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NITRATION BY

ANHYDROUS TRANSITION-METAL NITRATO

COMPOUNDS AND OXIDES OF NITROGEN

by

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A thesis submitted in part fulfilment of the
requirements for the degree of Doctor of Philosophy

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ABSTRACT

The nitration of aromatic compounds by anhydrous transition-metal nitrato compounds and oxides of nitrogen in carbon tetrachloride has been studied.

Tetranitratotitanium (IV) was found to nitrate some simple aromatic compounds of a wide range of expected reactivity in carbon tetrachloride at room temperature to give good yields of nitrocompounds. Results of direct rate measurements, competition studies and determinations of isomeric product proportions are reported. A combination of a low intermolecular selectivity and a high intramolecular selectivity of substitution was observed. A special mechanism of nitration is postulated proceeding by at least three stages of reaction and involving an intramolecular rearrangement within a co-ordination complex.

Nitro-product ratios are also reported for the reactions of the nitrato complexes of iron (III) and zirconium (IV) with some simple aromatic compounds at room temperature in the absence of solvent. The nitration of some heteroaromatic compounds by these transition-metal nitrato complexes was also investigated. Conditions were established where either 3- or mainly 4- nitropyridine was formed in the nitration of pyridine and either 7- or mainly 3- nitroquinoline produced from the nitration of quinoline.

A study of the nitration of aromatic compounds by dinitrogen pentoxide in carbon tetrachloride indicated that the nitronium ion was the effective electrophile in some reactions where previously it had been suggested that the dinitrogen pentoxide

molecule itself was involved. Product isomer data and competition studies supported this idea.

The nitration of some aromatic compounds with dinitrogen tetroxide in carbon tetrachloride at room temperature was investigated. Results from competition studies and product isomer ratios are reported. For toluene, an absence of intramolecular selectivity was associated with an intermolecular selectivity very similar to that observed for nitronium ion nitrations. The importance of a radical mechanism and nitrosation is discussed as are the effects of added species.

The reactions of both dinitrogen pentoxide and dinitrogen tetroxide with aromatic compounds in carbon tetrachloride showed characteristics of inter- and intramolecular selectivity very different from those observed with tetranitratotitanium (IV), and indicated that these nitrogen oxides were not intermediates in the reactions of tetranitratotitanium (IV).

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SECTION 1

INTRODUCTION

Studies of electrophilic substitution in aromatic compounds have made valuable contributions to the development of theoretical organic chemistry. Since Holleman[1] laid the foundations of our ideas of orientation in aromatic substitution. nitration has occupied a major role in this field.

Nitration can be performed on compounds of differing reactivity under a wide variety of conditions. It can usually be stopped cleanly after the first stage because of the strong deactivation produced in the aromatic nucleus by the nitro group. The characteristics of the reactions vary with reagents used, but the surprising fact has emerged that the nitronium ion (NO_2^+) is the most commonly effective electrophilic species. This supremacy of one electrophile is not characteristic of other electrophilic substitutions and explains the utility of nitration as a model reaction in the determination of structure - reactivity relationships.

There would be, however, considerable interest in a viable nitrating system where a different effective species was involved. In this connection, the nitrato compounds of the transition - metals appeared to be of interest. Some of these compounds were reported to react rapidly with both aromatic[2] and aliphatic[3] systems, and their unusual reactivity suggested that a special mechanism of nitration might well apply. If this were indeed the case, a study of the mechanism of these reactions might be of general interest in the nitration field as providing a point of comparison for the

ubiquitous nitronium ion reaction. Also various synthetic possibilities might arise. It might be possible to prepare nitro compounds in different isomeric proportions from those usual for direct nitrations, and also to nitrate compounds normally considered unreactive. Such considerations might be of importance for both aromatic and nitrogen heteroaromatic compounds.

The object of this work was to study the nitration of a range of simple aromatic molecules, which have been very well studied under other nitration conditions, by some transition - metal nitrato compounds with the object of evaluating some of the above possibilities. Also, it was intended to investigate the reactions of dinitrogen pentoxide and dinitrogen tetroxide with aromatic compounds in carbon tetrachloride solution with the aim of identifying the reactive species.

CHAPTER 1

LITERATURE SURVEY

MECHANISMS OF AROMATIC NITRATION

The first suggestion that the nitronium ion was the reactive species came fron von Euler[4], but proof of its existence was not conclusively demonstrated until 1946[5]. The identification of the electrophile and elucidation of the mechanism have been achieved by examination of the media employed by physical methods and the determination of the kinetics of the reactions.

1.1 NITRATION IN CONCENTRATED AND AQUEOUS MINERAL ACIDS

1.1.1 NITRIC ACID

In concentrated nitric acid, the Raman[6] and infra-red[7] spectra show bands characteristic of the nitrate and nitronium ions. Further work from freezing point[8] and electrical conductivity[9] experiments was consistent with the existence of the following equilibrium:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

In aqueous solutions of nitric acid, the presence of water affects the equilibrium leading to the formation of the nitronium and nitrate ions. The intensity of the band associated with the nitronium ion in both the Raman[6a] and infra-red[7] spectra decreases with the progressive addition of water, and there is no evidence for the existence of measurable quantities of the nitric acidium ion ($H_2NO_3^+$).

In both concentrated and aqueous nitric acid, the mechanism of the reaction has been established as a first order

process for nitrosubstituted benzenes and anthraquinones[10]. These results show that the reactive species if not nitric acid, is formed so quickly from it as to bear a constant concentration ratio to it. Whether this be a large or small ratio cannot be deduced from these kinetic results alone. Conclusive evidence for the operation of the nitronium ion in this aqueous medium was obtained by Bunton and his co-workers[11] from studies made on rates of ^{18}O- exchange between nitric acid and water during some reactions. They observed in certain reactions an initial slow stage which was independent of the concentration of the aromatic compound being nitrated (zeroth-order), and this was identified with the formation of the nitronium ion because the initial rate under zeroth-order conditions was the same as the rate of ^{18}O- exchange in a similar solution;

$$HNO_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ + H_2O$$

$$ArH + NO_2^+ \overset{k_2}{\rightleftharpoons} [Ar\,HNO_2^+]$$

when $k_2 >> k_{-1} > k_1$;- Zeroth-order nitration

$$H_2\,{}^{18}O + NO_2^+ \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} H\,{}^{18}O.NO_2 + H^+$$

No correlations of reaction rates and ^{18}O- exchange rates should be observed in a mechanism involving the nitric-acidium ion.

1.1.2 NITRIC ACID IN SULPHURIC ACID

The existence of the nitronium ion in this medium has been proved in ways which do not depend on its behaviour in nitration. Hantzsch made a study of the effect of nitric acid

on the freezing point of sulphuric acid and suggested[12] that the following equilibria exist

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons H_3NO_3^{2+} + 2HSO_4^-$$

However, improved cryoscopic techniques later showed that the i-factor was about 4 times that of an ideal solute[13] and not 3 as determined by Hantzsch. These results and others obtained by conductivity measurements[14,15] confirmed that the following equilibrium existed

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

More evidence was obtained from spectroscopic studies of solutions of nitric acid in sulphuric acid. The Raman spectra of these solutions[16] provided an easy way of estimating the concentrations of nitronium ions, and it was found that in anhydrous sulphuric acid, the above conversion was complete.

Some related work by Hantzsch[17a,17b] showed the existence of salts formed by the interaction of nitric and perchloric acids. A correct identification of these compounds was made by Ingold and his workers[17c] who showed that a mixture of nitronium and hydroxonium perchlorates was produced. Other conveniently stable nitronium salts have since been prepared by Schmeisser and Elischer[18], and Olah[19]. Both X-ray analyses[20] and Raman spectra[21] of these salts have proved conclusively the existence and linear form of the nitronium ion.

The nitration characteristics of nitric acid in sulphuric acid depend upon the strength of the latter. In concentrated acid of greater than 89% by weight, nitric acid is completely converted to the nitronium ion[16b]. Martinsen[27] discovered in his work on the nitration of some aromatic compounds with this medium, that a maximum in the rate of nitration occurred at 89-90% sulphuric acid.

As the sulphuric acid concentration decreases, a fall in nitration rates is observed. The second order rate coefficient for nitration based on the stoicheiometric concentration of nitric acid, decreases about 10^4 times for each decrease of 10% sulphuric acid below 85%. The rate decrease is attributed to the fall in nitronium ion concentration which cannot be detected by Raman spectroscopy below 85% sulphuric acid [5].

Several investigations have been performed to establish whether the nitronium ion is still effective in these aqueous systems. It is easy to show that molecular nitric acid is not the active electrophile under these conditions because the variation of rate is not similar to the corresponding change in concentration of this species determined both by vapour pressure[23] and spectroscopic measurements[24].

By comparing the dependence of rate on the concentration of sulphuric acid, with the acidity dependence of the ionisation of model compounds, the continued effectiveness of the nitronium ion has been indicated.

The ionisation of a series of tri-aryl carbinols occurs by,

$$XOH + H^+ \rightleftharpoons X^+ + H_2O$$

from which the H_R acidity scale is defined.[25,26] Primary aromatic amines ionising according to,

$$B + H^+ \rightleftharpoons BH^+$$

however, define a different scale known as the H_o acidity function[27]. The applicability of these relationships assumes that nitric acid behaves like the organic indicators mentioned which must be open to doubt. However, the scales H_R and H_o are so different, and the fact that nitration rates follow more closely the H_R function[28] than the H_o function showed clearly the effectiveness of the nitronium ion. Any contributions from the nitric acidium ion would have produced sudden and more significant deviation from the relationship, so the effectiveness of the nitronium ion is suggested even when it is only present in small concentrations.

1.1.3 ENCOUNTER RATE IN AQUEOUS SULPHURIC ACID

For a series of benzene derivatives with activating substituents, a limiting maximum rate of nitration by the nitronium ion is reached[29]. Beyond this limit, which is believed to be the rate of encounter between nitronium ions and aromatic molecules, the inclusion of further activating substituents does not affect the rate. The limit is already reached with the xylenes, for in 68.3% sulphuric acid at 25°C

they are all nitrated about 38 times as fast as benzene. Mesitylene is nitrated at an identical rate.

For reactions in solution the two reacting species remain in proximity for a finite time and an encounter pair (e.p.) can be considered as a transient intermediate. A typical reaction scheme can be represented by:

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O$$

$$NO_2^+ + ArH \rightleftharpoons (e.p.)$$

$$(e.p.) \rightarrow \text{products}$$

In comparisons of reactivity, the question of encounter control is of direct importance when we consider benzene as a basis for comparisons of aromatic reactivities. It has been shown[29] that below 68% sulphuric acid, benzene is unaffected by encounter control. But between 68 and 82% sulphuric acid, the rate approaches that of the rate of encounter. This shows that any accurate comparisons of aromatic reactivities by observed relative rates to benzene in this region are not meaningful. This work also implies another important principle. If the reactivity of an aromatic compound in a substitution reaction is increased, a plateau in rate constant for the reaction may be attained which can be identified as the rate constant of encounter for the reacting species. If further structural changes for increasing reactivity are made, and the rate constant is raised above this plateau then a new electrophile must be active.

1.2 NITRATION IN INERT ORGANIC SOLVENTS

The identification of the nitronium ion in organic solvents is not possible by physical methods[30], and the evidence for its existence and effectiveness has been obtained largely from detailed kinetic studies in these media.

The first correct interpretation of the features of nitration in these solvents came from Ingold and his co-workers[10]. This arose from studies of nitric acid in nitromethane and acetic acid. Reactions were performed with a large excess of nitric acid.

For sufficiently reactive substrates, the nitration rates were found to show zeroth-order kinetics[31]. Under such conditions, the rate is independent of the nature and concentration of the substrate.

A reaction scheme can be envisaged:

$$HNO_3 \underset{(2)}{\overset{(1)}{\rightleftharpoons}} NO_2^+ \xrightarrow{(3)} ArNO_2$$

The kinetic order of nitration depends on the fate of the nitronium ion. If the rate of process (3) is very fast, then zeroth-order kinetics will be observed, but if the process (2) is important, a first-order dependence on substrate concentration will be observed. Process (2) becomes important when the reactivity of the aromatic compound is decreased or if the concentration of the particular compound decreases. The deviation from zeroth to first order kinetics has been observed in several compounds[32] and is often a consequence of the decrease in the concentration of the aromatic towards the end of the reaction.

The reaction scheme for the production of the effective electrophile was obtained from a consideration of the effects that certain species had on the nitration rate. The addition of nitrate ions[10] produced anticatalysis without changing the kinetic form of the reactions.

Small additions of water depressed the zeroth-order rate without disturbing its kinetic form. Only when larger concentrations were added did the kinetics deviate from zeroth-order to first-order.

The results of nitrate ion addition showed that its effect was not exerted by consuming a proportion of the reactive species. Nitrate ions must be affecting the precursor to the nitronium ion, the precursor formed in equilibrium with nitric acid. The effect of water addition showed that appreciable concentrations of the electrophile were reacting with water. Both these facts are consistent with the acceptance of the following reaction scheme and the nitronium ion as the effective electrophile:

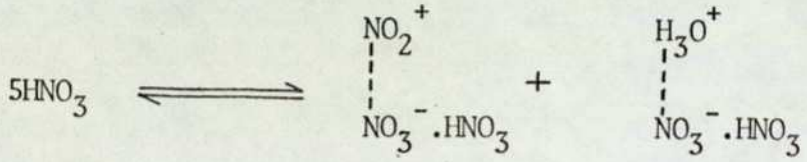
$$2HNO_3 \overset{\text{fast}}{\rightleftharpoons} H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \overset{\text{slow}}{\rightleftharpoons} NO_2^+ + H_2O$$

$$NO_2^+ + ArH \longrightarrow \text{Products}$$

The fact that nitrations in acetic acid[10], sulpholan[33] and carbon tetrachloride[34,35] were kinetically similar to that in nitromethane is important because it removes any possibility of chemical involvement of the solvent in the slow step of the reaction.

In recent work on nitration of reactive substrates in carbon tetrachloride[34], it was found that the zeroth-order rate constant depended approximately on the nitric acid concentration to the fifth power. This suggested that five molecules of nitric acid were associated with the pre-equilibrium stage or present in the transition state. Nitronium ion formation was represented by,



This scheme was used to explain temperature effects on the rates of nitration. At lower temperatures, enhanced rates of nitration were correlated with the increased production of molecular aggregates.

1.2.1 ENCOUNTER RATE IN INERT ORGANIC SOLVENTS

In sulphuric acid of greater than 68%, the observed rates of nitration for a series of substituted benzenes could not be raised above about 40 times that observed for benzene itself, despite the introduction of activating substituents. This limiting rate, or the rate of encounter between the substrate molecules and nitronium ions, has also been detected in several organic solvents[33]. In both nitromethane and sulpholan as well as some aqueous solutions of these solvents, similar effects were detected. Also in carbon tetrachloride [34] and acetic anhydride[36,37], nitration at encounter rate has been observed but not yet fully examined. In organic media, the

limit appears less sharply defined than that observed in mineral acids, but the factors controlling the point of onset of encounter control are not fully understood.

1.2.2 ACETIC ANHYDRIDE

Nitration by nitric acid in acetic anhydride is considered separately because, of all the media used in nitrations, this has proved the most controversial and least understood. Acetic anhydride differs from most of the organic solvents used, in that it reacts with nitric acid;

$$(CH_3CO)_2O + HNO_3 \rightleftharpoons CH_3CO\,NO_2 + CH_3COOH$$

A further much slower reaction finally produces tetranitromethane[34].

The kinetics of nitration in this medium are complex[32,38], and acetoxylation which occurs at the same time as nitration adds to the complications. From much of the early work in this medium, the existence of the effective electrophile was not convincingly established, and the involvement of such electrophiles as acetyl nitrate and the nitronium ion have been suggested[39,40,41,42].

