensitiser is obtained from the finding[4] that the limiting quantum yield of singlet oxygen production from 9,10-dicyanoanthracene approaches a value of 2 in both benzene and acetonitrile solutions. The results in Chapter 3 revealed that the interaction between the excited singlet states of the aromatic hydrocarbons and electron rich substrates, e.g. sulphides, can lead to an increase in the yield of triplet excited aromatic hydrocarbons. Consequently, the processes outlined in Scheme 9.4 represent routes which have been shown to lead, at least in part, to the generation of triplet excited states. Although Foote and co-workers[14] reported the observation of triplet formation when 9,10-dicyanoanthracene is irradiated in the presence of thioanisole our results suggest that the triplet enhancement is highly inefficient (see Chapter 3).

An interesting electron transfer photo-oxidation has recently been reported by Schaap and co-workers[15]. They found that the rate of the 9,10-dicyanoanthracene (DCA) sensitised photo-oxidation of tetraphenyloxirane (1) is dramatically enhanced in the presence of biphenyl (BP). The following scheme was proposed in order to account for the observed rate enhancement:-

$$\mathrm{DCA} \xrightarrow{h\nu} {}^{1}\mathrm{DCA}^{*} \qquad (1)$$

$${}^{1}\mathrm{DCA}^{*} + (1) \longrightarrow (1)^{+\cdot} + \mathrm{DCA}^{\overline{\cdot}} \qquad (2)$$

$${}^{1}\mathrm{DCA}^{*} + \mathrm{BP} \longrightarrow \mathrm{BP}^{+\cdot} + \mathrm{DCA}^{\overline{\cdot}} \qquad (3)$$

$$(1) + \mathrm{BP}^{+\cdot} \longrightarrow (1)^{+\cdot} + \mathrm{BP} \qquad (4)$$

$$\mathrm{DCA}^{\overline{\cdot}} + {}^{3}\mathrm{O}_2 \longrightarrow \mathrm{O}_2^{\overline{\cdot}} + \mathrm{DCA} \qquad (5)$$

$$(1)^{+\cdot} + \mathrm{O}_2^{\overline{\cdot}} \longrightarrow \text{oxidation products} \qquad (6)$$

Scheme 9.5

Because biphenyl, which was not appreciably consumed during the reaction, has a lower oxidation potential than (1) it will be the more effective quencher of singlet excited DCA ($k_q = 3.1 \times 10^{9}\ M^{-1}s^{-1}$)[15] to generate $\mathrm{DCA}^{\overline{\cdot}}$. The main drawback of the mechanism outlined in Scheme 9.5 is that subsequent electron transfer from (1) to $\mathrm{BP}^{+\cdot}$ (path 4) is highly endothermic. In the absence of biphenyl the reaction is extremely inefficient due to the inability of (1) to effectively quench the fluorescence of DCA in acetonitrile. Although (1) was chosen as a substrate which exhibits low reactivity towards singlet oxygen diphenyl sulphide has been described as "unreactive towards singlet oxygen" ($k_q \sim 1 \times 10^{5}$) but does undergo dye sensitised photo-oxidation. The possibility therefore arises that fluorescence quenching of DCA by BP can lead to intermediate exciplex formation, decay of which may lead to the production of triplets. To evaluate the feasibility of such a process a solution of DCA in acetonitrile was interrogated by laser flash photolysis and the effects of added biphenyl (10^{-2}M) determined. The results revealed that not only was the triplet yield of DCA enhanced (the triplet-triplet absorption increased from an OD of 0.023 to 0.032 at 465nm) when biphenyl was present in solution, but triplet biphenyl was also produced. The latter was identified by its triplet-triplet absorption spectrum (λ_{max} = 358nm). It is therefore proposed that the acceleration of the DCA sensitised photo-oxidation of (1), in the presence of biphenyl, is due to the production of triplets and subsequent singlet oxygen production. For such an explanation to be valid the efficiency with which (1) reacts with singlet oxygen must exceed the ability of the endothermic electron transfer from (1) to $BP^{+\bullet}$ to occur, under the reaction conditions.

The generation of excited biphenyl triplet states cannot have occurred via energy transfer from DCA triplet states because biphenyl triplets are of higher energy than their DCA counterparts. Consequently, the excitation of DCA provides firm evidence for the intermediacy of a non-relaxed or an equilibrium exciplex. The finding that even though decay of such an exciplex to yield triplet DCA is favoured over triplet BP formation, on energetic grounds, both decay routes are operative was of interest. In order to determine whether such behaviour is a widespread phenomenon a solution of DCA to which naphthalene or 1,1′-binaphthyl (both 10^{-2}M) had been added was flash photolysed, under conditions where DCA was the only species which absorbed the incident light. Although enhancement of triplet DCA formation was minimal both triplet naphthalene and triplet 1,1′-binaphthyl were generated. Similar experiments using 9-cyanoanthracene as the sensitiser also yielded triplets from both compounds present in solution, but the yields of aromatic hydrocarbon triplets were lower

SENSITISER	ADDITIVE (CONCENTRATION M)	TRIPLET-TRIPLET ABSORPTION λ_{max} (nm)	OPTICAL DENSITY AT λ_{max}	QUENCHING OF SENSITISER FLUORESCENCE (%)
9,10-Dicyanoanthracene	None	465	0.023	0
"	Biphenyl (10^{-2})	358	0.09	34
"	Naphthalene (10^{-2})	412	0.041	72
"	1,1′-Binaphthyl (10^{-2})	620	0.10	73
9-Cyanoanthracene	None	465	0.031	0
"	Biphenyl	358	0.042	47
"	Naphthalene (10^{-1})	412	0.027	64

TABLE 9.2 OPTICAL DENSITIES OF TRIPLET-TRIPLET ABSORPTIONS BY AROMATIC HYDROCARBONS RESULTING FROM FLUORESCENCE QUENCHING OF 9,10-DICYANOANTHRACENE AND 9-CYANOANTHRACENE BY THE HYDROCARBONS, IN DEGASSED ACETONITRILE SOLUTION

even though a similar proportion of DCA and 9-cyano-anthracene excited singlet states were quenched in each case. As the extinction coefficients for the triplet-triplet absorption of these compounds, in acetonitrile solution, are not known absolute quantum yields of triplet production could not be determined. These results are summarised in Table 9.2.

9.3 Conclusions

Excimer and exciplex forming systems can give rise to triplet formation and subsequent generation of singlet oxygen even in highly polar solvents. Consequently, excited complexes have proved to be of use as sensitisers for the photo-oxidation of sulphides and alkenes. In the case of exciplex forming systems the reactions may be complicated by competing dissociation of the excited complex to yield radical ions which results in electron-transfer oxidation processes. 9,10-Dicyanoanthracene (DCA) sensitised photo-oxidations should not automatically be interpreted as electron-transfer oxidation processes because not only can DCA sensitise singlet oxygen formation[4], but it can also form exciplexes with aromatic hydrocarbons. Triplet production and subsequent generation of singlet oxygen from such exciplexes provides an explanation for the observed enhancement of DCA sensitised photo-oxidation reactions in the presence of biphenyl[15] and, at least in part, for the observation that DCA sensitised photo-oxidation of dimethoxynaphthalene gives rise to products consistent with the involvement of both electron-transfer and singlet oxygen mediated mechanisms[3].

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CHAPTER 10

THE USE OF TITANIUM DIOXIDE AS A SENSITISER FOR ELECTRON TRANSFER PHOTO-OXIDATION REACTIONS

CHAPTER 10

THE USE OF TITANIUM DIOXIDE AS A SENSITISER FOR ELECTRON TRANSFER PHOTO-OXIDATION REACTIONS

The basis of the use of semiconductors, such as titanium dioxide, as photo-catalysts for electron transfer photo-oxidations combines semiconductor band theory[1a-d] with recent developments in synthetic applications of photo-induced electron-transfer reactions.

10.1 Semiconductor band theory

The theory of how a semiconductor and electrolyte, in contact with each other, can drive useful chemical reactions upon illumination is not complete and is constantly being modified. A brief outline of the currently accepted theory is provided below.

A semiconductor is a solid substance whose resistance decreases upon irradiation. In order for an electric current to flow energy has to be provided to promote electrons from the valence band, where no net movement of charge can occur, to the vacant conduction band. Once in the conduction band the electron is free to move and the material becomes a semiconductor. The band gap, i.e. the energy difference between the valence and conduction bands, determines the wavelength of light required to cause promotion of electrons. There are two types of semi-conductors; n-type where electrons in the conduction band are charge carriers and p-type where electron vacancies (positive holes) in the valence band are the charge carriers.