Some work carried out with reactive aromatic substrates[43] in acetic anhydride has shown that the kinetics of the reaction decrease from first order to zeroth order when the substrate concentration is increased. This was explained in terms of nitronium ion attack giving zeroth order kinetics when the substrate concentration is high, and attack by a solvated nitronium ion [NO_2^+ (HNO_3)] at low aromatic

concentrations giving first-order kinetics. These observations were reinvestigated by Ridd and his co-workers[44], who showed that the change in order was mainly due to a medium effect and not the rate determining formation of the electrophile.

1.3 NITRATION WITH NITRONIUM SALTS

The first isolated nitronium salt was prepared by Hantzsch[17a,45] since when largely through the efforts of Olah and his collaborators[46], a large number of these salts have been made available. Nitronium salts of the type NO_2^+ Cl O_4^- and NO_2^+ $HS_2O_7^-$ are relatively unstable but fluoro complex salts e.g. NO_2^+ BF_4^- and NO_2^+ PF_6^-, are quite stable and are now commercially available nitrating agents.

Despite solubility problems in inert solvents, these nitronium salts have been shown to exist as ion pairs in sulpholan[46,47]. They are found to give high yields of nitro-products with a wide range of aromatic compounds[19] whether they are used in the solid state or solution. When reactions are carried out with nitrogen heterocyclic compounds however, only N-nitration is observed[48].

Studies of nitrations of aromatic systems with nitronium salts have been used in quantitative comparisons of reactivity. Olah and his co-workers have published extensive data obtained from competitive nitrations of series of alkyl[49] and halogenobenzenes[50]. The results obtained differed in several respects from those observed by other methods of nitration[32].

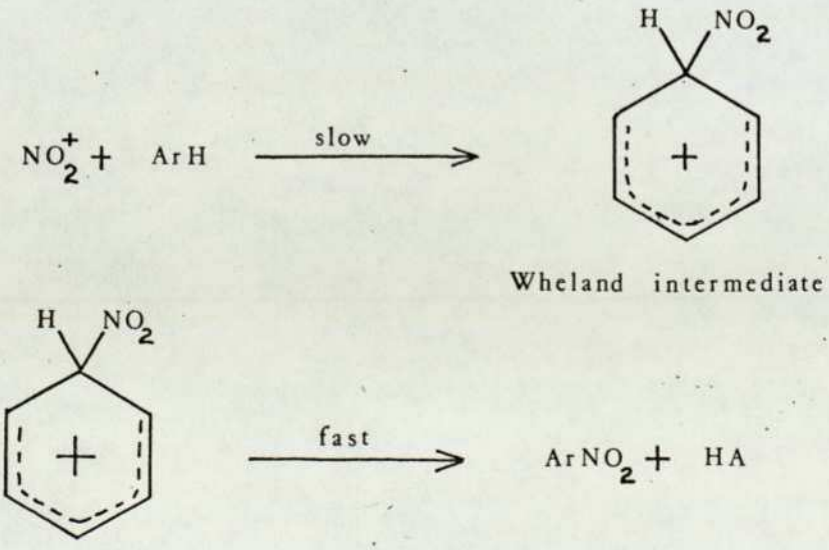
It is possible to regard the relative reactivities

obtained as a consequence of diffusion control of the reaction rates. The competition method has been criticised when the rate of mixing of reactants is comparable or slower than the rate of reaction[51], and there is evidence that in Olah's experiments, this objection is justified[52,53]. The small changes in orientation can be plausibly explained in terms of medium effects and do not indicate that any different electrophile is operating.

1.4 MECHANISM OF SUBSTITUTION

Except for possibly acetic anhydride, in the nitrating conditions discussed the electrophile has been found to be the nitronium ion. In some cases however, there is evidence that dinitrogen pentoxide is capable of operating as the nitrating agent when used in organic solvents. This will be discussed in Section 1.5.

It is necessary to consider the process by which the nitronium ion reacts with the aromatic substrate resulting in nitration. The accepted process[54], an SE2 mechanism, is described by two stages:



This process has been confirmed from studies of solvent effects[10] and isotope effects[55].

1.4.1 NITROSATION

The significance of this process to the nitration of certain aromatic compounds was first appreciated by Ingold and his co-workers[31,56]. In a study of the reactions of a series of aromatic compounds in different organic solvents, they observed an anti-catalytic process, the strength of which could be enhanced by an increase in the concentrations of nitrous acid. Stronger forms of the anticatalytic process found when either large nitrous acid concentrations or quantities of water were present were attributed to the formation of dinitrogen trioxide[10], heterolysis of the latter yielding the nitrosonium and nitrite ions,

$$2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3$$

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

The production of the nitrosonium ion from dinitrogen tetroxide in a variety of solvents has since been established spectroscopically[57,58].

As well as an anti-catalyst, nitrous acid has been found to catalyse the nitration of some very reactive aromatic compounds e.g. phenol, aniline and their derivatives. Some of these compounds are oxidised under the conditions of reaction, and the consequent formation of more nitrous acid leads to autocatalysis. A mechanism for the catalysed nitration has been suggested;

$$ArH + NOX \xrightarrow{slow} ArNO + HX$$

$$ArNO + HNO_3 \xrightarrow{fast} ArNO_2 + HNO_2$$

where NOX represents the nitrosating species. This reaction accounts for the constant concentrations of nitrous acid throughout the reaction. Nitric acid has been considered responsible for the oxidation of the nitroso compound but Bonner and his co-workers[35] have obtained evidence that dinitrogen tetroxide may function both as a nitrosating and oxidising agent. In studies of the catalysed nitration of p-dimethoxybenzene in carbon tetrachloride, they showed that the following reactions had taken place,

$$N_2O_4 + ArNO \longrightarrow ArNO_2 + N_2O_3$$

$$N_2O_3 + 2HNO_3 \longrightarrow 2N_2O_4 + H_2O$$

The data obtained by many workers who ignored the possibility of nitrosation have often given a misleading picture of the relative reactivity of certain reactive substrates to nitration[32]. The importance of the effect can be illustrated by some recent work on the relative rates of nitration of some naphthalenederivatives[36,38]. The relative rate of reaction of naphthaleneto benzene was found to be 62, whereas that of 1-methylnaphthalenewas found to be 20,600 which suggested an unreasonable activating property of methyl group. In both cases, the concentration of nitrous acid was low (ca. 5×10^{-4} mole $l.^{-1}$) but the result was wholly ascribed to nitrosation

effects.

Nitrosation is also an important factor affecting o- : p- ratios for nitration of certain aromatic compounds. The results obtained for nitration of anisole in sulphuric acid[37] illustrate this point. The o- : p- ratio of 1.5 was decreased to 0.065 in the presence of sodium nitrite showing that under the latter conditions nitration *via* nitrosation had occurred producing a preferential attack at the p- position.

Effects due to nitrosation can usually be removed by addition of suitable quantities of urea or sulphanilic acid to the reaction solutions.

1.5 NITRATION WITH OXIDES OF NITROGEN

1.5.1 DINITROGEN PENTOXIDE

The determination of the structure of dinitrogen pentoxide both in the solid state and in solution was first attempted by Chédin[59]. He showed by Raman spectroscopy, later to be confirmed by other techniques[13,60], that dinitrogen pentoxide is undissociated and covalent in both the gas phase and in solvents of low dielectric constant; whereas in the solid state and in solution with solvents of high dielectric constant, it is ionized to $\left(NO_2^+\right)\left(NO_3^-\right)$.

Further proof was afforded by Grison and his co-workers in an x-ray crystallographic investigation of solid dinitrogen pentoxide which confirmed its ionic structure[61].

Although a number of workers have published data recording structural and decomposition properties[62], surprisingly little early work was done on properties of dinitrogen pentoxide

as a nitrating agent. Gibson[63] used solid dinitrogen pentoxide to obtain a dinitrate of tartaric acid. Lothar Meyer[64] also used solid dinitrogen pentoxide to convert benzene into dinitrobenzene below 55°C. Trinitrobenzene was obtained on addition of sulphuric acid and increasing the temperature.

Bamberger[65] studied the reactions of dinitrogen pentoxide with ethereal solutions of aniline at -20°C. He found conversion was mainly into N-nitroaniline but mono-nitroanilines together with the nitrates of aniline and diazobenzene were also found.

Hoff[66] used a solution of dinitrogen pentoxide in carbon tetrachloride to investigate the reactions of aromatic amines. His results were similar to those obtained by Bamberger, showing the formation of N-nitration products together with diazo-amino compounds and amine nitrates.

Before 1913, dinitrogen pentoxide was described as having a melting point of 30°C and a boiling point of 45-50°C. However, it was shown that the pure compound had neither a melting point nor a boiling point[67], and that above 0°C would decompose[68]. Accordingly care has to be taken in interpreting these early results.

Some of the early preparative work was reinvestigated by Haines and Adkins[69] who used both solid dinitrogen pentoxide and a 0.1% solution in carbon tetrachloride. The latter was found to nitrate benzene to give good yields of nitrobenzene. Solid dinitrogen pentoxide converted nitrobenzene into dinitro-benzene but no trinitrobenzene was obtained even at 75°C. Other

conversions obtained with the dinitrogen pentoxide solution include, bromobenzene into p-nitrobromobenzene, toluene into o- and p-nitrotoluenes and phenol into picric acid. In the case of pyridine, an addition product was obtained which was insoluble in carbon tetrachloride. No nitropyridines were produced.

In an investigation into the orientation effects of nitration by dinitrogen pentoxide, Spreckels[70] studied the reaction with benzotrichloride. Using a carbon tetrachloride solution, he established that the mixture of products contained 70% of the m-nitro isomer. Cooper and Ingold[62b] employed dinitrogen pentoxide for the same reason in the reaction with benzoyl chloride, the m-nitro isomer being formed.

A study of the kinetics of nitration by dinitrogen pentoxide in sulphuric acid in the reaction with m-xylene-4, 6-disulphonic acid[71] showed that the dinitrogen pentoxide acted like twice as many molecules of nitric acid. This has since been shown[16a, 13] to be due to the conversion by the solvent of the two solutes into nitronium ions, one ion in the case of each molecule of nitric acid and two such ions in the case of dinitrogen pentoxide;

$$N_2O_5 + 3H_2SO_4 \rightleftharpoons 2NO_2^+ + 3HSO_4^- + H_3O^+$$

The first systemmatic study of the kinetics of nitration by dinitrogen pentoxide in organic solvents, mainly carbon tetrachloride, was made by Gold[72] and continued by Williams[73]. Kinetics of reactions were followed by dilatometric techniques.

Because the reactions of benzene and toluene were too fast to study by this technique, series of halogenobenzenes and aromatic esters were chosen.

From the results of the dilatometric runs made with the aromatic in an excess, it was possible to establish the presence of three broad classes of reaction. In the first, the reaction rate followed an exponential path corresponding to a first-order form. In the second, reactions remained linear and stopped abruptly when the aromatic had been consumed. In the third, rates followed sigmoid relationships suggesting that they were susceptible to varying intensities of auto-catalysis. This classification suggested that when the aromatic compound was in a constant excess, there was a first-order, a zeroth-order and an autocatalytic reaction either separately or superimposed upon one another. But a careful study showed that the whole series could be more simply and consistently regarded as a single series formed by the mixing of a non-catalysed first-order reaction with an autocatalytic reaction.

The non-catalytic reaction was favoured at higher temperatures and with low concentrations of dinitrogen pentoxide. In a series of reactions carried out between 10^{o}-20^{o}C with concentrations of dinitrogen pentoxide between 0.03-0.1 mole l^{-1} and containing a large excess of aromatic compound, the reaction rate obeyed the following law,

$$\text{Rate} = k \left[\text{ArH} \right] \left[N_2O_5 \right]$$

It was also noted that there were differences from characteristics established for nitric acid in organic solvents. The change in solvent polarity from carbon tetrachloride to nitromethane only changed the rate by a factor of 6, whereas nitronium ion reactions are accelerated by factors of the order of 40 when the solvent is changed from acetic acid to nitromethane[10]. Also small quantities of nitrate ions had a marked catalytic effect on the reaction rate.

The auto-catalytic reaction was favoured by lower temperatures or higher concentrations of dinitrogen pentoxide. A similar effect was observed on addition of either sulphuric or nitric acid. The addition of nitric acid at lower temperatures resulted in a strong catalysis and a modification of the auto-catalytic form. This effect was not so pronounced at higher temperatures. The effects observed with sulphuric acid were more pronounced.

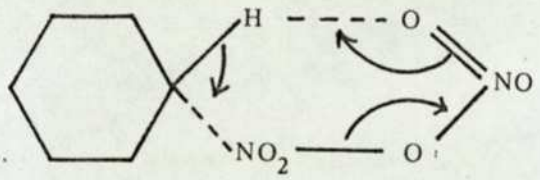
It was suggested that the catalytic effect was caused by the heterolysis of dinitrogen pentoxide induced by aggregates of nitric acid to yield nitronium and nitrate ions. The reactions are autocatalytic because as nitration proceeds, the water produced reacts with the dinitrogen pentoxide giving nitric acid. The observation that an increase in temperature diminishes the importance of the catalytic reaction relative to the non-catalytic one is attributed to the breaking up of the nitric acid aggregates. A similar temperature effect on reaction rates has since been observed for nitration by nitric acid in carbon tetrachloride[34].

In the non-catalytic reaction, the acceleration of

reaction rate observed when nitrate is added is not consistent with the formulation of the nitronium ion as the effective electrophile. Any possible equilibrium say, between the nitronium ion and dinitrogen pentoxide would result in a depression of rate by addition of small amounts of nitrate[10], but this was not the case. The authors conclude that the uncatalysed reaction of aromatic compounds by dinitrogen pentoxide in aprotic media is a single stage bimolecular process involving direct attack by the dinitrogen pentoxide molecule;

$$ArH + NO_2.O.NO_2 \longrightarrow ArNO_2 + HNO_3$$

They also suggested a cyclic transition state;



This sort of transition state has since been shown to be unlikely following the absence of any kinetic isotope effect in the nitration of certain aromatic compounds with benzoyl nitrate[74].

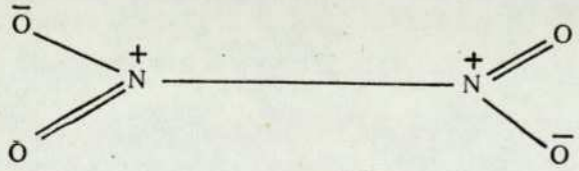
Another piece of evidence supporting the operation of an electrophile other than the nitronium ion in these non-catalytic reactions was obtained from a study of the isomer distribution of the nitroproducts found in the case of chlorobenzene. The nitration in the non-catalysed reaction gave 57% o- and 43% p-nitrochlorobenzenes whereas for nitronium ion nitrations the

percentage isomers reported are from 27-35% o- and 73-65% p-nitrochlorobenzenes[32]. Similar results to these latter ones were observed in the catalysed reactions. However, the formation of oxidation products such as nitrophenols in the non-catalytic reactions was an added complication. Some of these conclusions have been reconsidered in the present work.

Many of the recent studies of the reactivity of dinitrogen pentoxide, have been on benzoyl nitrate where dinitrogen pentoxide was believed to be the effective electrophile. Studies using benzoyl nitrate in carbon tetrachloride[15] and acetonitrile[76] have shown the formation and effectiveness of dinitrogen pentoxide in these systems mainly by comparisons to the reactions of dinitrogen pentoxide itself. Certain characteristics of the reactions of benzoyl nitrate have been observed in the reactions of acetic anhydride-nitric acid mixtures[75] for example, high o : p ratios, and effects of certain added salts. However reactions of acetyl nitrate in acetic anhydride as solvent are now not believed to involve dinitrogen pentoxide[38].

.5.2 DINITROGEN TETROXIDE

Dinitrogen tetroxide can be represented by a single structure (I) in the solid and gaseous states and this structure is also found in the liquid state;



(I)

This symmetrical structure has been proposed on the basis of x-ray[77], magnetic susceptibility[78] and spectroscopic measurements[79].