Contact between the semiconductor and a liquid solution (or electrolyte) induces the required potential gradient for electrons to flow within the semiconductor. The energy of electrochemical reactions of the electrolyte can be related to the redox potentials of the species, e.g. ions of a dissolved salt, in solution. Semiconductors have a Fermi level which is defined as the highest filled level at absolute zero, where all electrons fill up the lowest levels, whereas the electrolyte counterpart of a Fermi level is equal to ΔG^o where:-

$$A^{+}_{(solvated)} + e^{-}_{(vacuum)} \rightleftharpoons A_{(solvated)} \qquad \Delta G = \Delta G^{o} \qquad (10.1)$$

For n-type semiconductors the Fermi level (of energy E_f) is close to the conduction band (of energy E_c) and for p-type semiconductors is close to the valence band (of energy E_v) as illustrated in Figure 10.1.

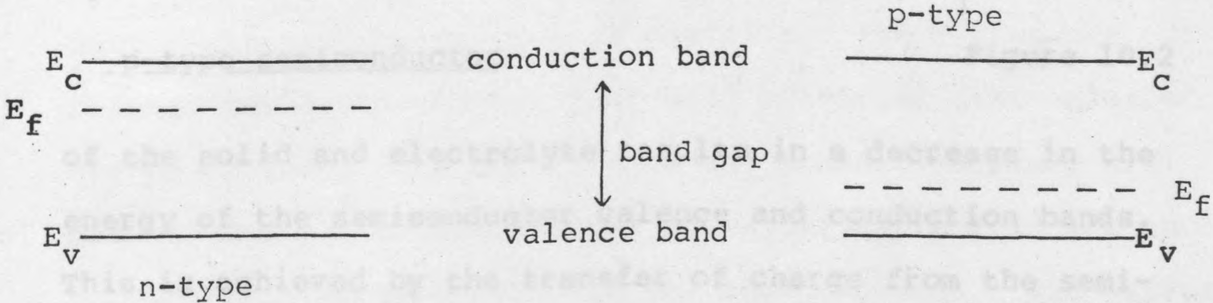


Figure 10.1

The relative positions of the semiconductor and electrolyte Fermi levels determines whether the required potential gradient to cause charge flow in the semiconductor can be obtained. If the two Fermi levels are of equal energy no potential gradient will exist within the semiconductor.

An n-type semiconductor can be made into a photoconductor by putting it in contact with an electrolyte containing a redox couple whose Fermi level lies below that of the semiconductor (Figure 10.2, process (A)). In this situation equilibration of the solid and electrolyte results in a decrease in the energy of the semiconductor valence and conduction bands. This is achieved by the transfer of charge from the semiconductor bulk to the electrolyte which results in a lower semiconductor Fermi level. As a result of adsorption of electrolyte species at the semiconductor surface the band edges remain "pinned" at their original value resulting in a space-charge layer beneath the surface of the semiconductor (represented by curved bands in Figure 10.2). The space-charge

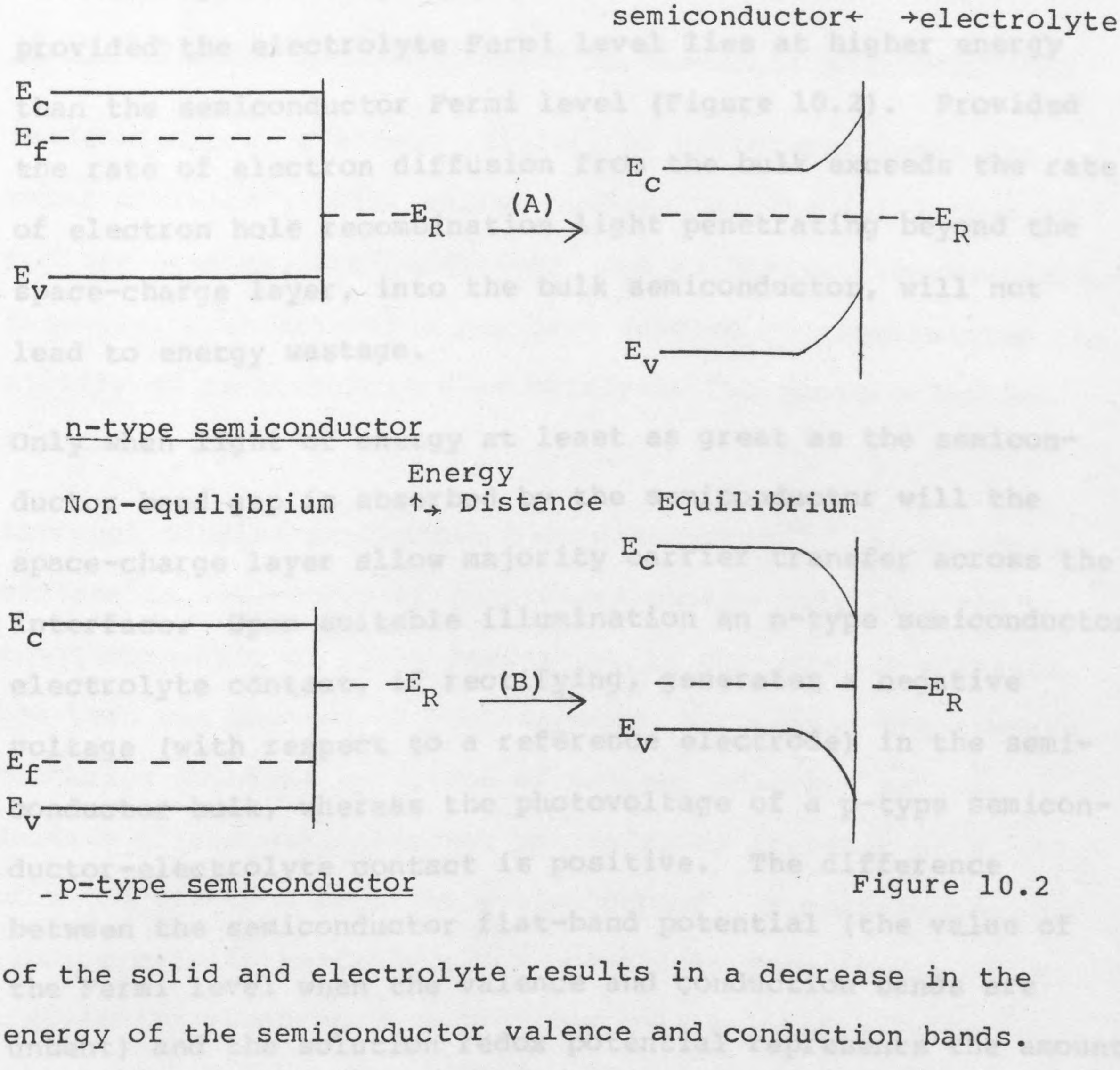


Figure 10.2

layer provides the driving force for charge flow, within the irradiated semiconductor, of electrons into the semiconductor bulk and positive holes to the surface. Thus charge carrier generation and separation is neatly effected by a very simple chemical system. A p-type semiconductor behaves similarly, provided the electrolyte Fermi level lies at higher energy than the semiconductor Fermi level (Figure 10.2). Provided the rate of electron diffusion from the bulk exceeds the rate of electron hole recombination light penetrating beyond the space-charge layer, into the bulk semiconductor, will not lead to energy wastage.

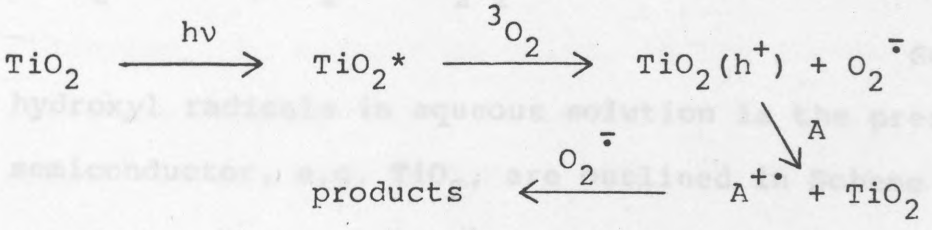
Only when light of energy at least as great as the semiconductor band gap is absorbed by the semiconductor will the space-charge layer allow majority carrier transfer across the interface. Upon suitable illumination an n-type semiconductor-electrolyte contact, if rectifying, generates a negative voltage (with respect to a reference electrode) in the semiconductor bulk, whereas the photovoltage of a p-type semiconductor-electrolyte contact is positive. The difference between the semiconductor flat-band potential (the value of the Fermi level when the valence and conduction bands are unbent) and the solution redox potential represents the amount of band-bending obtainable in the semiconductor. The greater the band-bending the larger the field in the space-charge layer, hence electron hole separation will be more effective. The adsorption of ions, of opposite sign to the charge induced in the electrode, on the semiconductor surface affects the flat-band potential and hence influences band-bending. Semiconductor band theory therefore predicts that photocatalysed oxidation or reduction should occur with acceptors, e.g. oxygen, or donors, whose redox potentials lie within the range between the valence and conduction bands of the semiconductor.

10.2 The generation of superoxide anions by semiconductors

Semiconductors have been utilised as photosensitisers for water cleavage[2], solar energy conversion, the initiation of cycloreversions, cycloadditions[3] and oxidative decarboxylations[4]. Recently, much attention has been devoted to ascertaining the utility of semiconductors as catalysts for photo-oxidation reactions.