The dissociation of the dinitrogen tetroxide molecule has been postulated to occur in several ways,

a) $N_2O_4 \rightleftharpoons 2NO_2$

This rapid equilibrium occurs in the liquid, the dimer predominating at lower temperatures.

b) In mineral acids, dinitrogen tetroxide is completely ionized according to,

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

This has been confirmed by conductivity measurements[31,80], and infra-red spectroscopy[58]. In sulphuric acid, ionization is complete;

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

This solution has been shown to have nitrating properties[86]. The existence of the nitronium ion in this medium has been established by Raman spectroscopy[16a] and cryoscopy[13]. The ionization of dinitrogen tetroxide increases with dielectric constant of the solvent, so that ionization is complete in sulphuric acid, considerable in nitric acid and very small in organic solvents.

It has long been known that when dinitrogen tetroxide reacts with organic compounds, nitration, oxidation and

diazotisation reactions are likely to take place. Hasenbach[81] first studied the reaction of benzene and dinitrogen tetroxide and obtained nitrobenzene and oxalic acid as products. Similarly Leeds[82] obtained both nitration and oxidation products from a series of benzene derivatives. Wieland[83] demonstrated that polynitro aromatics could be obtained by carrying out reactions in sealed tubes at elevated temperatures.

The main disadvantages noted by these and subsequent workers were the slowness of reaction and the undesirable formation of oxidation products. Schaarschmidt and his co-workers[84] investigated some reactions using dinitrogen tetroxide in organic solvents. They found that some unreactive compounds could not be nitrated by dinitrogen tetroxide alone, but that on addition of certain Lewis-acid type catalysts (e.g. $AlCl_3$) or sulphuric acid, good yields of nitrocompounds could be obtained. This was later confirmed by other workers and much of thesubsequent work has been carried out in the presence of these catalysts[46,85].

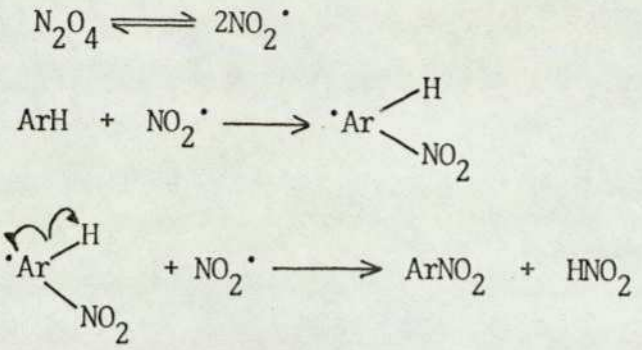
Pinck[86] showed that good yields of nitrobenzene could be obtained from benzene using dinitrogen tetroxide in sulphuric acid. Battegay[87] extended work with this nitrating solution to obtain high yields of nitrocompounds from a range of aromatic compounds, i.e. benzene, toluene, o-, m- and p-xylenes, chlorobenzene and nitrobenzene. Schaarschmidt[84,88] and Titov[89] obtained equally good yields from the same series of aromatic compounds in the presence of metallic chlorides e.g. $AlCl_3$, $FeCl_3$. The most extensive work using the complexes obtained from dinitrogen tetroxide and Lewis acids was reported by Olah

and his co-workers[46]. Their work suggested that, for example when boron trifluoride was used as catalyst, the complex obtained appeared to behave as a mixture of both nitronium and nitrosonium salts[90].

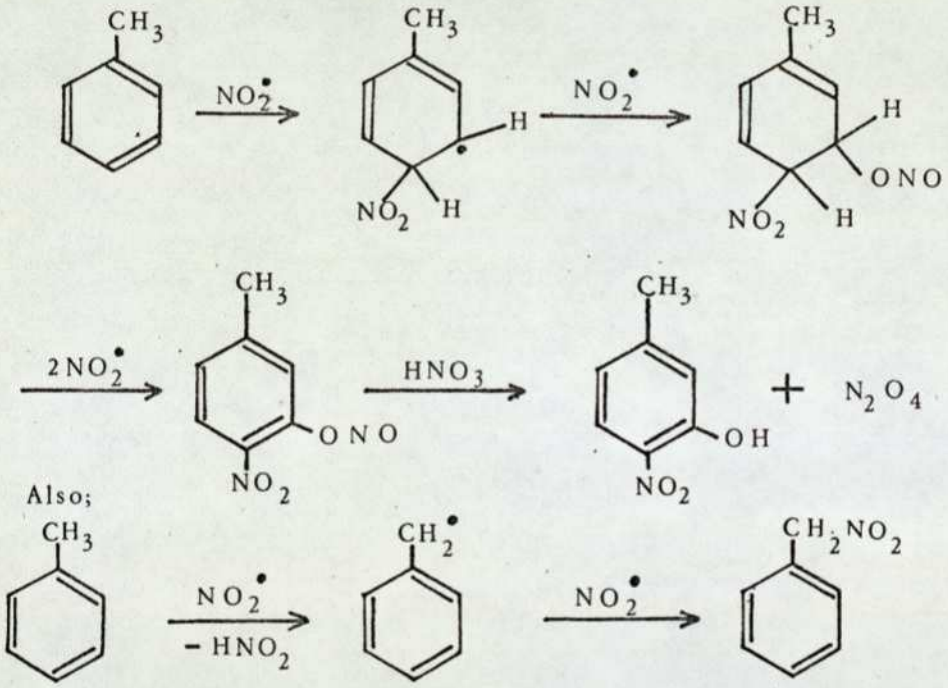
A more recent study of the reactions of dinitrogen tetroxide alone with aromatic compounds was carried out by Underwood and his co-workers[91]. They attempted to study of some characteristics of the reaction mechanism. Using dinitrogen tetroxide in aprotic solvents, it was found that aromatic compounds could be nitrated cleanly and give good yields of nitroproducts. From some competition experiments performed, a similar intermolecular selectivity to that of the nitronium ion was observed.

From product analysis in the nitration of anisole, it was observed that attack had occurred preferentially at the p-position. The latter result was suggested as a consequence of nitration *via* nitrosation. This phenomenon had previously been observed by Bonner and his workers[35] in reactions of dinitrogen tetroxide in carbon tetrachloride with p-dimethoxybenzene (Section 1.4.1).

As well as the reaction sequences mentioned, much of the literature information concerning attack by dinitrogen tetroxide in similar systems has been explained in terms of mechanisms involving free radicals. In his extensive surveys of nitrations, Titov[92] postulates the formation of nitroproducts from aromatic systems as follows:



A similar explanation for the formation of oxidation products was proposed,



1.6 ANHYDROUS TRANSITION-METAL NITRATO COMPOUNDS

1.6.1 INTRODUCTION;

Compounds of metals (M) and the nitrate group can be divided into two classes depending on the nature of the metal-nitrate bond. A compound which is ionic is termed nitrate, whereas one in which the bonding is covalent through one or more of its oxygen atoms is termed nitrato.

Until recent years the known anhydrous metal nitrates (i.e. alkali metals, alkaline earth metals) were all ionic compounds. The nitrates of other metals were known only in the form of their hydrates, and attempts to remove water commonly resulted in the formation of oxides or hydroxide nitrates with the evolution of nitric acid. This gave rise to the belief that the anhydrous nitrates of many metals (particularly the transition metals) would be unstable. However, the majority of the anhydrous nitrates which have recently been prepared are found to have high thermal stability, and to exhibit covalent bonding. In aqueous solution the covalent bonds cannot withstand the solvating power of water molecules and ionic species are formed. When prepared under non-aqueous conditions however, metal nitrato compounds can be strongly covalent and in some cases are volatile.

1.6.2 PREPARATIVE METHODS

The methods which have the widest general application involve the use of dinitrogen tetroxide or dinitrogen pentoxide. Chlorine nitrate has also been used successfully[93] but often oxidation-reduction reactions occur leaving products of indefinite composition.

1.6.2.1 DINITROGEN TETROXIDE

Liquid dinitrogen tetroxide reacts with a few metals (e.g. Na, K, Ag, Pb and Zn) to form nitrates and addition complexes. The liquid itself is non-polar and so displays very poor solvent properties for metal salts, and with metals reaction is very slow. However the nitrating ability can be enhanced when the dinitrogen tetroxide is used dissolved in a dipolar aprotic solvent, e.g. ethyl

acetate or acetonitrile. Extensive work with this system has been reported by Addison and his co-workers who prepared a series of anhydrous compounds as shown in Table 1.1.

Several metal salts react with dinitrogen tetroxide solutions to form addition compounds. The anhydrous nitrato compound can often be obtained by heating the adduct in vacuo.

1.6.2.2 DINITROGEN PENTOXIDE

The use of dinitrogen pentoxide dissolved in nitric acid for dehydrating hydrated nitrates and thus isolating anhydrous compounds was first appreciated by Guntz and Martin[102]. They prepared anhydrous nitrates of manganese, copper, nickel and cobalt by this method. Further work by Schmeisser[103], Field and Hardy[104] and Addison and his co-workers[105, 106, 107, 108, 109] resulted in the preparation of an extensive series of anhydrous nitrates, chiefly the transition-metal nitrato compounds. This is summarised in Table 1.2.

Although in many cases the same reaction product is obtained using dinitrogen pentoxide and dinitrogen tetroxide, the pentoxide addition complexes are generally weaker than those of the tetroxide[80] and this is an important consideration in the choice of reagent for preparative work.

The anhydrous nitrates known to exist are indicated in the following Table 1.3.

1.6.3 STRUCTURES

The nitrate group has long been recognised as a versatile ligand and several modes of co-ordination to transition-metals have been proposed;

TABLE 1.1

NITRATO COMPOUNDS FROM REACTION WITH DINITROGEN TETROXIDE

Starting material	Product	Reference
Metal	$Cu(NO_3)_2$	94
	$Cd(NO_3)_2$, $Co(NO_3)_2$, $Hg(NO_3)_2$,	95
	$Mn(NO_3)_2$	95
	$Ca(NO_3)_2$, $Mg(NO_3)_2$.	96
	$Zn(NO_3)_2$	97
	$UO_2(NO_3)_2$	98
Anhydrous chloride	$Be(NO_3)_2$, $Be_4O(NO_3)_6$	99, 96
	$Fe(NO_3)_3$, $FeNO(NO_3)_4$	100
	$Ni(NO_3)_2$	101
Carbonyl	$Fe(NO_3)_3$, $FeNO(NO_3)_4$	100
	$Co(NO_3)_3$, $Ni(NO_3)_2$	101

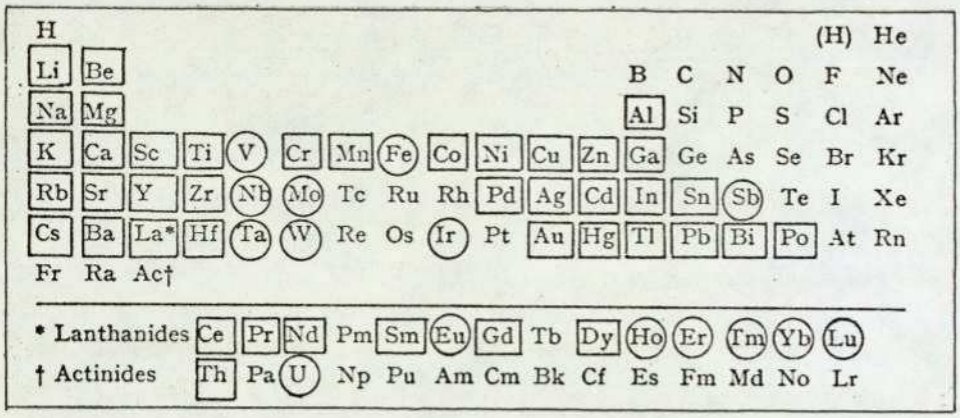
TABLE 1.2

NITRATO COMPOUNDS PREPARED FROM DINITROGEN PENTOXIDE

Starting material	nitrato-product	Reference
Metal oxides or chlorides	$CrO_2(NO_3)_2$, $VO(NO_3)_3$, $MoO(NO_3)_2$, $WO_2(NO_3)_2$, $SbO(NO_3)_2$, $Ti(NO_3)_4$.	103
Metal, Anhydrous choride, or Hydrated nitrate.	$Cu(NO_3)_2$, $Zn(NO_3)_2$ $Pd(NO_3)_2$, $Zr(NO_3)_4$, $Ti(NO_3)_4$, $Hf(NO_3)_4$. N_2O_5, $NbO(NO_3)_3$, $Au(NO_3)_3$, $In(NO_3)_3$, $Hg(NO_3)_2$ $Fe\,NO(NO_3)_4$, $Be_4O(NO_3)_6$	104
Carbonyl, Anhydrous Chloride, or Hydrated Nitrate	$Cr(NO_3)_3$, $Al(NO_3)_3$. N_2O_5, $Al(NO_3)_3$. 0.4 N_2O_5, $Sn(NO_3)_4$, $NO_2^+[Ni(NO_3)_4]^-$, $Au\,NO(NO_3)_4$	105, 106, 107, 108, 109
Scandium chloride	$Sc(NO_3)_4$	110
Manganese trifluoride	$Mn(NO_3)_3$	111
Cobalt trifluoride	$Co(NO_3)_3$	112

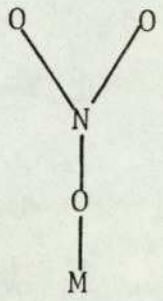
TABLE 1.3

The known anhydrous nitrates and nitrato compounds arranged on the basis of the Periodic Table.

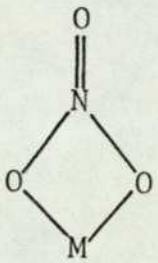


□ Anhydrous nitrate and nitrato compound known

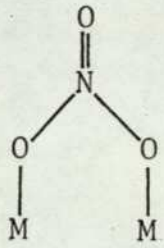
○ Only oxide nitrates known



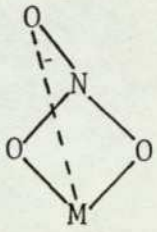
UNIDENTATE BONDING



BIDENTATE BONDING



BONDING AS A BRIDGING GROUP



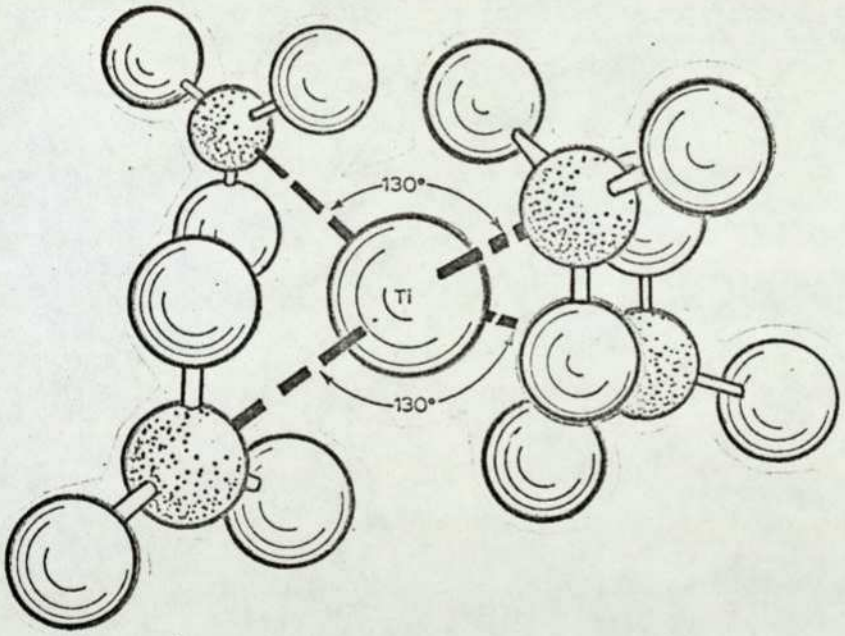
TERDENTATE BONDING

Structural studies carried out so far have identified all but terdentate bonding. Much of the evidence for the existence of a particular bond in a compound has been based on analysis of infra-red spectra, and has been largely of a tentative nature. However, extensive applications of X-ray diffraction techniques by Addision and his associates[113] have enabled unequivocal structures to be established.

Tetranitratotitanium (IV) was chosen as a model compound for many of the early studies mainly due to its volatility and because the simplicity of its infra-red spectrum suggested a structure composed of single molecules with probably a single mode of bonding of the nitrate groups. This was in fact observed[114] and the four bidentate nitrato groups were found to be arranged symmetrically in a tetrahedral manner around the central titanium atom as shown below in Figure 1.1.