Although singlet oxygen has been discounted[5a,b] as an intermediate in semiconductor sensitised photo-oxidations the exact mechanism of these reactions, in non-aqueous solvents, has been the subject of much debate. At present the favoured mechanism involves reduction of oxygen, adsorbed on the surface of the semiconductor particle, by transfer of a promoted electron from the semiconductor. Similarly organic substrates with suitable redox potentials (see above) can transfer an electron to a positive hole to generate the substrate radical cation. The radical cation of trans-stilbene has been identified spectroscopically[6] upon irradiation of trans-stilbene in the presence of colloidal TiO_2 in both degassed and oxygenated acetonitrile solution. Subsequent interaction between the superoxide anion and the substrate radical cation can ultimately lead to the formation of oxidation products. Such a mechanism, as outlined for TiO_2

in Scheme 10.1, can account for many of the reported photo-oxidations using platinised and metal-free semiconductors. In some cases the interaction of oxygen with the substrate radical cation and/or reaction of the superoxide anion with the neutral substrate can also lead to the generation of oxidation products (see Chapter 5, section 5.2.1). Mechanistic investigations[5b] of the semiconductor catalysed photo-oxidation of alkenes indicate that these reactions occur at the semiconductor-liquid interface rather than in bulk solution. The low quantum efficiency of alkene oxidation was attributed[7] to pathways for the deactivation of the excited semiconductor such as electron-hole recombination within the semiconductor and rapid back electron transfer from the adsorbed alkene radical cation.



where $TiO_2(h^+)$ represents a positive hole in a titanium dioxide particle.

Scheme 10.1

In aqueous solution $\dot{H}O$ radicals are considered to be the major oxidant[8] and their generation has been proposed[9] to involve the Haber-Weiss reaction (Equation 10.2). The generation of hydrogen peroxide can be readily achieved, in aqueous solution,

$$H_2O_2 + O_2^{\bar{\cdot}} \longrightarrow \dot{H}O + OH^- + O_2 \qquad (10.2)$$

by disproportion of $H\dot{O}_2$ radicals which are the conjugate acids of superoxide anions (Scheme 10.2). Other possible sources of

$$H^+ + O_2^{\overline{\cdot}} \longrightarrow H\dot{O}_2 \qquad pKa = 4.69$$

$$2\,H\dot{O}_2 \longrightarrow O_2 + H_2O_2$$

Scheme 10.2

hydroxyl radicals in aqueous solution is the presence of a semiconductor, e.g. TiO_2, are outlined in Scheme 10.3.

$$H_2O_2 \xrightarrow[\lambda\ 365nm]{h\nu} 2H\dot{O}$$

$$H_2O_2 + e^-(TiO_2) \longrightarrow H\dot{O} + OH^-$$

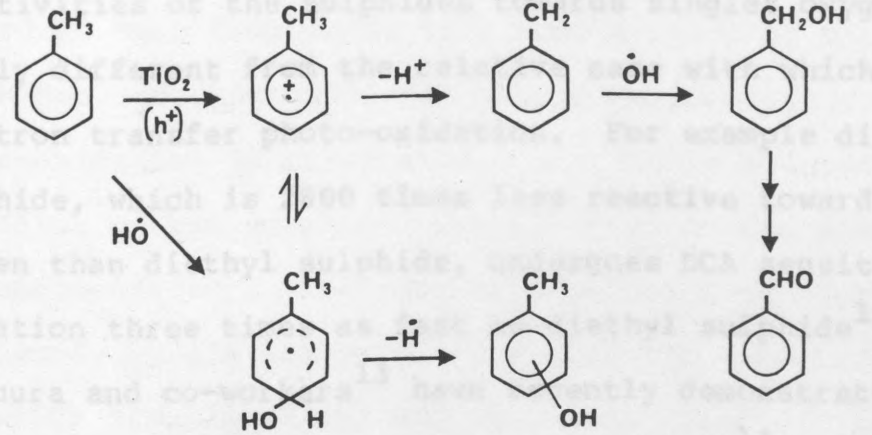
$$H_2O\ (adsorbed) + h^+(TiO_2) \longrightarrow H\dot{O} + H^+$$

Scheme 10.3

10.2.1 Examples of photo-oxidation reactions in the presence of semiconductors

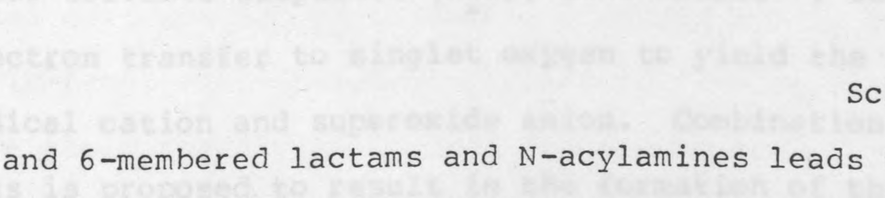
Recognition of the importance of photoinduced electron transfer reactions in synthetically useful transformations has led to investigations of semiconductors as potential sensitisers for redox reactions of organic substrates. The semiconductors which have received most attention are TiO_2 (anatase), ZnO and CdS in their platinised, metal free or in the case of TiO_2 colloidal forms. The simple removal of particulate semiconductors by filtration is of considerable advantage for reactions of utility in synthetic organic chemistry.

Irradiation of a wide range of semiconductors, suspended in either protic or non-protic solvents, in the presence of alkenes leads to selective oxidation of the latter to generate epoxides and carbonyl compounds in high yields[5a,b,7]. The reactivity of the alkenes tended to be reduced as the π-electron donating ability of the double bond decreased[5a,7]. Secondary alcohols undergo semiconductor catalysed oxidations to ketones, dehydration to alkenes and C-C bond cleavage to yield lower aldehydes. In aqueous solution, in the presence of TiO_2, light and oxygen, toluene is converted to benzaldehyde and cresol[9] as outlined in Scheme 10.4. Similar treatment[10] of



Scheme 10.4

5- and 6-membered lactams and N-acylamines leads to the generation of imides as illustrated for lactams in Equation 10.3. Photocatalylic oxidation of primary and secondary



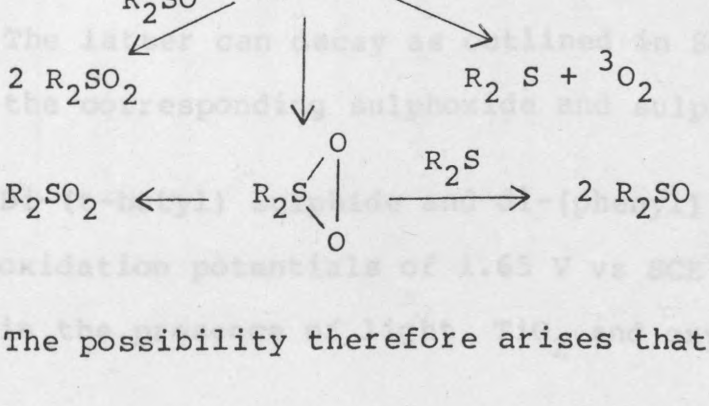
(10.3)

(where R = H or CH_3, n = 1 or 2)

aliphatic amines on irradiated TiO_2 powders, suspended in oxygenated solution, has been reported[11] to result in N-formylation and α-C-N oxidative cleavage products along with small amounts of other cleavage products.

10.3 Electron-transfer photo-oxidations of sulphides

Organic sulphides have relatively low ionization potentials (see Chapter 5, Table 5.3) and readily undergo 9,10-dicyanoanthracene (DCA) sensitised electron transfer photo-oxidation[12a,b]. The products of the DCA sensitised photo-oxidation of sulphides are identical to those obtained under conditions where singlet oxygen is the oxidizing species. However, the relative reactivities of the sulphides towards singlet oxygen are often widely different from the relative ease with which they undergo electron transfer photo-oxidation. For example diphenyl sulphide, which is 2800 times less reactive towards singlet oxygen than diethyl sulphide, undergoes DCA sensitised photo-oxidation three times as fast as diethyl sulphide[12a]. Matsuura and co-workers[13] have recently demonstrated that in polar solvents sulphides (R_2S), like amines[14], can undergo electron transfer to singlet oxygen to yield the sulphide radical cation and superoxide anion. Combination of these ions is proposed to result in the formation of the same intermediates as the singlet oxygen mediated photo-oxidation[15] (Scheme 10.5).



Scheme 10.5

The possibility therefore arises that sulphides can undergo semiconductor catalysed photo-oxidation. As the redox potentials of many sulphides lie between the energy of the valence band (E = 2.35 V) and the conduction band (E = 0.88 V) of TiO_2[16], the latter should represent a feasible photocatalyst for their oxidation.

10.4 Results and discussion

It can be seen from Table 10.1 that a range of organic sulphides underwent TiO_2 (an n-type semiconductor) catalysed photo-oxidation in oxygenated acetonitrile solution. No oxidation of the sulphides was observed in the absence of the semiconductor. The rate of disappearance of the sulphides was found, by glc analysis, to exceed the combined rate of formation of sulphoxides and sulphones (Table 10.1). The rates of formation of oxidation products are in the order di-(n-hexyl)>>di-(n-butyl)~diphenyl>di-(t-butyl) which differs from their reactivity towards singlet oxygen di-(n-butyl)>> di-(t-butyl)~diphenyl sulphide . Consequently, singlet oxygen can be ruled out as the species responsible for oxidation of the sulphides. Formation of oxidation products can be rationalised on the basis of the mechanism outlined in Scheme 10.1 followed by interaction of the radicals (Scheme 10.4, path b) to yield the intermediate $[R_2\overset{+}{S}OO^-]$. The latter can decay as outlined in Scheme 10.4 to generate the corresponding sulphoxide and sulphone.

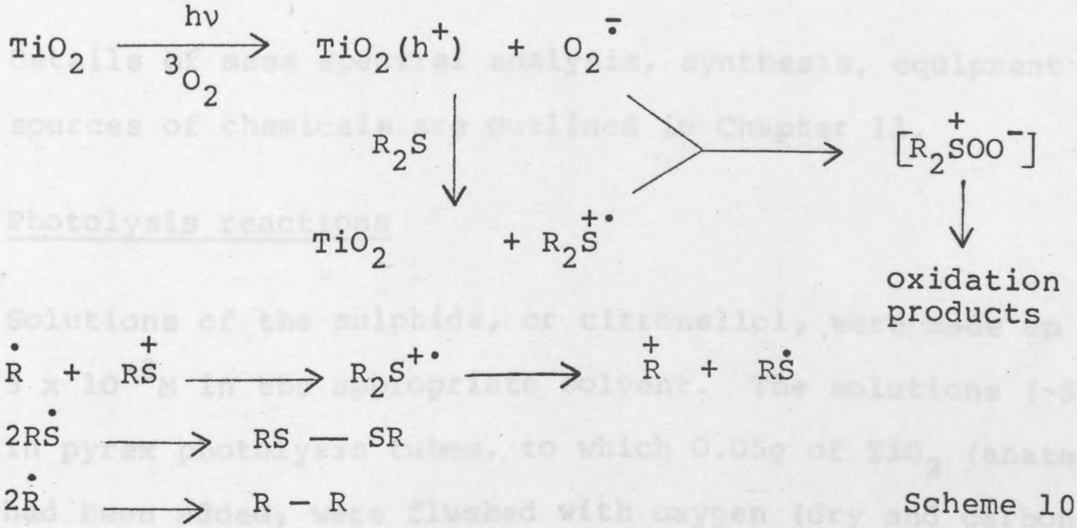
Di-(t-butyl) sulphide and di-(phenyl) sulphide both have oxidation potentials of 1.65 V vs SCE[18] and undergo reaction in the presence of light, TiO_2 and oxygen at similar rates,

SUBSTRATE	RATE (Ms^{-1})	REACTION LEADING TO OXIDATION (%)	k_r (s^{-1})
Di-(n-butyl) sulphide	8.9×10^{-7}	42	9.1×10^{6}
Di-(t-butyl) sulphide	4.4×10^{-7}	21	$\sim 1.5 \times 10^{5}$
Di-(n-hexyl) sulphide	2.3×10^{-6}	100	a
Diphenyl sulphide	6.4×10^{-7}	62	1×10^{5}
1,4-Dithiane	5.1×10^{-7}	a	1.5×10^{6}

a - not determined

TABLE 10.1 RATE OF CONSUMPTION OF SUBSTRATE AND PERCENTAGE OF REACTION WHICH LEADS TO OXIDATION PRODUCTS FOR THE TITANIUM DIOXIDE PHOTO-CATALYSED REACTION OF SULPHIDES (5×10^{-3} M) IN OXYGENATED ACETONITRILE SOLUTION AND REPORTED[17] RATE CONSTANTS (k_r) FOR THEIR REACTION WITH SINGLET OXYGEN but the proportion of reaction which leads to oxidation products is much less for the former. Mass spectral analysis revealed that n-butyl, t-butyl and phenyl disulphides were formed from the corresponding dialkyl sulphides upon TiO_2 catalysed photo-oxidation. This, coupled with the observation that some biphenyl is also formed from diphenyl sulphide, indicates that some C-S bond cleavage takes place. Dissociation of the intermediate $R_2\overset{+\bullet}{S}$ radical cation can account for the generation of these secondary products. Consequently, the extent of reaction which leads to oxidation products should decrease with increasing stability of the $R_2\overset{+\bullet}{S}$ radical. The increasing proportion of reaction leading to oxidation products in the order di-(t-butyl)<di-(n-butyl)<diphenyl<di-(n-hexyl) sulphide is consistent with dissociation of $R_2\overset{+\bullet}{S}$ intermediates. Further evidence for C-S bond cleavage in the TiO_2 catalysed photo-oxidation of the sulphides was provided by identification, using X-ray fluorescence spectrometry, of sulphur on the surface of the TiO_2 particles after irradiation in the presence of sulphides. The small quantity of sulphur gave rise to a slight yellow colouration to the initially brilliant white TiO_2 particles. It has been reported[19] that sulphur undergoes photocatalytic oxidation in the presence of TiO_2 (anatase) to generate SO_2^{2-} ions in aqueous solution. In some cases blue colouration of the TiO_2 particles was observed which was attributed to the presence of Ti^{3+} ions. Other products of the TiO_2 catalysed photo-oxidations of sulphides remain to be identified. Mass spectral analysis has shown that the most abundant unidentified peak from di-(n-butyl, di-(t-butyl) and diphenyl sulphides has an

m/e value of 64 which could be attributed to SO_2 ions perhaps derived from SO_4^{2-} ions. In the absence of a complete product analysis the following mechanism is proposed for the TiO_2 catalysed reaction of dialkyl sulphides in oxygenated acetonitrile solution (Scheme 10.6).



Scheme 10.6

Titanium dioxide was also found to photo-catalyse the oxidation of citronellol. However, in the absence of any product studies it is not clear whether the double bond or the hydroxyl group preferentially undergo oxidation. The negligible solvent isotope effect upon the rate of this reaction and the analagous reaction of di-(t-butyl) sulphide (1.0 and 1.5 respectively) in CD_3CN/CH_3CN indicates that a diffusional process of singlet oxygen is not responsible for the observed loss of substrate.

10.5 Conclusions

Titanium dioxide can be used as a photo-catalyst for the oxidation of a range of dialkyl sulphides in oxygenated acetonitrile solution. In many cases competing reactions of the intermediate $R_2\overset{+\bullet}{S}$ radical cations lead to a considerable reduction in the yield of oxidation products. Consequently, the utility of semiconductor sensitised photo-oxidation as a convenient route to the production of sulphoxides and sulphones from sulphides is severely limited.

10.6 Experimental

Details of mass spectral analysis, synthesis, equipment and sources of chemicals are outlined in Chapter 11.

Photolysis reactions

Solutions of the sulphide, or citronellol, were made up to 5×10^{-3}M in the appropriate solvent. The solutions (~5mls) in pyrex photolysis tubes, to which 0.05g of TiO_2 (anatase) had been added, were flushed with oxygen (dry and carbon dioxide-free) prior to being irradiated within a circular array of 16 Sylvania black light lamps of maximal output at 350nm. The loss of substrate and appearance of oxidation products was followed by glc analysis using a 10% SE 30 column. Oxidation products were identified by comparison with authentic samples by both glc and mass spectral analysis. The products other than sulphoxides and sulphones were identified by mass spectrometry. Prior to each period of irradiation the contents of the tubes were thoroughly shaken in order to disperse the particles of TiO_2.

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CHAPTER 11

EXPERIMENTAL

CHAPTER 11

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11.1 Instrumentation

11.1 (i) I.R. spectra These were recorded as Nujol mulls or as neat films using a Perkin-Elmer 157G grating spectrophotometer.

11.1 (ii) U.V./visible spectra These spectra were recorded using a Perkin Elmer 402 UV/visible spectrophotometer. If a solution was being made up to a known optical density or the loss of a substrate was being followed by the decrease in its UV absorption a Cecil Instruments CE 272 Linear readout ultraviolet spectrophotometer was used.

11.1 (iii) ^{1}H NMR spectra These were measured on a Jeol JNM-MH 100 NMR spectrometer, using an external lock, tetramethylsilane (TMS) as the internal standard and deuterochloroform ($CDCl_3$) as the solvent. The following abbreviations are used in the spectral interpretations:- s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet.

11.1 (iv) Mass spectra Measurements were carried out by [redacted], using a Kratos MS 30 Electron Impact mass spectrometer, linked to a Kratos DS 50 data system. Samples were run at 70eV. GC / mass spectra were carried out using a Pye-Unicam 104 gas liquid chromatograph.