FIGURE I.I

STRUCTURE OF TETRANITRATOTITANIUM (IV)



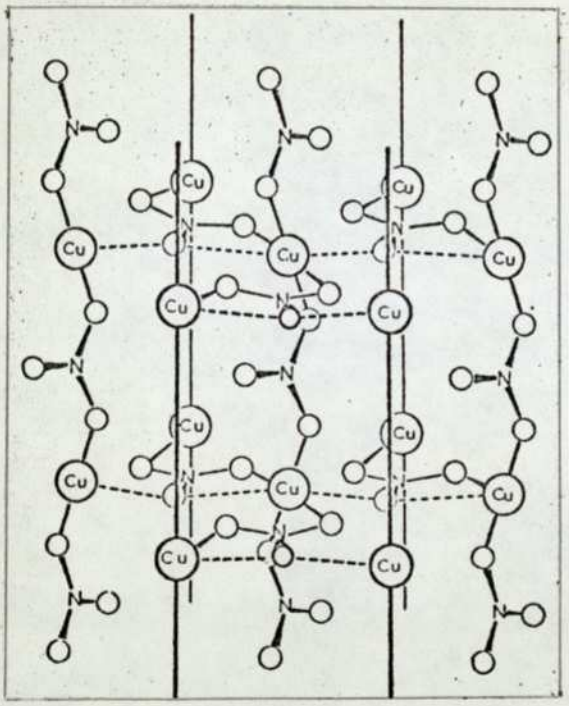
Mainly on the basis of infra-red data it has been established that tetranitratozirconium (IV) has a structure very similar to that of the titanium (IV) compound[115]. Other transition-metal nitrato compounds e.g. Mn $(NO_3)_2$, Ni $(NO_3)_2$ and Zn $(NO_3)_2$ have been shown to exhibit unidentate nitrato group bonding[113].

Nitrato compounds of chromium have been shown to exhibit both unidentate and bidentate bonding[115].

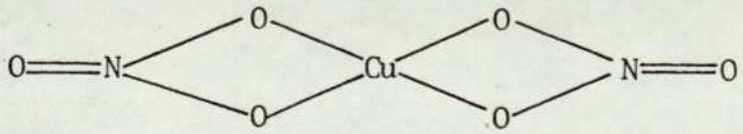
The first direct evidence of the existence of bridging nitrate groups was obtained from a study of the structure of dinitrato copper (11)[116, 117]. The main feature of the crystalline structure is the presence of infinite chains formed by alternate copper atoms and nitrate groups. The chains are linked via Cu - O bonding as shown below in Figure 1.2.

FIGURE 1.2

STRUCTURE OF DINITRATOCOPPER (II)



In the vapour state, this compound exhibits a monomeric structure with bidentate nitrato-group bonding:



The nitrato complexes of iron present similar structural anomalies. The products obtained from reactions iron (III) salts with nitrogen oxides can be represented as $Fe(NO_3)_3 \cdot N_2O_4$. On the basis of hydrolysis characteristics and infra-red evidence, this compound is better represented by the structure $NO^+ Fe(NO_3)_4^-$ [100]. Infra-red evidence also indicates that the nitrate groups are bonded in an unsymmetrical bidentate manner to the metal atom[118]. It was shown that if the compound $NO^+ Fe(NO_3)_4^-$ was heated <u>in vacuo</u> for several hours, the sublimate then has the structure $NO_2^+ Fe(NO_3)_4^-$ [119], but the metal-nitrate bonding was still found to be bidentate.

Although the study of covalent bonding in transition-metal nitrato compounds is of structural importance, the manner in which covalency influences chemical reactivity is more significant and this will be discussed in the next Section.

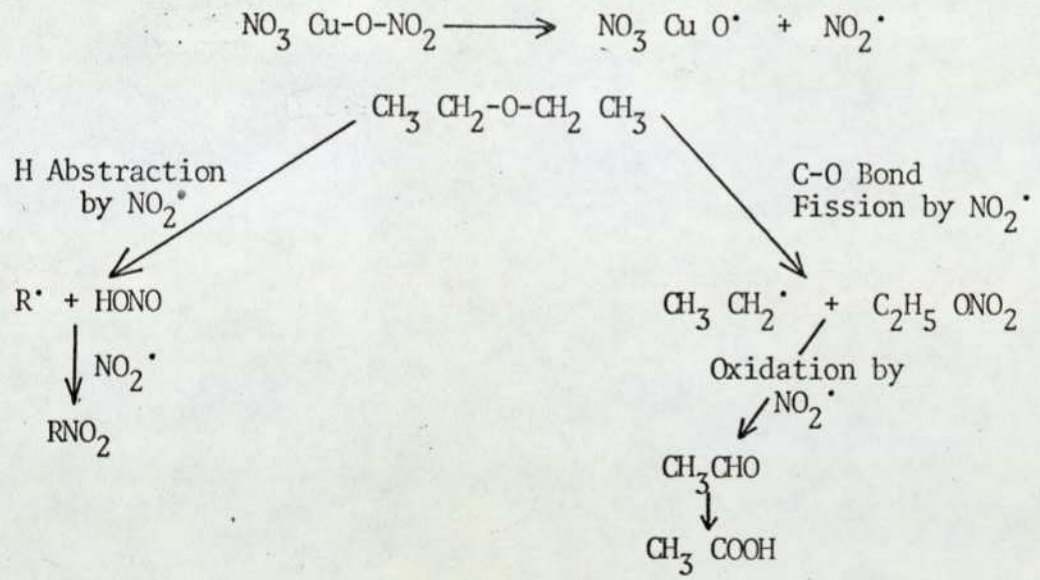
1.6.4 REACTIONS

The high reactivity associated with bidentate covalent bonding of the nitrate group quickly became apparent as the nitrato compounds of the transition-metals became available. When Field and Hardy[3] first prepared tetranitratotitanium (IV) they reported an unusual reactivity of the compound towards alkanes used to prepare infra-red mulls. They reported that an alkyl nitrate, a nitroalkane and a carboxylic acid were formed from n-dodecane, and proposed a radical mechanism for the reaction. $NO_2^{\bullet}$ was produced from the dissociation of the nitrato compound,

$$M - O - NO_2 \longrightarrow MO^{\cdot} + NO_2^{\cdot}$$

A similar mechanism was proposed for the reaction of anhydrous dinitratocopper (II) and diethyl ether[2]. This mechanism, of course ignores the fact that $NO_2^{\cdot}$ does not react with alkanes under these conditions. There is no reaction when a solution of dinitrato copper (II) in a solvent (e.g. ethyl acetate) was added to ether. But when dinitratocopper (II) was added to ether alone a reaction was observed. The solvents were thought to co-ordinate so strongly to copper that dissociation to radicals could not occur. Dissociation however was possible when no solvents were present and the reaction of the nitrato compound and ether was represented by Figure 1.3,

FIGURE 1.3



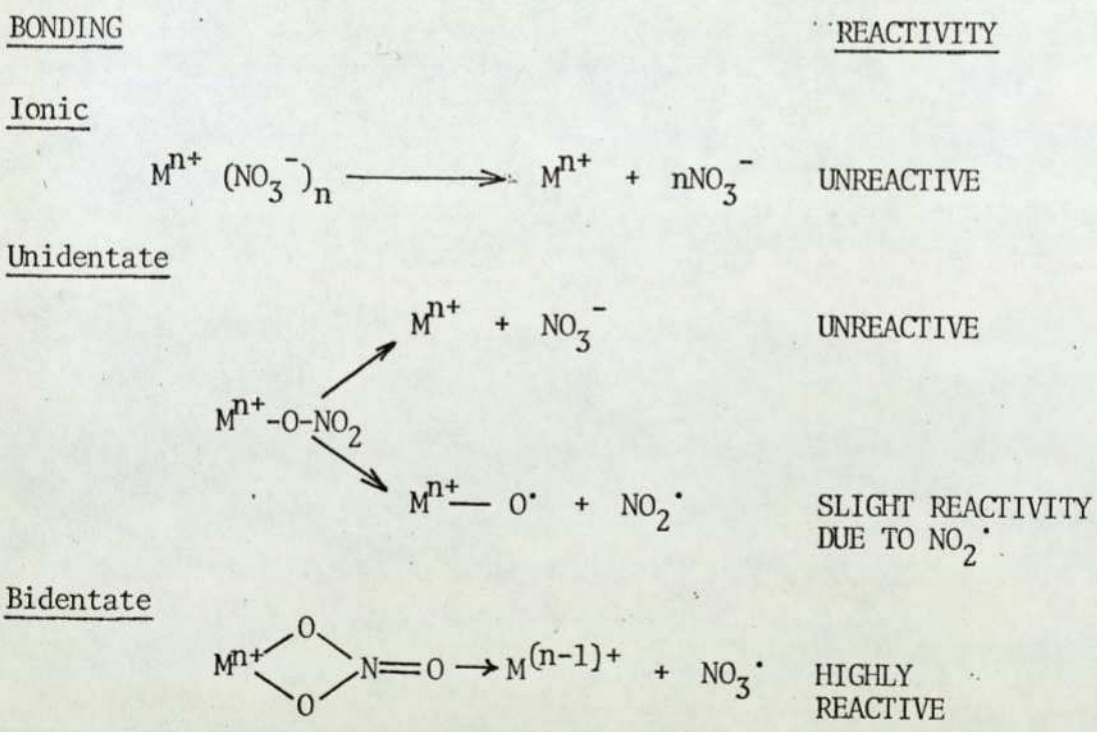
The anhydrous dinitratocopper (II) is regarded in this scheme as a low temperature source of $NO_2^{\cdot}$ radicals, but a similar mechanism based on a dissociation to $NO_3^{\cdot}$ radicals has also been suggested.[2]

The reactions with alkanes and ethers already described

however are not characteristic of all transition-metal nitrato compounds. For example, although tetranitratotitanium (IV) will explode or inflame with organic compounds such as ethers or aniline as well as nitrate aliphatic hydrocarbons, the dinitrato salts of manganese, nickel and zinc are inert.

The relationship between chemical reactivity and the nature of the metal-ligand bond was investigated by Addison[115]. He concluded thatchemical reactivity was dependent on the multiplicity of the metal-nitrate bond i.e. bidentate nitrate was more reactive than unidentate nitrate. It was also suggested by Addison that the species formed during a reaction were as follows, in Figure 1.4.

FIGURE 1.4



He therefore postulated that the species responsible for oxidation of organic compounds by anhydrous nitrato compounds

was the $NO_3^{\cdot}$ radical. It follows from his studies, that

1) The metal should have a lower valency state available if reactive.

11) Bidentate nitrates should be more reactive than unidentate nitrates, and change of bidentate to unidentate bonding should result in a loss of chemical reactivity.

The first of these predictions can be shown to be true. Copper (II) can be reduced to copper (I) very easily which could explain the reactivity towards ethers. Similarly the reductions of Ti (IV) to Ti (III) and Zr (IV) to Zr (III) are not difficult. In contrast nitrates of Co (II), Ni (II) and Zn (II) do not have a lower available valency state and are not reactive.

The change of reactivity associated with a change from bidentate to unidentate bonding can be illustrated by reference to tetranitratotin (IV)[108]. This contains four bidentate ligands but on formation of the pyridine adduct i.e. $Sn(NO_3)_4 . 2\ py$, all the nitrate groups are unidentate. A comparison of reactions of both tin (IV) nitrate and the adduct shows that the former rapidly reacts with hydrocarbons whereas the adduct is inert.

1.6.5 AROMATIC NITRATION BY METAL NITRATO COMPOUNDS

An early study of the aromatic nitration properties of covalent nitrates was performed by Menke[119]. He showed that iron, copper, nickel cobalt, aluminium, cerium and uranium nitrates could easily nitrate aniline and phenol whereas nitrates of the alkali or alkaline-earth metals failed to react. This work was confirmed by Bacharach[120] who further investigated reactions of anhydrous nitrates of the alkali metals and managed in the presence

of aluminium trichloride to obtain nitro-products from aromatic compounds[85]. In all these reactions, the anhydrous covalent nitrates were prepared in solution by addition of a hydrated nitrate to acetic anhydride.

A study of the correlation between the covalency of nitrato compounds and their efficiency as nitrating agents towards aromatic molecules was attempted by Davey and Gwilt[121]. Using the hydrated metal nitrates dissolved in acetic acid, the efficiency of nitration of benzylidene diacetate was observed. The yields of the p-nitro derivative obtained were reported to change as follows,

$$Cu > Zn > Fe > Ni > Mg > Co$$

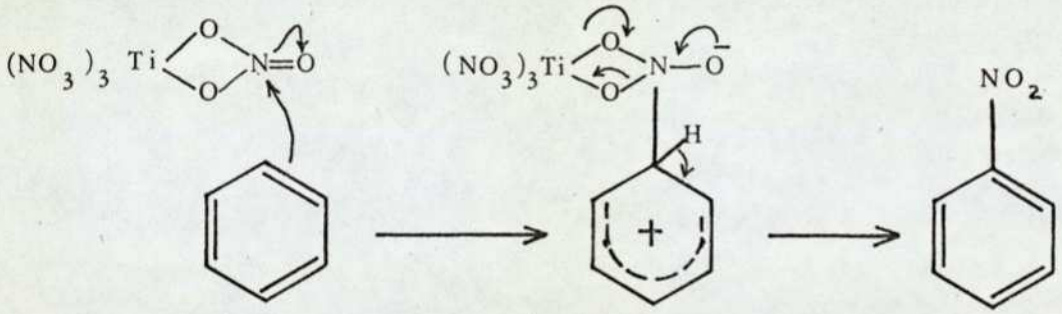
The efficiency of the nitrato-compound of copper far exceeded that of the other nitrates tested.

Reactions of simple aromatic compounds such as benzene and toluene[122] with transition-metal nitrato compounds have since been reported only briefly and it was the object of the present work to investigate such reactions extensively. Indeed the reactions reported with aliphatic compounds and oxygen-containing molecules suggested a special mechanism of nitration might well be involved. The apparent speed of reaction in the absence of solvent suggested that reactions should be studied in dilute solutions and this was also essential for any meaningful comparisons with other nitrating agents to be made.

As this work was nearing completion a communication by Amos and his co-workers[123] reported some observations on the

nitration of benzene, nitrobenzene, chlorobenzene and toluene with tetranitratotitanium (IV) in the absence of any solvent. The products obtained are shown in Table 1.4

It was also shown that,under these conditions, one molecule of tetranitratotitanium (IV) carries out two nitrations of benzene with 82% efficiency. The similarity of the isomer proportions obtained to those observed under mixed acid nitrations was mentioned, and it was noted that the reaction seemed too selective for a radical mechanism to be operating. The following mechanism was proposed,



The authors at this point reached two conclusions which require comment. They tentatively proposed by analogy, that in the mixed acid system the species 'SO_2 $(NO_3)_2$' may be responsible for the nitration of simple aromatic compounds. However the operation of the nitronium ion as the effective electrophile in this medium is surely beyond reasonable doubt. Thus any similarities between the results from tetranitratotitanium (IV) nitration and those for mixed acid systems could be more simply interpreted in terms of nitronium ion involvement in the former

TABLE 1.4

NITRATION OF AROMATIC COMPOUNDS BY TETRANITRATOTITANIUM (IV) IN THE ABSENCE OF SOLVENT

Aromatic substrate	Product	Isomers obtained
Benzene	Nitrobenzene	-
Toluene	Nitrotoluenes	o- = 48% m- = 5% p- = 47%
Nitrobenzene	Dinitrobenzenes	o- = 8% m- = 92% p- = -
Chlorobenzenes	Nitrochloro-benzenes	o- = 32% m- = - p- = 68%

system also.