11.1 (v) Elemental analysis CHN analyses were performed by Mr. P. Hemming using a Carlo Erba Model 1106 Elemental Analyser.

11.1 (vi) Melting points/boiling points Melting points were recorded using a Kopfler block melting point apparatus and are uncorrected. All compounds prepared as liquids were distilled under reduced pressure using a Büchi Kugel Oven. Boiling points are uncorrected.

11.1 (viii) Gas liquid chromatography (GLC) All glc analyses were carried out using a Perkin Elmer Sigma 3 gas-liquid chromatograph fitted with a flame ionisation detector and a Perkin Elmer 10% SE 30, chromosorb W 60-80 mesh column. The gas flow was maintained at 30mls/min and the temperatures for each compound analysed by this method are given in Table 11.1. No internal standard was used; this was due to the difficulty in obtaining a standard which did not absorb any of the incident light or interact with the sensitiser, substrate or products in their ground or excited states, but had a retention time comparable with that of the substance being analysed. As the samples for analysis were < 0.5mls addition of a standard to each solution, at such a concentration that its peak was comparable with that of the substrate (at 5 x 10^{-3}M) or the product (<< 5 x 10^{-3}M), would be difficult to achieve with a great deal of accuracy. Calibration curves were usually linear over the small concentration range associated with the first 10-30% of reaction studied for kinetic analyses. Each sample was analysed at least twice in non-chronological order. In the early work

COMPOUND	OVEN TEMPERATURE (^{o}C)	COMPOUND	OVEN TEMPERATURE (^{o}C)
Anthracene	200	Citronellol	150
Biphenyl	130	(+)-Limonene	100
Naphthalene	120	Di-(n-butyl)sulphide	120
Phenanthrene	200		
Pyrene	200	Di-(n-butyl)sulphoxide	200
9-Bromoanthracene	210	Di-(n-butyl)sulphone	200
1-Bromonaphthalene	130	Di-(t-butyl)sulphide	90
9-Chloroanthracene	210	Di-(t-butyl)sulphoxide	150
4-Chlorobiphenyl	150	Di-(t-butyl)sulphone	150
4-Chlorobenzonitrile	140	Di-(n-hexyl)sulphide	135
1-Chloronaphthalene	130	Di-(n-hexyl)sulphoxide	200
Benzonitrile	120	Di-(n-hexyl)sulphone	200
9-Cyanoanthracene	200	Diphenyl sulphide	140
9-Cyanobiphenyl	160	Diphenyl sulphoxide	200
1-Cyanonaphthalene	140	Diphenyl sulphone	200
4-Cyanophenanthrene	220	1,4-Dithiane	100
4-Cyanopyridine	120		
9,10-Dicyanoanthracene	250		

TABLE 11.1 OVEN TEMPERATURES USED FOR THE GLC ANALYSIS OF A RANGE OF COMPOUNDS, USING A 10% SE 30 COLUMN (SEE ABOVE) AND A CARRIER GAS FLOW OF 30mls/min

peak areas were calculated by measuring the peak height and the width at half the height and multiplying the two values. Later a Pye Unicam DP88 computing integrator was used to determine the peak areas.

11.2 Sources of chemicals

11.2.1 Spectroscopic solvents

These were obtained from the following suppliers and used without further purification:-

Aldrich Chemical Co. Ltd. - acetonitrile (99.5%), benzene and methanol (99.9%) (all spectrophotometric grade, Gold Label).
Hopkin and Williams - cyclohexane (Spectrosol^R).
E. Merck - benzene and acetonitrile (Uvasol^R) - used for laser experiments.

11.2.2 Reagents

The following reagents were used as supplied unless otherwise stated:-

Aldrich Chemical Co. Ltd. Benzonitrile, 9-bromoanthracene, 1-bromonaphthalene, 4-chlorobenzonitrile, 4-chlorobiphenyl, citronellol (distilled prior to use), 9-cyanoanthracene, 9-cyanophenanthracene, 4-cyanopyridine, di-(n-butyl)sulphide, di-(s-butyl)sulphide, di-(t-butyl)sulphide, dichlorodicyanobenzoquinone, α,α-dichloromethyl methyl ether, 1,4-dicyanobenzene, di-(n-hexyl)sulphide, 4-dimethylaminobenzonitrile, 9,10-dimethylanthracene, 2,6-dimethylnaphthalene, N,N-dimethylpiperazine, 9,10-diphenylanthracene, diphenyl sulphide, 1,3-dithiane, 1,4-dithiane, eosin Y, ethyl pyruvate, ethyl sulphide, indole, α-keto-glutaric acid, (+)-limonene, lithium aluminium hydride, 2-methylanthracene, 9-methylanthracene, methylene blue (metal-free), 3-methyl indole, 2-methylnaphthalene, methyl pyruvate, methyl viologen hydrate, 1-naphthaldehyde, 1-naphthylacetic acid, 2-naphthylacetic acid, pentamethylene sulphide, phenyl sulphone, 3-phenyl toluene, pyruvic acid, sodium azide, tetracyanoethylene, thioanisole and triphenylamine.

<u>BDH Chemicals Ltd.</u> Anthracene, barium hydroxide, biphenyl (recrystallised from acetonitrile), calcium chloride (anhydrous), cuprous cyanide, hydrogen peroxide, malonic acid, naphthalene, phenanthrene, potassium chromate, potassium hydroxide (pellets), rhodamine B, rose bengal (BDH) and sodium nitrate.

<u>BOC Ltd.</u> Air, argon (research grade), fluorine (2% in helium), helium (research grade), nitrogen (oxygen-free and commercial), oxygen (research grade), Xenon (research grade).

<u>Ciba Geigy Ltd.</u> Tinuvin 770.

<u>Eastman Kodak Co. Ltd.</u> 9-Chloroanthracene, 9,10-dicyanoanthracene and rose bengal (unless otherwise stated).

<u>Fisons Chemical Co. Ltd.</u> Acetonitrile, benzene, chloroform, cyclohexane, dichloromethane and methanol (all AnalaR grade), acetic acid, ethyl acetate, conc. hydrochloric acid, magnesium sulphate (anhydrous), N-methylaniline, pyridine (distilled prior to use and stored over potassium hydroxide pellets) and methylamine.

Goss Scientific Instruments Acetonitrile-d_3, benzene-d_6, chloroform-d_1, deuterium oxide, methanol-d_1 and methanol-d_4.

Koch-Light Chemicals Ltd. Diethylamine, 1-naphthaldehyde, oxalyl chloride, phosphorous pentoxide and thionine.

May and Baker Co. Ltd. Diethyl ether, ethanol and petroleum ether (40-60° and 60-80°).

Oxford Organic Chemical Co. Ltd. 1,3-diphenylisobenzofuran.

Ralph N. Emanuel 1-Chloronaphthalene, 1-cyanonaphthalene, 1,4-diazabicyclo[2.2.2.]octane, hexamethylphosphoramide and 4-nitrobiphenyl.

Sigma Chemical Co. Ltd. Erythrosin B and α-keto-octanoic acid.

The author is most grateful to the following individuals for providing the materials listed below:-

[redacted] for the 1,3-diphenyl-2-pyrazoline, 1,3,5-triphenyl-2-pyrazoline and derivatives of the latter.

[redacted] for the di-(1-naphthylmethyl)ether and the N-(2-(1′-naphthyl)ethyl)-N′-(2-(1-aza-4-oxa-cyclohexyl)ethyl-1,4-diazocyclohexane.

[redacted] for the 1,2-dimethyl-1,3-dithiopropane and the 1,2-dimethyl-1,2-dithioethene.

[redacted] for the 1,3-dimethylindole, ethyl benzoyl formate and the isopropyl, t-butyl, n-hexyl, n-butyl and benzyl pyruvates.

[redacted] for the titanium dioxide.

[redacted] for the 1-(4-cyanophenyl)-3,5-diphenyl-2-pyrazoline.

[redacted] for the tetraphenylporphyrin.

[redacted] for the tris-ruthenium(II)-(2,2′-bipyridyl)-chloride, hexahydrate, 1-(1′-naphthyl)-4-diethylaminobutane and 1-(1′-naphthyl)-4-(N-methylanilino)butane.

11.3 Preparation of materials

11.3.1 Dimers of anthracene, 9-chloroanthracene, 9-bromoanthracene and 9-cyanoanthracene

Photolysis of anthracene compounds (~12hrs), in degassed toluene solution (flushed with a stream of dry argon for 20 mins) using Sylvania fluorescent black-light lamps having a maximal output at 350nm afforded crystals of the appropriate dimers. These crystals were filtered, washed with toluene and dried. The dimers had melting points corresponding to the appropriate monomer and the following IR spectra which do not correspond to the IR spectra of the monomers. Crystals formed in the photolysis reactions of anthracene compounds under degassed conditions were compared with these authentic samples of the dimers using IR spectroscopy.