Their arguments against the operation of the nitronium ion were that, in the media used, the dielectric constants were so low that spontaneous release of the electrophile from tetranitratotitanium (IV) would be unlikely. Also there was the absence of any bands in the infra-red or Raman spectra of solutions of tetranitratotitanium (IV) in carbon tetrachloride[124] characteristic of the nitronium ion. However, the nitronium ion need not be present in detectable quantities to be effective and it can be the reactive species for nitration in carbon tetrachloride[34]. It is significant in this work however that the values reported for the nitration of toluene by tetranitratotitanium (IV) lie well outside the narrow range of values known for various nitrations over a wide range of conditions involving the nitronium ion[32].

The second point which they report is that approximately two moles of the aromatic compound are nitrated by each mole of tetranitratotitanium (IV). It must follow therefore that two stages of nitration are involved and that unless a common intermediate is effective, the isomer ratios reported are an average value of those caused by two different nitrating species. The mechanism proposed by the authors involves an electrophilic attack by a species less reactive[125] and hence more selective than the nitronium ion. If proton loss from the Wheland intermediate is fast then intramolecular selectivities different from those found should have been observed whether or not the mechanism is intended to apply for both of the nitrating species

that stoicheiometric results would indicate are effective.

A further clarification of some of the points raised in this paper was also attempted in the present work.

1.7 NITRATION OF HETEROCYCLIC NITROGEN COMPOUNDS

1.7.1 PYRIDINE

The pyridine nucleus has proved to be very resistant to nitration. Although pyridine itself was isolated in 1849, it was not until 1912 that the nitration of pyridine was first successfully performed by Friedl[126] using solid potassium nitrate and fuming sulphuric acid. Although his conditions were vigorous, only a 15% yield of 3-nitro-pyridine was obtained. Friedl[127] later improved his method, and using potassium nitrate in fuming nitric acid added to pyridine in sulphuric acid, obtained 3-nitropyridine with a slightly improved yield.

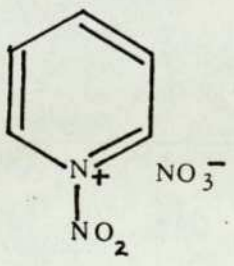
Both Murmann[128] and Kirpal and Reiter[129] repeated the work of Friedl. The yields they obtained were very low but they discovered that the reactions were catalysed by iron and with this knowledge, managed to obtain yields of 22% of 3-nitropyridine. A very careful investigation of this reaction however by Den Hertog and Overhoff[130] failed to obtain the high yields already mentioned. They showed that a mixture of nitropyridines was obtained during the reaction, the isomer proportions of which changed when the reaction temperature was increased. The percentage yields of 3-nitro and 2-nitropyridine obtained at 300°C were 4.5% and 0.5% whereas at 450°C they were 0% and 2.5% respectively. It was thought that the mechanism of substitution changed from

electrophilic to free radical attack as the temperature increased.

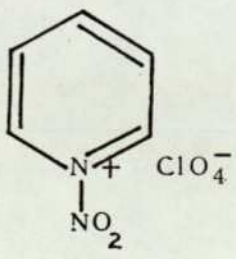
Electrophilic attack would be expected to occur m- to the electron deficient nitrogen atom. The observed deactivation of the 3-position compared with benzene is very much greater than would have been expected from the relative electronegativities of carbon and nitrogen. This is due to the fact that most of these electrophilic reactions take place under acid conditions and the entity then being substituted is probably the pyridinium ion. This will be much more deactivated than the neutral molecule.

A vapour phase nitration of pyridine using dinitrogen tetroxide was first performed by Schorygin and Topchiev[131]. Between 115-120°C, they obtained a yield of 5-10% 3-nitropyridine. Sisler and his co-workers[132] showed that the adduct, $N_2O_4 \cdot 2\ C_5H_5N$ was produced at low temperatures in such reactions.

Very little work has been reported on the nitration of pyridine in aprotic solvents. Foster[133] studied the reactions of dinitrogen pentoxide and some nitronium salts with pyridine in carbon tetrachloride and nitromethane. He reported the absence of any nitropyridines but the formation of some N-nitropyridinium salts e.g.



and



A similar result was reported by Jones and Jones[48a] who studied the reaction of pyridine and nitronium salts in sulpholan. Using various spectroscopic techniques they showed the formation of N-nitropyridinium fluoroborate, and the absence of any nitro pyridines. Olah and his co-workers[48b] extended these studies and investigated reactions in various solvents. Substitution was found to be exclusively at the N position and no evidence for any N→C nitro group migration was obtained.

Reactions of metal nitrates and pyridine have not been extensively studied. However, Dewar and Maitlis[134] observed a reaction between pyridine and lithium nitrate in the presence of some copper nitrate using acetic anhydride as solvent. At 100°C, a 1% yield of 3-nitro pyridine was obtained.

1.7.2 QUINOLINE

Nitration of quinoline is governed by,

a) the relative ease of substitution of the different positions in the corresponding hydrocarbon, and

b) the effect of the nitrogen atom.

Effects due to (a) should favour substitution as in naphthalene in the α-positions whereas effects due to (b) should strongly deactivate the pyridine ring favouring attack on the benzenoid ring. One would expect therefore nitration of quinoline to occur at the 5- and 8- positions.

Many workers have studied the nitration of quinoline but much of the early work employed very drastic conditions. These included nitric acid in oleum or hot concentrated sulphuric acid. However good yields of mononitroquinolines were obtained and

consisted of the 5- and 8- isomers in roughly equal amounts[135]. Dewar and Maitlis [136] reinvestigated the reaction products of nitration of quinoline and confirmed that only 5- and 8- nitro-quinolines had been prepared. Isomer proportions were reported for reaction at 0°C; 5- nitroquinoline = 52.3%, 8-nitro-quinoline = 47.7%. Less than 1% of the 3-, 6- and 7-nitroquinolines were reported. The most recent and very accurate determination of isomer proportions was performed by Schofield and his co-workers[137]. Using an isotopic dilution technique, they determined the product ratios for reaction of quinoline by nitric acid in 80.05% sulphuric acid at 25°C and found,

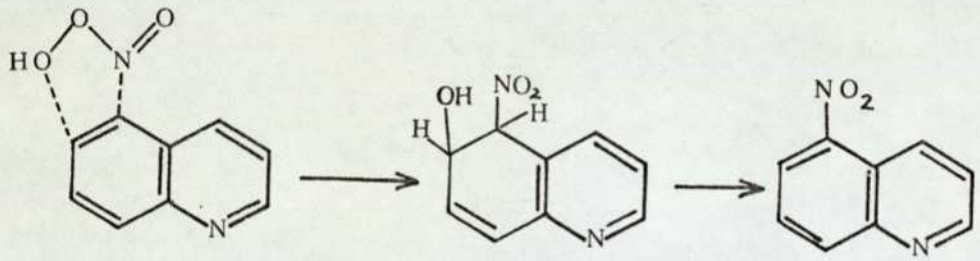
3 - nitroquinoline	=	0.0014	%
5 - "	=	53.3	%
6 - "	=	1.71	%
7 - "	=	0.015	%
8 - "	=	44.98	%

A study of the kinetics of nitration of quinoline in sulphuric acid has shown that the nitronium ion reacts with a protonated quinoline molecule, and that the proton is still present in the transition state [138]. Schofield and his co-workers[139] confirmed these observations for both quinoline and isoquinoline.

Nitrations of quinoline have been reported however where 5- and 8- nitroquinolines are not the major products. Bacharach, Haut and Caroline[140] reported that on heating quinoline with lithium nitrate, copper nitrate and acetic anhydride gave

7-nitroquinoline. Schorygin and Topchiev[141] obtained the same product and some 5,7- dinitroquinoline when quinoline was nitrated with dinitrogen tetroxide.

Laville and Waters[142] studied the reactions of the free radical reagent pernitrous acid with quinoline and obtained 6- and 7- nitroquinolines in roughly equal amounts. Dewar and Maitlis[143] reinvestigated this work and obtained 5 -, 6 -, 7- and 8- nitroquinolines. They suggested that pernitrous acid was the attacking entity undergoing a selective reaction with the 5:6- and 7:8- bonds i.e.,



(I)

The variety of elimination reactions which (I) should undergo was used to explain the copious formation of by-products.

Dewar and Maitlis[143] also studied some nitration reactions of quinoline when a mixture of metal nitrates, nitric acid or nitrogen dioxide were used as nitrating agents. The most surprising feature of these experiments was the isolation of 3- nitroquinoline as the major mononitration product. The results are summarised in Table 1.5

In all cases the yield of mono-nitro-quinolines was very low and up to 70% of unreacted quinoline was recovered.

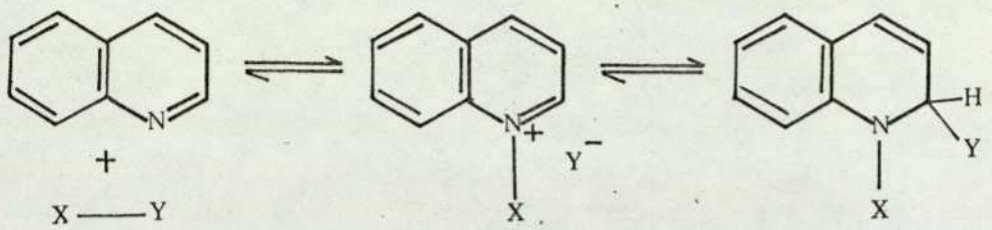
A mechanism for the formation of 3-nitroquinoline and only 6- and 8- nitroquinolines as side products was suggested

TABLE 1.5

NITRATION PRODUCTS OF QUINOLINE

Nitrating reagent	Nitroquinolines formed		
$Li(NO_3$ - Cu $(NO_3)_2$ - Ac_2O (100°C)	3	6	8
HNO_3 - Ac_2O (100°C)	3	6	8
HNO_3 - Ac_2O (20°C)	3		
N_2O_4 (100°C)	3	6	8
N_2O_4 - Ac_2O (20°C)	3		
HNO_3 - $(F_3C$ - $CO)_2O$ (20°C)		6	8

involving an addition elimination sequence;



(I)

The adduct (I) would be expected to be nitrated o - and p - to the nitrogen atom (i.e. positions 6- and 8-) while addition of oxides of nitrogen to the styrene-like double bond of (I) followed by elimination would give the 3-nitroisomer. The product of 3-nitroquinoline has also been considered by Ridd[144] who suggested that it arises from the nitration of quinoline as the free base.

The reaction of quinoline and dinitrogen pentoxide was studied by Foster [133]. Using solutions of the reactants in carbon tetrachloride, he observed the formation of N-nitroquinolinium nitrate, but no nitration of the benzenoid ring had occurred.

1.7.3 ISOQUINOLINE

The nitration of isoquinoline has not been extensively studied. Much of the earlier work on this reaction was performed with mixed acids[145], and in every case both 5- and 8- nitroisoquinolines were observed. Although the 5-nitroproduct was found to be the dominant isomer, the products were not isolated and the relative proportions not determined.

Dewar and Maitlis performed the first quantitative studies of isoquinoline nitrations in sulphuric acid[136]. They determined isomer proportions and also compared the reactivities of quinoline and isoquinoline by competition experiemnts. The isomer data they reported are shown below,

Reaction Temp	5- nitro	8- nitro
0°C	90.4%	9.6%
100°C	84.8%	15.2%

In all their experiments, only the 5- and 8- nitro- products were observed. The relative reactivities were shown to be,

Quinoline: Isoquinoline = 1 : 24.5

The isomer proportions arising from the nitration of isoquinoline show how the hetero group at a β position selectively deactivates the 8- position of the parent naphthalene skeleton.

Ochiai and his co-workers[146] obtained 5-nitroisoquinoline from reactions of potassium nitrate in sulphuric acid solutions.

SECTION II

INTRODUCTION TO SECTION II

CHAPTER 2

This chapter describes in detail the results obtained from kinetic, product and competitive rate measurements of the reactions of tetranitratotitanium (IV) in carbon tetrachloride with a series of aromatic compounds. The inter and intramolecular selectivities of this reagent are discussed, and a possible mechanism of nitration suggested.

CHAPTER 3

This chapter describes how compounds of a wide range of aromatic reactivity are nitrated by the nitrato complexes of zirconium (IV) and iron (III). Product isomer ratios are reported. In addition, studies of the nitration of pyridine, quinoline and isoquinoline with these reagents and with tetranitratotitanium (IV) are reported, and conditions for the formation of reasonable quantities of nitroproducts are established.

CHAPTER 4

A study of the nitration of a series of aromatic compounds by dinitrogen pentoxide in carbon tetrachloride is described in this chapter. Conditions where both the nitronium ion and the dinitrogen pentoxide molecule had previously been thought to be effective were studied. Using competition and product measurements, the inter and intramolecular selectivities

of the reagent are established, and the nature of the effective species over the range of conditions employed is discussed.

CHAPTER 5

A study of the nitration of a series of aromatic compounds by dinitrogen tetroxide in carbon tetrachloride is described. The results from a series of competition, kinetic and product measurements are used to describe the inter and intramolecular selectivities of the reagent, and the nature of the effective species is discussed.

CHAPTER 2

THE NITRATION OF AROMATIC COMPOUNDS BY TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE SOLUTION

2.1 RESULTS

Tetranitratotitanium (IV) was chosen for initial experimental work because it was known to be soluble in carbon tetrachloride to the extent of about 0.1 mole l^{-1} at 20°C. This was a factor which it was thought would enable meaningful mechanistic studies of aromatic nitration to be made under homogeneous conditions. The stability of these solutions was determined by infra-red spectroscopy, and it was found that the spectra remained constant for several weeks. Results obtained from reactions with certain aromatic molecules will now be described.

2.1.1 BENZENE

The addition of benzene to solutions of tetranitratotitanium (IV) was found to lead to the formation of a small amount of a precipitate and slow conversion of the benzene into nitrobenzene accompanied by further precipitation. The infra-red spectra of solutions on mixing and during reaction showed only changes due to the addition of benzene and its conversion into nitrobenzene. The course of some typical reactions is shown in Figures 2.1.1 and 2.1.2, obtained by quantitative gas-liquid chromatography.

The rate of reaction shows an initial increase with time which is general for these reactions. The yields of nitrobenzene obtained after more than five half lives, based on the assumption of a reaction between one mole of benzene and one mole of tetranitratotitanium (IV), were between 86 and 98%.