Anthracene dimer; IR (Nujol mull), 1295, 1225, 1200, 1165, 1110, 1035, 950, 860, 820, 770, 760, 685cm^{-1}.

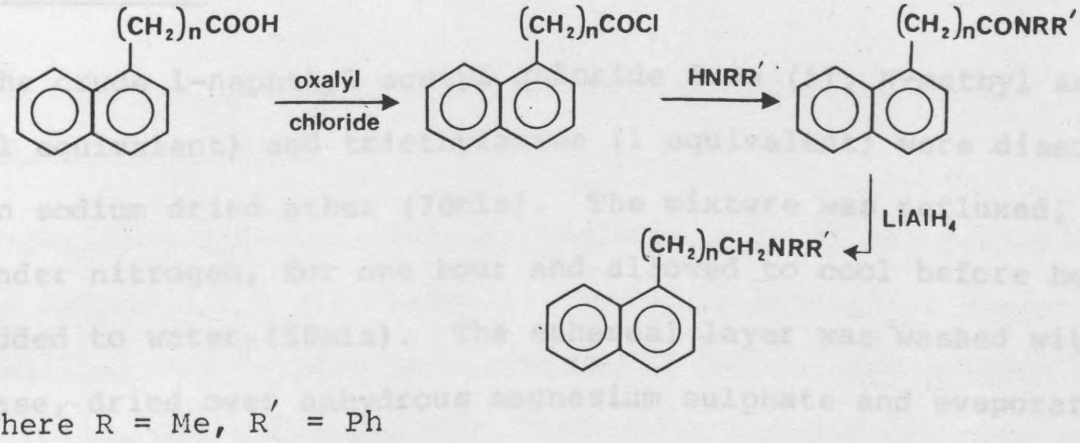
9-Chloroanthracene dimer; IR (Nujol mull), 1295, 1232, 1170, 1158, 1045, 940, 878, 866, 838, 780, 760, 743, 695, 665, 630cm^{-1}.

9-Bromoanthracene dimer; IR (Nujol mull), 1290, 1232, 1160, 1045, 937, 852, 825, 778, 756, 693, 625cm^{-1}.

9-Cyanoanthracene dimer; IR (Nujol mull), 2223, 1930, 1820, 1730, 1633, 1605, 1580, 1340, 1320, 1312, 1270, 1240, 1162, 1125, 1038, 950, 943, 910, 842, 785, 780, 765, 760, 740, 695, 670, 640cm^{-1}.

11.3.2 α-Naphthylalkylamines

A range of N-methylanilino- and diethylamino- α-naphthylalkylamines were prepared according to the procedures reported by Trethewey[1] as outlined in Scheme 11.1. All intermediate



where R = Me, R′ = Ph
or R = R′ = Et
and n = 0 - 3

Scheme 11.1

products were characterised using NMR spectroscopy.

11.3.2 (i) Preparation of 1-naphthyl acetyl chloride

1-Naphthyl acetic acid was purified by dissolving it in chloroform, adding 1.2 equivalents of potassium hydroxide (in aqueous solution) and after shaking the acid was liberated by addition of a 50/50 mixture of conc. hydrochloric acid and water. The 1-naphthyl acetic acid was filtered off and then washed with water prior to being dried over phosphorus pentoxide powder in a vacuum dessicator.

Oxalyl chloride (2g) was added dropwise to a solution of purified 1-naphthyl acetic acid (0.66 equivalents) in benzene solution and the mixture refluxed, under nitrogen, until the evolution of hydrogen chloride ceased (~2hrs). Any remaining oxalyl chloride and the solvent were removed by rotary evaporation. The crude 1-naphthyl acetyl chloride was used directly in the next stage.

11.3.2 (ii) Preparation of N-methyl-N-phenyl-1-naphthyl acetonitrile

The crude 1-naphthyl acetyl chloride from (i), N-methyl aniline (1 equivalent) and triethylamine (1 equivalent) were dissolved in sodium dried ether (70mls). The mixture was refluxed, under nitrogen, for one hour and allowed to cool before being added to water (50mls). The ethereal layer was washed with base, dried over anhydrous magnesium sulphate and evaporated to yield the product.

11.3.2 (iii) Preparation of N-methyl-N-phenyl-1-aminoethyl naphthalene (α2N)

Unpurified N-methyl-N-phenyl-1-naphthyl acetamide (0.9g, prepared as above) in sodium dried ether (60mls) was added dropwise to a cooled slush of lithium aluminium hydride (0.4g) in dry ether (40mls), under nitrogen. After warming to room temperature the mixture was vigorously refluxed for 2lhrs. Water was added dropwise to the cooled solution to destroy the $LiAlH_4$ and the mixture was filtered. An acid base wash, followed by extraction with ether yielded a solution of the product which was dried over magnesium sulphate, filtered and evaporated. The product was first recrystallised from diethyl ether and secondly recrystallised from methanol and dried over phosphorus pentoxide. (Yield; 85.7% from 1-naphthyl acetic acid.)

Melting point 84-85°C (literature[1] 85-86°C).

NMR ($CDCl_3$) δ,6.5-8.1 (12H, m); 3.6-3.8 (2H, m); 3.1-3.5 (2H, m); 2.84, (3H, s).

IR (Nujol), 3040, 1600, 1500, 1280, 1190, 1110, 1050, 1030, 990, 950, 860, 800, 780, 750, 690cm^{-1}.

11.3.2 (iv) Preparation of N,N-diethyl-(1'-aminoethyl) naphthalene (α2E)

Unpurified N,N-diethyl-1-naphthylacetamide (1.9g, prepared by method 11.3.2 (ii) using diethylamine instead of N-methylaniline) was reduced by method 11.3.2 (iii). The product was a yellow oil which was distilled under reduced pressure to yield a colourless oil. (Yield; 90.4% from the acid.)

Boiling point 85-88°C at unknown pressure (literature[1] 115-118°C at 0.05mm).

NMR ($CDCl_3$) δ,7.04-8.03 (7H, m); 2.35-3.3 (8H, m); 0.9-1.2 (6H, t).

IR (film), 3060, 2960, 2923, 2798, 1595, 1518, 1463, 1380, 1200, 1064, 800-770cm^{-1}.

11.3.2 (v) Preparation of 3-(1'-naphthyl) acrylic acid

1-Naphthaldehyde (27g) was added to malonic acid (27g) in pyridine (100mls) containing a few drops of pyridine as catalyst. The mixture was heated on a water bath for 1½ hours and then poured into water (1 litre) containing conc. hydrochloric acid (100mls). The precipitated product was filtered, washed with water and dried over phosphorus pentoxide.

11.3.2 (vi) Preparation of 3-(1'-naphthyl)-propionic acid

3-(1'-Naphthyl)-acrylic acid (10g) and palladium charcoal (1g) as catalyst were added to acetic acid (200mls). The mixture was stirred under hydrogen until the appropriate volume of hydrogen had been absorbed. The charcoal was removed by filtration and the acid removed under reduced pressure. The product was recrystallised from ethanol twice.

11.3.2 (vii) Preparation of 3-(1'-naphthyl) propionyl chloride

This compound was prepared from 3-(1'-naphthyl) propionic acid (4g) using method11.3.2 (i).

11.3.2 (viii) Preparation of N-methyl-N-phenyl-1-(3'-aminopropyl) naphthalene (α3N)

Unpurified N-methyl-N-phenyl-3-(1-naphthyl) propionamide (2.82g, prepared from 11.3.2 (vii) using method 11.3.2 (ii)) was reduced by method 11.3.2 (iii). The resultant oil was distilled under reduced pressure and crystallised in the fridge to yield white crystals. (Yield; 81% from the acid).

Boiling point 156-8°C at unknown pressure (literature[1] 170°C at 0.01mm).

Melting point 78-79°C.

NMR ($CDCl_3$) δ,6.7-8 (10H, m); 3.8-3.18 (5H, m); 2.6-2.4 (2H, t).

IR (Nujol), 2920, 2860, 1600, 1505, 1460, 1375, 1343, 1248, 1210, 1190, 1122, 992, 802, 782, 750, 700cm^{-1}.

11.3.2 (ix) Preparation of N,N-diethyl-3-(1'-naphthyl) propionamide

This compound was prepared from 3-(1'-naphthyl) propionyl chloride by method 11.3.2 (ii) using diethylamine instead of triethylamine.

11.3.2 (x) Preparation of N,N-diethyl-1-(3'-aminopropyl) naphthalene (α3E)

Unpurified N,N-diethyl-3-(1'-naphthyl) propionamide (2.3g) was reduced by method 11.3.2 (iii). The resultant oil was distilled under reduced pressure. (Yield; 85.9% from the acid.)

Boiling point 113-115°C at unknown pressure (literature[1] 135-137°C at 0.7mm).

NMR ($CDCl_3$) δ; 8.1-7.1 (7H, m); 3.18-2.9 (2H, t); 2.8-2.3 (6H, m); 2.1-1.7 (2H, m); 1.2-0.9 (6H, t).

IR (film), 3040, 2960, 2920, 2860, 2800, 1600, 1520, 1460, 1380, 1200, 1065, 800-770cm^{-1}.

11.3.3 α-Keto-carboxylic esters

These were prepared using the method described by Binkley[2] as outlined in Scheme 11.1. Intermediate compounds were characterised by NMR spectroscopy.

$$RCOCO_2H + Cl_2CHOCH_3 \xrightarrow{\Delta} RCOCOCl + HCO_2CH_3 + HCl$$

$$RCOCOCl + R'OH \xrightarrow[\text{pyridine}]{C_6H_6} RCOCO_2R'$$

Scheme 11.1

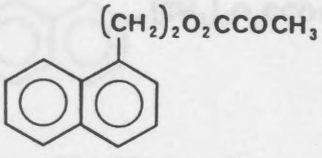
11.3.3 (i) Preparation of pyruvoyl chloride

The acid chloride of pyruvic acid was prepared using the method described by Ottenheijm and De Man[3] (Scheme 11.1). α,α-Dichloromethyl methyl ether (0.06 moles) was added dropwise, with stirring, to pyruvic acid (1 equivalent) under nitrogen. The mixture was heated at an oil bath temperature of 50°C for thirty minutes and used directly, without further purification, in the next stage. A yield of 54%, as obtained previously[3], was assumed.

11.3.3 (ii) Preparation of 1-(2'-hydroxy ethyl) naphthalene

This compound was prepared from 1-naphthylacetic acid (2g) using method 11.3.2 (iii). The product was recrystallised from petroleum ether (bp 60-80°C). (Yield; 36%).

11.3.3 (iii) 2-(1-Naphthyl) ethyl pyruvate



1-(2'-Hydroxy ethyl) naphthalene (0.62g) was added to a solution of pyridine (0.79g) in benzene (25mls) and cooled. Pyruvoyl chloride was added dropwise, under nitrogen, and the mixture stirred at room temperature for 2hrs. Pyridinium hydrochloride was removed by filtration and evaporation of the filtrate yielded a yellow oil which solidified on cooling. The ester was recrystallised from ethyl acetate to which a few drops of petroleum ether (bp 40-60°C) had been added, to give white crystals (yield 53%). Physical and spectral data confirmed the structure of the product.

Melting point 50-52°C.

NMR ($CDCl_3$) δ; 8.84-8.6 (2H, m); 8.6-8.28 (1H, m); 8.28-7.8 (4H, m); 5.1-4.87 (2H, t); 3.92-3.7 (2H, t); 2.64 (3H, s).

IR (Nujol); 1745, 1730, 1295, 1258, 1135, 950, 800, 760cm^{-1}.

$C_{15}H_{14}D_3$ requires % C, 74.36; H, 5.82 : found %C, 73.79; H, 5.75.

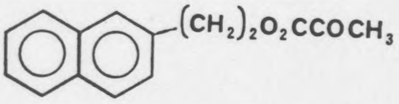
Mass spectrum m/e 242 (m^+).

11.3.3 (iv) Preparation of 2-(2'-hydroxy ethyl) naphthalene

This compound was prepared from 2-naphthylacetic acid using method 11.3.2 (ii). The product was recrystallised from petroleum ether (bp 60-80^{o}C). (Yield; 73%).

Melting point 67-67.5^{o}C (literature^{4} 68^{o}C).

11.3.3 (v) Preparation of 2-(2'-naphthyl) ethyl pyruvate



This compound was prepared from 2-(2'-hydroxy ethyl) naphthalene using method 11.3.3 (iii). The product was recrystallised from ethyl acetate to which a few drops of petroleum ether (bp 40-60^{o}C) had been added, to give white crystals (yield; 58%).

Melting point 82-83^{o}C.

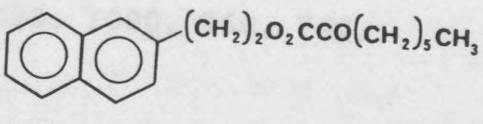
NMR ($CDCl_3$) δ; 8.48-8.1 (4H, m); 8.1-7.78 (3H, m); 4.98-4.82 (2H, t); 3.32-2.58 (2H, t); 2.61 (3H, t).

IR (Nujol); 1735, 1270, 1150, 960, 827, 752cm^{-1}.

$C_{15}H_{14}O_3$ requires % C, 74.36; H, 5.82 : found % C, 74.54; H, 5.78.

Mass spectrum m/e 242 (m^{+}).

11.3.3 (vi) Preparation of 2-(2'-naphthyl) ethyl-α-keto-octanoate



This compound was prepared from α-keto-octanoyl chloride (prepared from α-keto-octanoic acid by method 11.3.3 (i)) using method 11.3.3 (iii). The product was recrystallised from ethanol as a waxy solid. (Yield; 70.4%).

NMR ($CDCl_3$) δ; 8.0-7.68 (4H, m); 7.68-7.3 (3H, m); 4.75-4.5 (2H, t); 3.44-3.14 (2H, t); 2.84-2.66 (2H, t); 1.56-1.12 (8H, m); 1.04-0.78 (3H, m).

IR (Nujol); 1724, 1270, 1124, 1078, 948, 862, 790cm^{-1}.

$C_{20}H_{24}O_3$ requires % C, 76.92; H, 7.69 : found % C, 74.16; H, 7.8.

Mass spectrum m/e 312 (m$^+$).

11.4 Preparation of sulphoxides

The sulphoxides were prepared from the corresponding sulphides using the procedure reported by Leonard and Johnson[5]. Sodium metaperiodate in MeOH/H_2O at 0°C was added to the appropriate sulphide (1 equivalent) and stirred for ~24hrs on an ice-bath. The precipitate of sodium iodate was filtered off and the filtrate extracted with chloroform. The chloroform layer was dried over magnesium sulphate and the solvent removed to yield the sulphoxide as either a solid or an oil. Solid products were recrystallised from ethanol.

11.4 (i) Diphenyl sulphoxide (Ph_2S)

Melting point 67-68°C (literature[5] 69-71°C).

NMR ($CDCl_3$) δ; 7.72-7.5 (4H, m); 7.5-7.32 (6H, m).

IR (Nujol); 1585, 1445, 1090, 1040, 1025, 1000, 760, 740, 700, 690cm^{-1}.

Mass spectrum m/e 202.03 (m$^+$).

11.4 (ii) Di-(n-butyl)sulphoxide (n-Bu_2SO).

Colourless viscous oil (literature[4] 32°C).

NMR ($CDCl_3$) δ; 2.82-2.66 (4H, t); 1.94-1.30 (8H, m); 1.06-1.92 (6H, t).

IR (film), 2980, 2940, 2880, 1470, 1410, 1380, 1300, 1275, 1140, 1030, 920, 735cm^{-1}.

Mass spectrum m/e 162.09 (m^+).

11.4 (iii) Di-(t-butyl)sulphoxide ($t\text{-}Bu_2SO$)

Melting point 66-67°C (literature[6] 63.5-65°C).

NMR ($CDCl_3$) δ; 1.50, s.

IR (Nujol); 1090, 1020, 800, 690cm^{-1}.

Mass spectrum m/e 162.13 (m^+).

11.4 (iv) Di-(n-hexyl)sulphoxide ($(CH_3(CH_2)_5)_2SO$)

Melting point 58-59°C (literature[7] 58-59°C).

NMR ($CDCl_3$) δ; 2.8-2.5 (2H, t); 1.9-1.6 (2H, m); 1.6-1.1 (6H, m); 1.0-0.7 (3H, m).

IR (Nujol); 1415, 1310, 1245, 1095, 1050, 1020, 975, 880, 800, 730cm^{-1}.

Mass spectrum m/e 218.14 (m^+).

11.5 Preparation of sulphones

This was achieved using the procedure reported by Bell and Bennet[6] for the preparation of sulphoxides. It proved to be impractical to prevent further oxidation of the product sulphoxides to the corresponding sulphones. Hydrogen peroxide (1.5mls, 30% aqueous solution) in acetic acid (1.5 mls) was added dropwise to an ice-cooled solution of the sulphide (1g) in glacial acetic acid (20mls). The mixture was stirred at room temperature for 24hrs before removal of the volatile components by rotary evaporation. The resultant solids were recrystallised from ethanol in > 80% yield.

11.5 (i) Phenyl sulphone (Ph_2SO_2)

Melting point 125-126°C (literature[4] 128°C).

NMR ($CDCl_3$) δ; 7.92-7.84 (5H, m); 7.52-7.43 (5H, m).

IR (Nujol); 1585, 1320, 1312, 1300, 1188, 1160, 1110, 1070, 1005, 765, 732, 702, 695, 685cm^{-1}.

Mass spectrum m/e 218.04 (m^+).

11.5 (ii) Di-(n-butyl) sulphone (n-Bu_2SO_2)

Melting point 42-43°C.