It is clear, however, that simple kinetic behaviour cannot be expected from the reaction which involves a heterogeneous

FIGURE 2.1.1

NITRATION OF BENZENE BY TETRANITRATOTITANIUM (IV)

IN CARBON TETRACHLORIDE AT 20°C

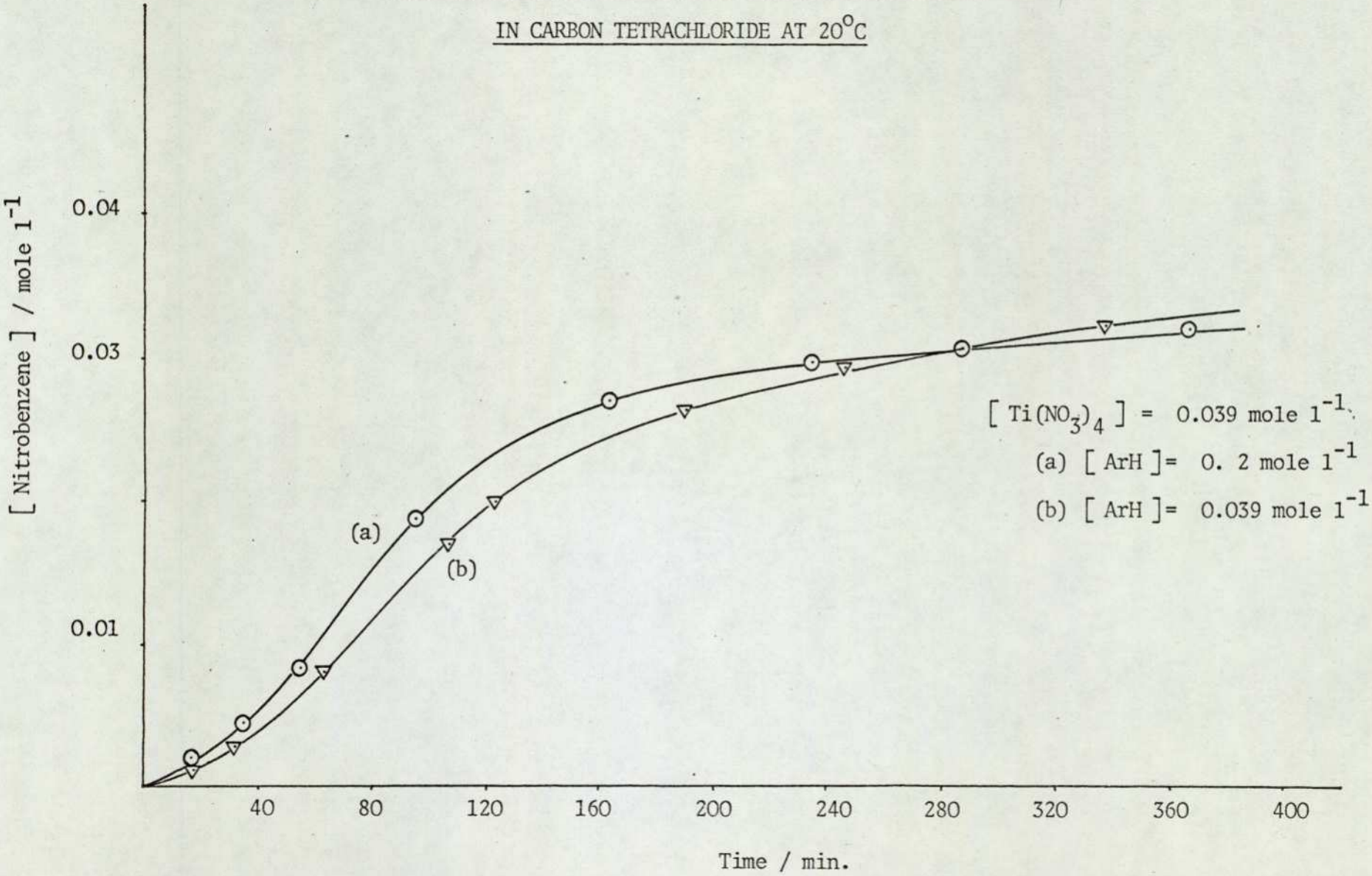
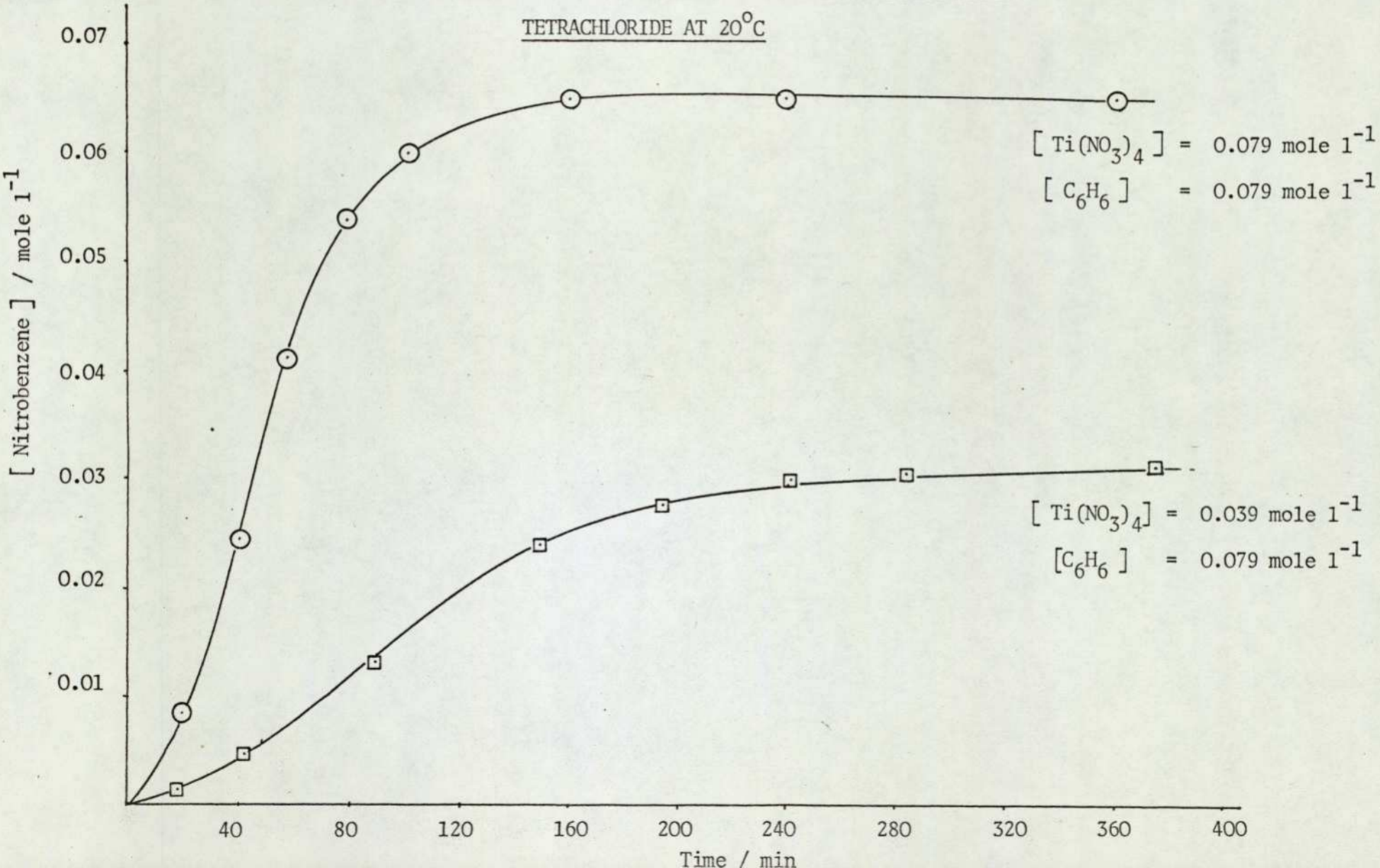


FIGURE 2.1.2

NITRATION OF BENZENE BY TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE AT 20°C



system. Other solvents were investigated including nitromethane, and chloroform, but it was not possible to find a solvent which was unreactive to tetranitratotitanium (IV) and in which no precipitate was formed. It was found however, that the results obtained were generally reproducible and so two parameters were chosen to describe the results approximately. These were the initial rate of production of nitro compounds measured over the first 5-7% of the reaction, and the half life for the reaction.

The data obtained from experiments performed with benzene are shown in Table 2.1.

The results shown in the table illustrate the reproducibility achieved by the method employed. As precise kinetic study of the reaction was not possible, broad trends in the changes in reaction rate with reactant concentrations were observed. In addition, any deductions on the effects of additives and other changes were made from runs carried out at the same time and under identical conditions. Such runs are bracketted together in the table.

It can be seen from Table 2.1 that the initial rate of reaction increased with the initial concentration of tetranitratotitanium (IV). By contrast the initial benzene concentration had little effect on the initial rate of nitration.

Up to approximately 5% of m - dinitrobenzene could be detected from some reactions. Its presence became apparent when reactions under equimolar conditions were left for over ten half lives, or in reactions where the tetranitratotitanium (IV) was in a large excess. It was also noted when attempts were

TABLE 2.1

REACTION WITH BENZENE AT 20°C

Run No	[Benzene] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	Initial Rate 10^{-6} mole $l^{-1}s^{-1}$	Half Life /10^3s.	% Yield
37	7.9 [a]	7.9	5.6	2.8	72
34	7.9	7.9	5.9	2.9	86
38	7.9	7.9	6.0	2.4	93
187	7.9 [b]	7.9	3.9	3.2	95
188	9.9 [c]	7.9	5.8	3.3	98
80	3.6	3.6	0.73	19.0	87
81	3.6 [b]	3.6	0.97	12.0	53
66	2.2 [e]	2.3	0.72	17.0	77
67	2.2	2.3	0.53	17.0	97
34	7.9	7.9	6.0	2.9	86
35	7.9	3.9	1.2	7.6	95
36	7.9	0.79	0.14	28.0	98
43	20	3.9	1.2	16.0	98
35	7.9	3.9	1.2	7.6	95
44	3.9	3.9	2.1	6.4	88
45	2.5	3.9	3.2	2.9	90
210	3.4	3.4	3.5	5.8	88
211	3.4f	3.4	3.5	6.0	99

a In the presence of Urea ($\sim 6 \times 10^{-3}$ mole l^{-1})

b $[H_2O] = 8 \times 10^{-3}$ mole l^{-1}

c $[H_2O] = 2 \times 10^{-4}$ mole l^{-1}

d In the presence of $Et_4N^+ NO_3^-$ ($\sim 4 \times 10^{-3}$ mole l^{-1})

e Hexadeuteriobenzene

f Rapidly stirred during entire reaction.

made to analyse the solid precipitate as described later.

There was also no change detected in the rate of reaction with benzene when the solution was rapidly stirred during the reaction. Similarly the presence of urea or tetraethylammonium nitrate at the maximum possible concentrations had no effect on the rates of nitration. The result from the nitration of hexadeuteriobenzene showed that there is no primary kinetic isotope effect on the rate determining step of the reaction.

Owing to the very hygroscopic nature of the anhydrous nitrato compounds, the effect of water in the carbon tetrachloride solvent was investigated. However, from the data quoted in Table 2.1, the presence of dissolved water did not have a detectable effect on the rate of reaction.

Accurate characterisation of the precipitate was made difficult because it was found to contain, after filtration under anhydrous conditions, 10-25% by weight of nitro compounds depending on the initial concentrations. The addition of water removed the organic compounds but it would be expected to alter the nature of the solid also. Therefore solids produced from reactions of a range of initial concentrations were separated by filtration under anhydrous conditions after various times during the reaction, and the percentages of titanium and nitrate group present were obtained. From this information, a NO_3: Ti ratio was obtained as shown in Table 2.2.

From runs 200-203 an average NO_3: Ti ratio of 2.7 ± 0.4 was obtained. Further analysis of the solid was attempted by

TABLE 2.2

ANALYSIS OF PRECIPITATED SOLID

Run No.	$[Ti(NO_3)_4]$ /10^{-2}mole l^{-1}	$[C_6H_6]$ /10^{-2}mole l^{-1}	$[C_6H_5NO_2]$ Found on solid /10^{-2}mole l^{-1}	% Ti	% NO_3	NO_3:Ti Ratio
151[a]	3.98	3.98	-	21.3	45.0	1.6
200[b]	8.70	8.70	0.08	20.1	65.0	2.5
201[b]	4.5	4.5	0.2	21.4	68.8	2.5
202[b]	8.3	90.0	0.36	17.3	69.6	3.1
203[c]	8.6	90.0	0.50	15.1	50.0	2.6

[a] Solid removed after 5 days reaction.

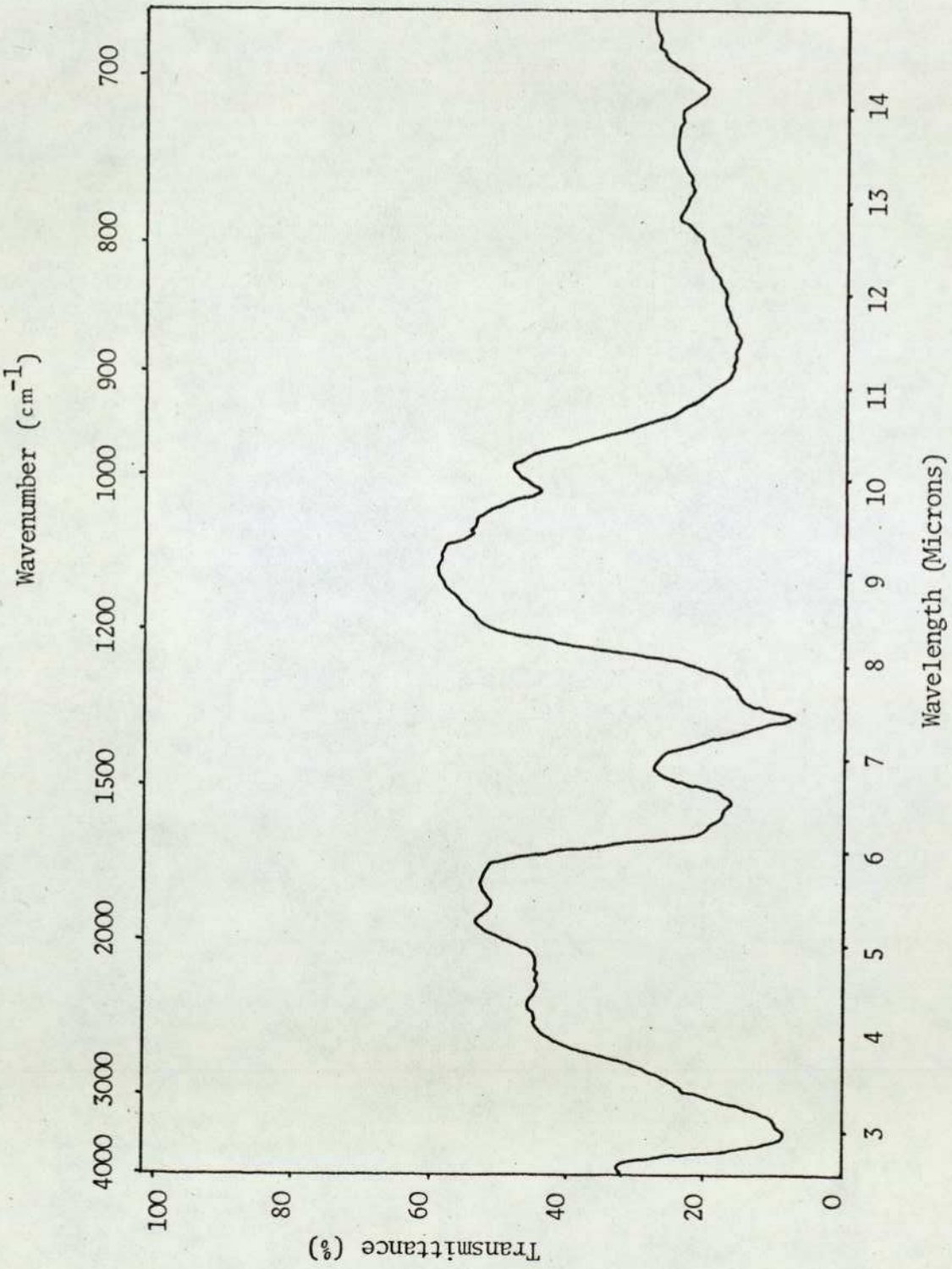
[b] Solid removed after 6 hours reaction.

[c] Solid removed after 2 days reaction.

infra-red spectroscopy, and a spectrum obtained from a typical residue is shown in Figure 2.2.

Very broad bands are observed in all of the solid spectra obtained. Water peaks at 3400, 2100 and in the region 1000-800 cm^{-1} were noticed, mainly due to the extremely hygroscopic nature of the solids. Bands characteristic of the tetranitratotitanium (IV) structure in the regions 1600 cm^{-1} and 1200 cm^{-1} were noticed, but it was not possible to determine any change in the nature of the covalent nitrato bonding which may have occurred during the reaction.

Figure 2.2. INFRA-RED SPECTRUM OF PRECIPITATED SOLID FORMED IN REACTION OF BENZENE AND TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE



2.1.2 TOLUENE

Most of the reaction characteristics observed in the reaction with toluene were found to be very similar to those of the benzene reaction. Figs. 2.3.1, 2.3.2 show the course of some typical reactions. Figure 2.4 shows a comparison of the toluene reaction with that of benzene under identical conditions.

Further similarities can be observed by a comparison of some toluene reaction rate data as shown in Table 2.3. with those obtained for benzene in Table 2.1.

The data in Table 2.3 compared with those in Table 2.1 show that toluene reacted at a rate which was related to that of benzene under similar conditions by a factor of between one and three. It is also clear in Table 2.3 that the initial rate of reaction once again fell with decreasing concentration of tetranitratotitanium (IV), and that it was approximately independent of the concentration of toluene.