NMR ($CDCl_3$) δ; 3.1-2.94 (4H, t); 2.1-1.3 (8H, m); 1.08-0.994 (6H, t).

IR (Nujol); 1320, 1290, 1260, 1130, 1100, 750, 740cm^{-1}.

Mass spectrum m/e 178.1 (m^+).

11.5 (iii) Di-(t-butyl)sulphone

Melting point 124.5-125.5°C (literature[9] 127-128°C).

NMR ($CDCl_3$) δ; 1.46, s.

IR (Nujol); 1270, 1180, 1110, 1020, 940, 800, 789cm^{-1}.

Mass spectrum no mass peak (major peak m/e 57.06).

11.5 (iv) Di-(n-hexyl)sulphone ($CH_3(CH_2)_5)_2SO_2$

Melting point 71-72°C (literature[10] 72.6-73°C).

NMR ($CDCl_3$) δ; 3.44-3.28 (2H, m); 2.34-2.2 (2H, m); 1.94-1.66 (5H, m); 1.36-1.24 (3H, t).

IR (Nujol); 1320, 1290, 1268, 1238, 1130, 1110, 770, 730cm^{-1}.

Mass spectrum m/e 234.16 (m^+).

11.6 Preparation of 4-cyanobiphenyl

This was achieved using the method reported by House and

Fischer[11] for the preparation of 2-cyanonaphthalene from 2-chloronaphthalene. A mixture of cuprous cyanide (10 molar excess) and hexamethylphosphoramide (10mls) was refluxed under nitrogen at 235-240°C, with stirring, for 3hrs. The resulting mixture was washed with water and the green solid extracted with dichloromethane. The green solution was filtered through decolourising charcoal and the solvent removed to yield a yellow solid which was distilled under reduced pressure. The resultant white solid was obtained in 45% yield.

Melting point 82-83°C (literature[4] 84-85°C).

NMR ($CDCl_3$) δ; 7.78-7.25 m.

IR (Nujol); ν_{max} 2185cm^{-1}.

11.7 Photophysical measurements

11.7.1 Fluorescence studies

All fluorescence measurements were made using a Perkin Elmer MPF-4 fluorescence spectrophotometer and are uncorrected. Spectrophotometric solvents were used and solvent blanks recorded, in each case, to ensure that they did not emit significantly over the wavelength ranges being monitored. Solutions were made up in 1cm path length quartz, rectangular, fluorimeter cells to an OD of 0.1 at the excitation wavelength. Degassing was achieved by thoroughly flushing the solution with a stream of dry argon (research grade) for ~5mins and stoppering the cell.

Quantum yields of fluorescence (ϕ_f) were determined relative to that from a degassed solution of 1-methylnaphthalene ($\phi_F = 0.21$). Quantum yields were calculated by weighing the areas bounded by the spectra of the compound and comparing them with the weights of the corresponding areas for the standard, recorded under similar conditions. Quantum yields derived from a range of settings were averaged out.

Solvent isotope effects were determined by weighing the areas bounded by the spectra of the compound in the deuterated and non-deuterated solvents and comparing the values obtained.

11.7.2 Fluorescence lifetime measurements

These were carried out by [redacted] at The Royal Institution, London. Solutions of the α-naphthylalkylamines and pyrazolines were each made up to an optical density of 0.1 at the excitation wavelength (300nm). The solutions were degassed by several freeze-pump-thaw-shake cycles. Lifetimes were measured using the single photon counting method with a pulsed laser excitation source. This source was a Spectra Physics (model 171) argon ion laser, mode locked on the 514nm line, and used to synchronously pump a Spectra Physics (Model 375) dye laser containing Rhodamine 6G (2g/litre) in ethylene glycol as the fluorescent dye. The output from the dye laser cavity was extracted at 4 MHz using a Spectra Physics (Model 344) cavity dumper. The second harmonic of the dye laser radiation was generated using a 90° matched angle and temperature tunnel ADP crystal (J.K. Lasers Ltd.). Fluorescence from the sample was focussed on the slits of a Hilger and Watts D330 monochromater through a Melles Griot WG345 filter (to remove scattered excitation light). The resolved emission was detected by a fast gain Mullard XP2020Q photomultiplier tube. The signal from the tube was sent to a constant fraction discriminator, Ortec Model 934, via electronic delays. The output from the discriminator provided the 'start' signal to the Ortec (Model 457) time to amplitude converter (TAC). The stop signal was derived from a signal, synchronised with the excitation pulse, from the electronics controlling the cavity dumper. The output from the TAC was fed to a Canberra Series 30 multichannel analyser interfaced to a Perkin Elmer Interdate Computer. Decay curves were deconvoluted using the non-linear least squares iterative reconvolution using a single exponential function to derive the lifetime of the sample. In general the decays did not fit this function well, as determined by the reduced chi square Durbin-Watson parameter as well as by inspection of the plots of the weighted residuals and autocorrelation function. The lifetimes presented in this thesis are therefore only used for comparison purposes rather than as absolute lifetimes.

11.7.3 Triplet-triplet absorption spectra

These were studied using the technique of nanosecond laser flash photolysis. The excitation pulse was provided by an Oxford Lasers Ltd., Model KX2 rare gas-halide excimer laser using krypton fluoride (to provide 27ns pulses each with an energy of 260 mJ and a wavelength of 249nm) or xenon fluoride (to provide 23ns pulses each with an energy of 114 mJ and a wavelength of 353nm) as the lasing gas. The excitation mechanisms of rare gas-halide lasers are thought to involve the processes outlined in Scheme 11.2 for krypton fluoride.

$$\mathrm{Kr} + \mathrm{e}\ (\text{fast}) \longrightarrow \mathrm{Kr}^{+} + 2\mathrm{e}\ (\text{slow})$$

$$\mathrm{F_2} + \mathrm{e}\ (\text{slow}) \longrightarrow \mathrm{F}^{-} + \mathrm{F}$$

$$\mathrm{F}^{-} + \mathrm{Kr}^{+} + \mathrm{He} \longrightarrow (\mathrm{KrF})^{*} + \mathrm{He}$$

$$(\mathrm{KrF})^{*} + h\nu \longrightarrow \mathrm{Kr} + \mathrm{F} + 2h\nu$$

Scheme 11.2

As the excited complex (KrF)* is dissociative in its ground state a build-up of ground state krypton fluoride is avoided. The following gases were used:- krypton (BOC speciality gases, research grade), 2% fluorine - 98% helium (research grade) as the buffer gas and xenon (research grade). The monitoring light source was provided by a 75W xenon lamp, linked to an arc lamp pulsing unit. The laser was used in a single shot mode and triggered by a synchronous signal from the arc lamp pulsing unit, employing a variable delay of 0.2-2.0 µs. All solutions were made up to an OD of 1.0 at the excitation wavelength and thoroughly degassed by repeated freeze-pump-thaw-shake cycles. Two shutters, manually operated by the activation of solenoid coils, were utilised to prevent either the laser pulse or xenon monitoring light from falling on the sample compartment. The xenon lamp shutter could be left permanently open when the pulsing unit was in use to enable the use of minimum slit widths on the monochromater inlet and outlet (no problems were encountered with PM tube (Hamamatsu TV Co. Ltd., Type R928) saturation). The signal from the PM tube, at the wavelength of maximum absorption of the triplet species being investigated, was transmitted to a storage oscilloscope (Tektronix 466) and the decay of the triplet-triplet absorption spectrum displayed on the screen using variable time base settings. The information was recorded on Polaroid 667 black and white land film, using a Shackman (Model 7000) oscilloscope camera. The information on the photograph was then digitised using a Textronix 4662 interactive digital plotter and analysed using a Commodore Pet micro-computer. The rate constant for the triplet-triplet absorption decay (k_T) was calculated from the slope of a plot of $\log_{10}$ OD (where OD = optical density) against time. For cases where two components contributed to the triplet-triplet absorption decay curve the initial and final sections of the decay curve were analysed separately. Triplet lifetimes (τ_T) were determined using Equation 11.1.

$$\tau_T = 1/k_T \qquad (11.1)$$

11.8 Photochemical reactors

(i) Daylight reactor This reactor contained a circular array of eight 20W, Chryselco daylight fluorescent lamps which were kept cool by means of a fan fitted to the base.

(ii) 350nm reactor This reactor contained in circular array of sixteen, 8W, F8T5/BLB Sylvania black-light fluorescent lamps (having a maximum emission at 350nm) which were kept cool by means of a fan fitted to the base. The reactor was fitted with a merry-go-round apparatus to ensure that each of several samples irradiated simultaneously received the incident light at similar intensities.

(iii) 300nm reactor This reactor contained a circular array of sixteen Rayonet PRP 3000Å fluorescent lamps, but in all other respects was similar to the 350nm reactor.

(iv) 254nm reactor This adapted Applied Photophysics reactor contained a circular array of twelve Sylvania G15T8 lamps (having a maximum emission at 254nm) but in all other respects was similar to the 350nm reactor.

11.9 References

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