Once again the addition of both urea and tetraethylammonium nitrate at the maximum soluble concentrations in carbon tetrachloride, had no effect on the reaction rate. In addition, the reaction was not found to be catalysed or initiated by light.

The isomer distribution of mono-nitro toluenes produced in these reactions is shown in Table 2.4. The proportion of the m- isomer was always very low (0.5 ± 0.4%). The average o : p ratio obtained from the values quoted in Table 2.4 was found to be 0.72 ± 0.18, but there were apparently random variations over this range which lay well

FIGURE 2.3.1

NITRATION OF TOLUENE BY TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE AT 20°C

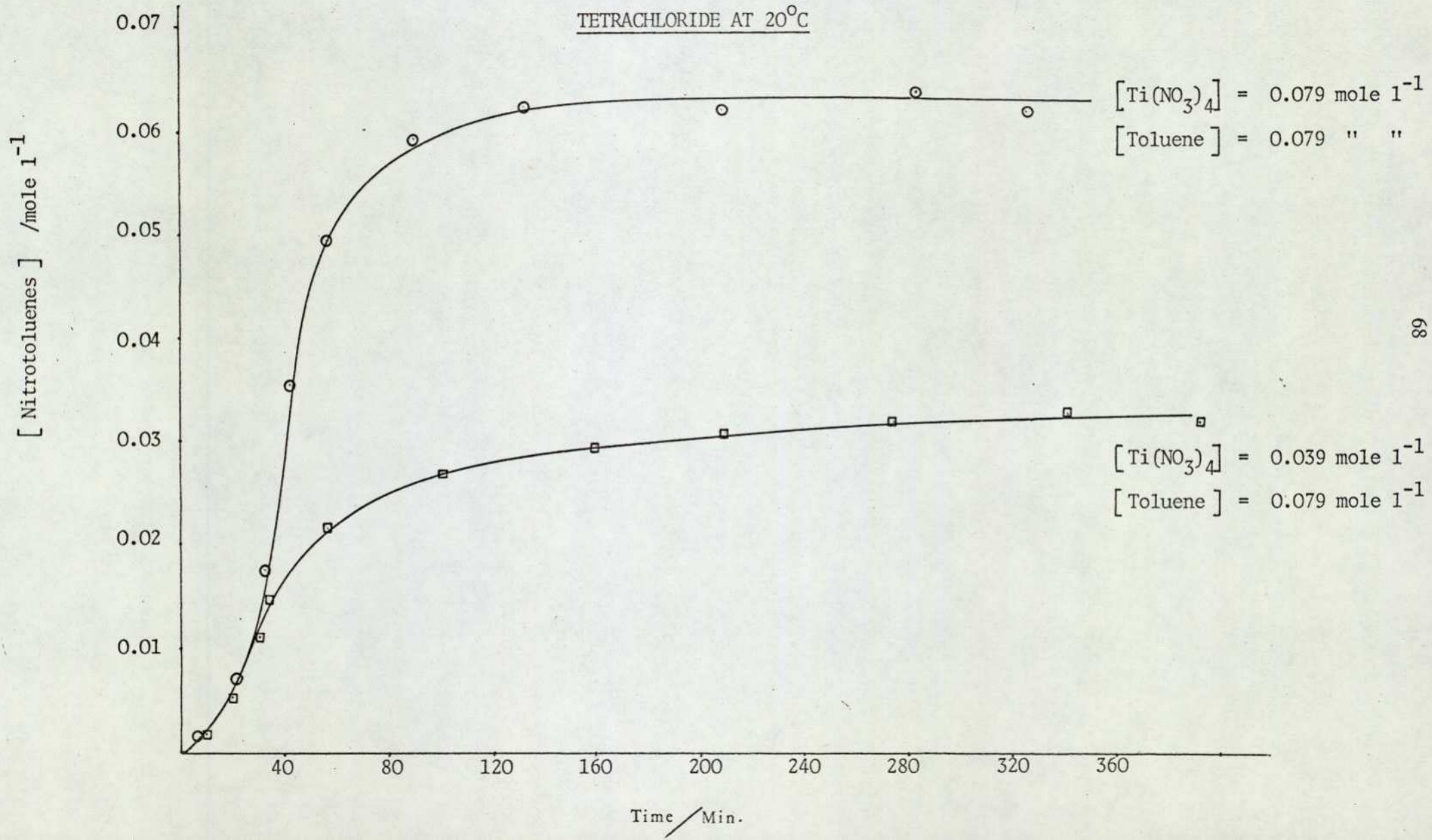


FIGURE 2.3.2

NITRATION OF TOLUENE BY TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE AT 20°C

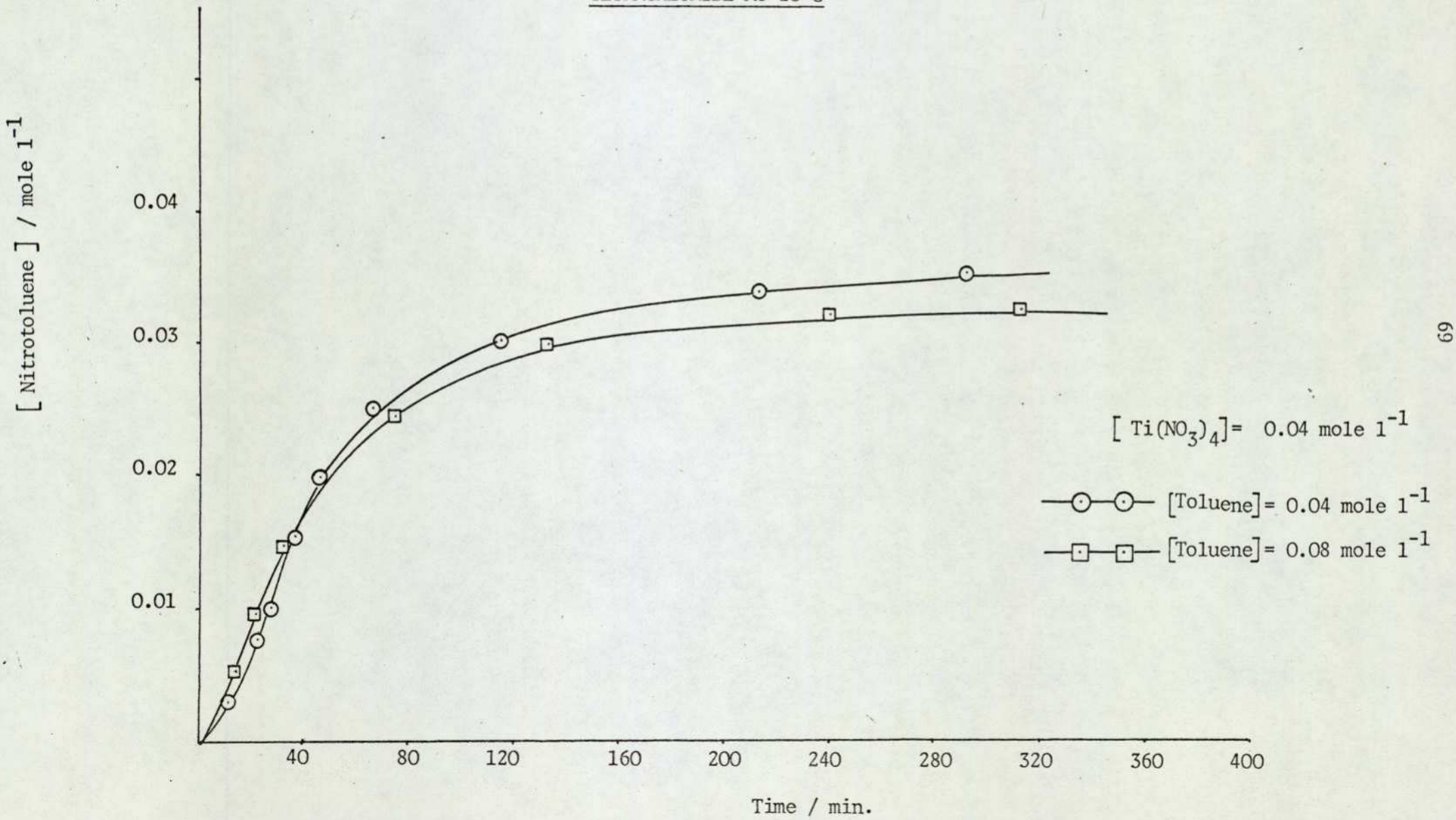


FIGURE 2.4: NITRATIONS OF BENZENE AND TOLUENE BY TETRANITRATOTITANIUM (IV) IN CARBON TETRACHLORIDE AT 20°C

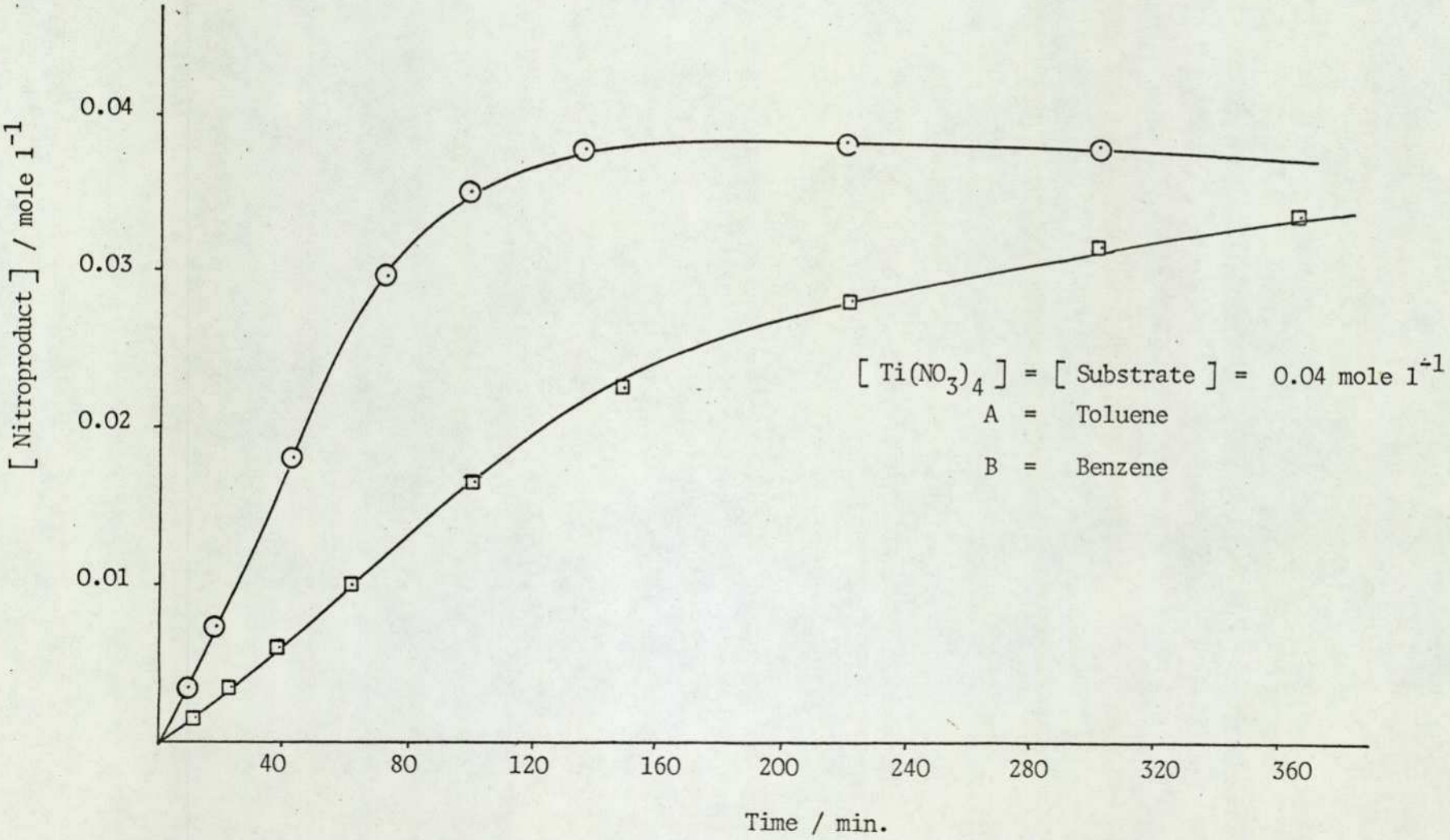


TABLE 2.3

REACTION WITH TOLUENE AT 20°C (±1°C)

Run No.	[Toluene] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	Initial Rate /10^{-6} mole $l^{-1}s^{-1}$	Half Life /10^3 s	% Yield of mononitro products
39	7.9	7.9	5.0	1.8	90
40	7.9 [a]	7.9	4.0	2.2	72
82	4.7	3.4	2.4	5.3	89
83	4.7 [b]	3.4	3.5	5.5	83
10	4.1	4.5	12.0	2.3	94
10X	4.1 [c]	4.5	12.0	2.3	91
10H	45.0	3.5	12.0	2.3	94
39	7.9	7.9	5.0	1.8	90
41	7.9	3.9	2.5	2.6	95
42	7.9	0.79	0.4	7.0	95
41	7.9	3.9	2.5	2.6	95
47	3.9	3.9	4.7	2.8	98
48	1.9	3.9	2.5	3.2	99
10H	45.0	3.5	12.0	2.3	94

a In the presence of urea ($\sim 6 \times 10^{-3}$ mole l^{-1})

b In the presence of $Et_4N^+ NO_3^-$ ($\sim 4 \times 10^{-3}$ mole l^{-1})

c Reaction carried out in the absence of light.

TABLE 2.4

NITRATION PRODUCT ISOMER DISTRIBUTION - VARIATION WITH INITIAL CONCENTRATIONS

Run No.	[Toluene] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	Nitrotoluenes[abc] % o-	% p-
9	70.0	7.0	35	65
10	40.0	4.5	47	53
10X[d]	40.0	4.5	44	56
8	9.0	9.0	37	63
91	9.4	3.4	44	56
39	7.9	7.9	36	64
40[e]	7.9	7.9	44	56
41	7.9	3.9	44	56
42	7.9	0.79	46	54
12	6.9	6.9	36	64
82	4.7	3.4	39	61
83[f]	4.7	3.4	42	58
47	3.9	3.9	45	55
48	1.9	3.9	41	59
281[gh]	18	4.3	46	54

a all values ± 2%

b All yields of mononitrotoluenes 87 - 98%

c % m- = 0.5 ± 0.4% in all cases

a In the absence of light

e In the presence of Urea (≈ 6×10^{-3} mole l^{-1})

f In the presence of $Et_4 N^+NO_3^-$ (≈ 4×10^{-3} mole l^{-1})

g Analysis of complete product including any associated with the precipitated solid.

h % m- = 0.8 ± 0.1% in this case.

outside any experimental uncertainties.

A study was also made of the variation of isomer distribution during the course of a reaction and this is shown in Table 2.5. From this table it appears that the proportion of nitrotoluenes formed did not vary during the course of the reaction. It is also clear from this table that dinitration was not important and in fact in all the reactions of toluene quoted, less than 2% of dinitration was observed.

In one case in table 2.4 (i.e. Run 281), a reaction was allowed to go to completion before the entire product was treated with water and analysed. In so doing, any organic material associated with the solid would also have been analysed. However no change in the o : p ratio was apparent, and the percentage of m- nitro toluene was established as 0.8 ± 0.1% in this case.

2.1.3 OTHER AROMATIC COMPOUNDS

The rates of nitration and the product distributions observed in the reactions of several alkyl- and halogenated aromatic compounds with tetranitratotitanium (IV) were also investigated. Similarly nitrobenzene, anisole and biphenyl were studied but these will be considered separately.

Reactions of mesitylene, o- and m- xylenes, ethyl and tert-butyl benzenes, chloro-, bromo- and p-dichlorobenzenes were all studied under conditions where they could be compared both amongst themselves and also with benzene and toluene. The kinetic data are shown in Table 2.6.

A comparison of the results shown in Table 2.6 with those obtained for benzene and toluene in Tables 2.1, and 2.3

TABLE 2.5

PRODUCTS OF REACTION WITH TOLUENE -

VARIATION DURING A TYPICAL EXPERIMENT

RUN NO. 47

$[Ti(NO_3)_4]$ = 3.9×10^{-2} mole l^{-1}

[Toluene] = 3.9×10^{-2} mole l^{-1}

Temperature = $20^{o}C \pm 1^{o}C$

Time /10^3s.	% Nitrotoluenes [a] [b]		Yield %
	o-	p-	
0.6	47	53	7
1.5	47	53	21
2.8	47	53	50
4.0	47	53	66
6.1	48	52	89
9.3	47	53	98
12.0	44	56	98
19.0	45	55	98
72.0	45	55	98

[a] % m- = 0.5 ± 0.4 in all cases

[b] ± 2%

TABLE 2.6

RATES OF REACTION WITH AROMATIC COMPOUNDS

Run No.	Substrate	[Substrate] /10^{-2}mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2}mole l^{-1}	Initial Rate /10^{-6}mole $l^{-1}s^{-1}$	Half Life /10^{3}s	% Yield
50	Mesitylene	3.9	3.9	3.8	2.9	98
51	o-xylene	3.9	3.9	1.6	5.5	67
18	Ethylbenzene	35.0	3.5	4.6	2.9	91
17	Tert-butyl benzene	35.0	3.5	4.6	4.0	98
52	Chloro-benzene	3.9	3.9	0.12	17.0	94
22	Chloro-benzene	60.0	6.0	4.6	5.7	98
53	Para-dichloro benzene	3.9	3.9	0.12	18.0	87

Reactions all carried out at 20°C (±1°C)

shows that a factor of about 3 covers all these results under comparable conditions with the exceptions of chlorobenzene and p- dichlorobenzene. The initial rate here was an order of magnitude slower than that of benzene, and the plots analogous to figure 2.1 for these compounds show clearly larger initial curvature. This is illustrated by figure 2.5.

The products obtained in the reactions of the substrates already mentioned are reported in Table 2.7.

Other compounds which were studied included nitrobenzene, anisole, and biphenyl. These are considered separately from those compounds already mentioned because they gave results which seemingly did not accord with broad patterns already established. In particular, these compounds gave low and where studied variable yields of nitro compounds at complete reaction.

The results of rate studies of these compounds are shown in Table 2.8 and the nitro products obtained together with the yields observed in Table 2.9.

The differences in reaction rate with these substrates can be observed by comparison of Table 2.8 with previous data for aromatic substrates. Nitrobenzene is shown to react several times more slowly than benzene under similar conditions whereas anisole was found to react much more rapidly than any of the other compounds. These points can be emphasised by comparison of a plot of a typical reaction for anisole and nitrobenzene with one observed for toluene under similar conditions as shown in figure 2.6.

2.1.4. INTERMOLECULAR SELECTIVITY BY COMPETITION EXPERIMENTS

This work was conducted between pairs of aromatic compounds

FIGURE 2.5

NITRATION OF SOME AROMATIC COMPOUNDS BY TETRANITRATOTITANIUM (IV) AT 20°C

$[\ Ti(NO_3)_4\ ] = [\ \text{Substrate}\ ] = 0.04\ \text{mole}\ l^{-1}$

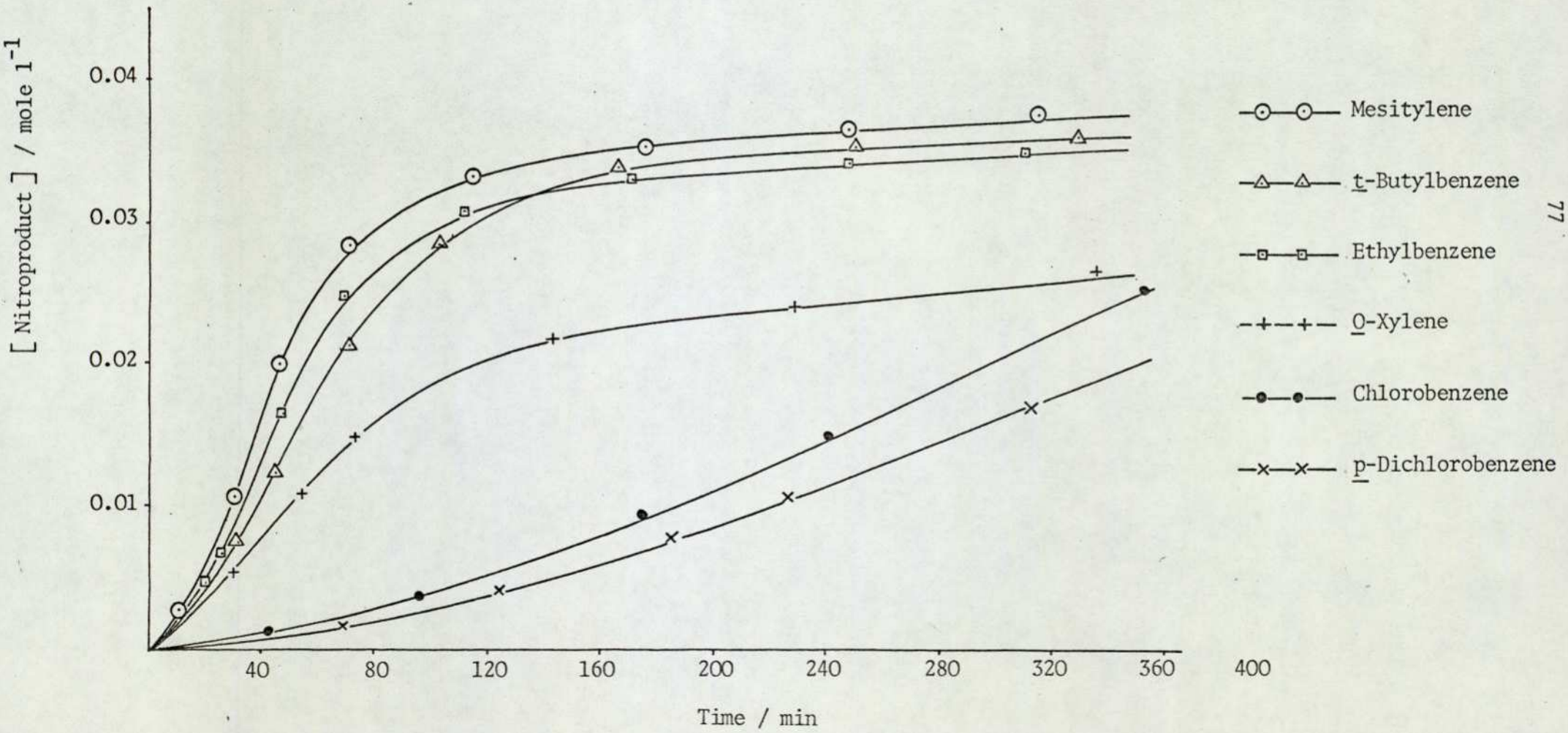


TABLE 2.7

PRODUCTS OF REACTIONS WITH AROMATIC COMPOUNDS

Substrate	[Substrate] /10^{-2}mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2}mole l^{-1}	Nitroproducts %			Yield %
			2-	3-	4-	
o-xylene	50.0	5.0	—	28.0	72.0	87
	3.9	3.9	—	27.0	73.0	67
m-xylene	90.0	9.0	12.0	—	88.0	*
Ethylbenzene	35.0	3.5	37.2	2.0	60.8	91
	45.0	4.5	34.0	2.2	63.8	89
t-butyl benzene	35.0	3.5	9.3	4.0	86.7	98
	90.0	9.0	7.4	4.1	88.5	*
Chlorobenzene	3.9	3.9	20.0	<0.5	80.0	94
	4.1	4.1	21.3	<0.5	78.7	*
	60.0	6.0	20.5	<0.5	79.5	*
	100.0	10.0	23.5	<0.5	76.5	*
Bromobenzene	36.0	3.6	23.5	d	76.5	90

[a] % m- = 0.5 ± 0.4%

* Not determined.

Reaction temperature = 20°C (±1°)

TABLE 2.8

REACTION RATES OF ANOMALOUS SUBSTRATES

Run No.	Substrate	[Substrate] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	initial rate /10^{-6} mole $l^{-1}s^{-1}$	half life /10^{3}s	yield %
20	nitrobenzene	31.7	3.0	0.04	17.0	10
55	"	3.9	3.9	1.3	12.0	20
19	"	4.0	4.0	0.2	22.0	20
21	"	0.16	3.1	0.007	16.0	14
25	anisole	64.0	6.4	33.0	2.4	78
24	"	4.0	4.0	52.0	0.8	28
56	"	3.9	3.9	19.0	0.7	48
15	biphenyl	6.7	6.7	11.9	1.5	50

Reaction temperature = $20^{o}C$ ($\pm 1^{o}$)

TABLE 2.9

ISOMER DISTRIBUTIONS OBTAINED FROM ANOMALOUS SUBSTRATES

Substrate	[Substrate] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	nitroproducts 2-	3-	4-	Yield %
Nitrobenzene	3.9	3.9	4	96	<0.1	20
	31.7	3.0	3	97	-	10
Anisole	63.5	6.3	41	b	59	78
	36.0	3.6	30	b	70	*
	20.4	4.1	32	b	68	*
	4.1	4.1	41	b	59	*
	4.0	4.0	41	b	59	28
	3.9	3.9	45	b	55	48
	2.7	2.7	41	b	59	30
	[a]2.7	2.7	44	b	56	33
	0.8	4.1	64	b	36	*
Biphenyl	6.7	6.7	48	<0.1	52	50
	30.0	3.0	41	<0.1	59	*

[a] In presence of Urea ($\sim 6 \times 10^{-3}$ mole l^{-1}).

[b] m- isomer would not be detected.

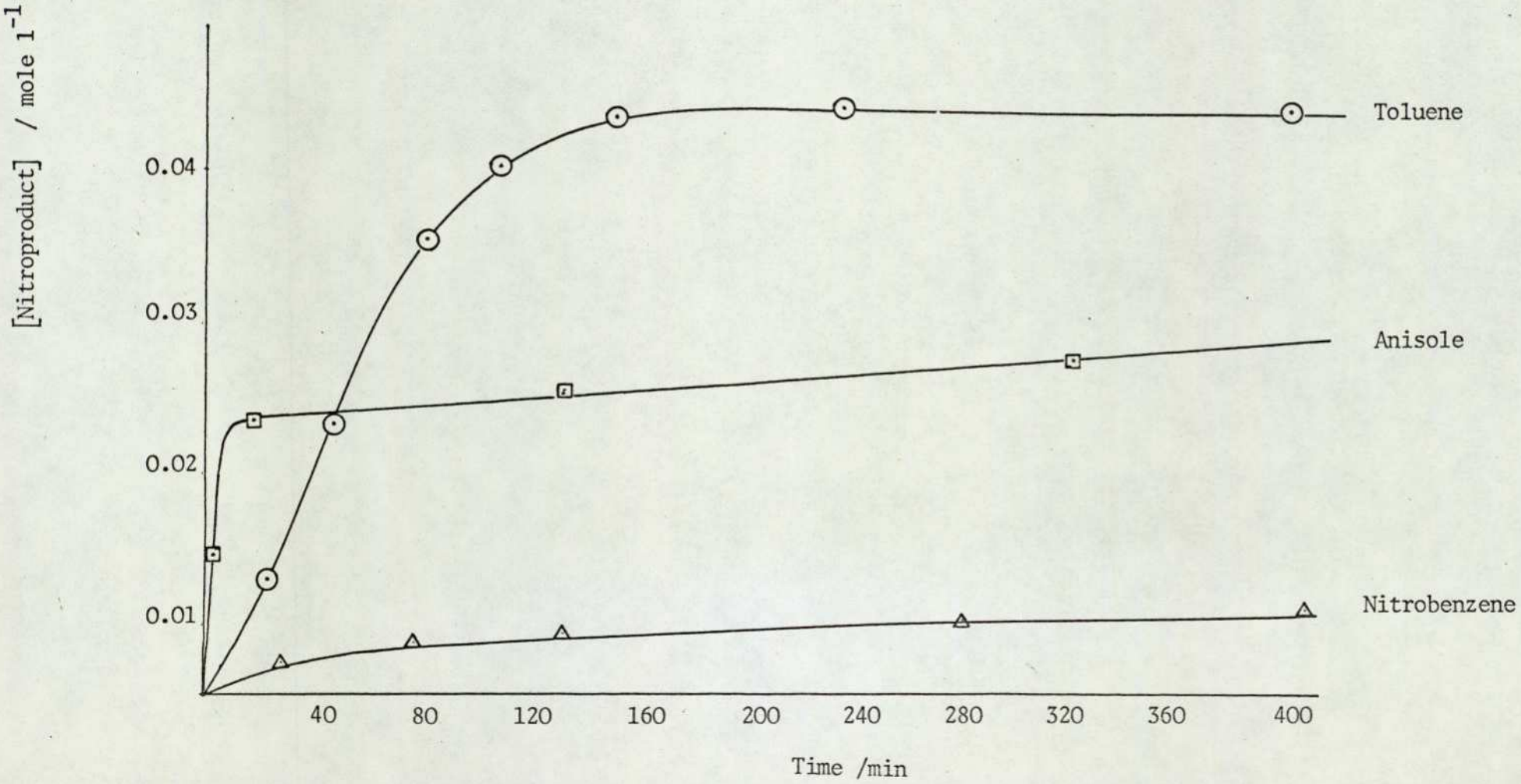
* not determined.

Reaction temperature = 20°C (± 1°)

FIGURE 2.6

NITRATION OF SOME ANOMALOUS SUBSTRATES BY TETRANITRATOTITANIUM (IV) AT 20°C

$[Ti(NO_3)_4]$ = [substrate] = 0.04 mole l^{-1}



selected from those mentioned previously to establish a scale of reactivity relative to benzene. In each case, equimolar mixtures of the two substrates in usually at least a ten fold molar excess were added to a solution of tetranitratotitanium (IV) in carbon tetrachloride, and the composition of the mixture of nitro compounds was determined. The detailed results are shown in Table 2.10.

In several cases, the ratio of nitroproducts of the competing substrates was followed during the course of the reaction. These results can be seen in Table 2.11. This shows that the nitroproduct ratio does not show significant variation during the reaction. In all competition experiments performed, the figures quoted as the nitroproduct ratio of the two competing substrates were determined after ten half lives.

As can be seen from Table 2.10, the amount of water dissolved in the solvent used did not affect the relative reactivity of the substrates. Also it is apparent that no primary kinetic isotope effect was found when hexadeuteriobenzene was used. Using the data obtained from Table 2.10, it was then possible to construct a scale of reactivity relative to benzene and this is shown in Table 2.12.

2.1.5 REACTION OF TETRANITRATOTITANIUM (IV) WITH n-PENTANE

A brief investigation into the reaction of the nitro compound with n-pentane was carried out. It was found that although in the absence of solvents many nitration and oxidation products were noticed, when a solution of tetranitratotitanium (IV) in carbon tetrachloride was used, very small yields of

TABLE 2.10

COMPETITION OF AROMATIC COMPOUNDS FOR TETRANITRATO TITANIUM (IV)

Run No.	Substrate A	Substrate B	[A] = [B] /mole l^{-1}	$[Ti(NO_3)_4]$ /10^{-2} mole l^{-1}	Nitro product ratio A : B
69	Toluene	Benzene	0.15	3.26	4.1
73			0.26	3.60	4.2
189			0.26[a]	3.6	5.7
190			0.26[b]	3.6	5.5
64			0.17	1.3	7.3
68		c	0.15	3.3	4.9
74		c	0.26	3.6	5.1
71	Mesitylene	Benzene	0.26	3.6	20.3
118			0.37	3.7	18.8
70	Mesitylene	Toluene	0.17	3.3	5.7
77	t-Butyl Benzene	Benzene	0.26	3.6	1.3
108	Mesitylene	O-xylene	0.30	3.2	2.7
72	Chlorobenzene	Benzene	0.26	3.6	0.12
76	p-dichloro Benzene	Benzene	0.26	3.6	0.02

[a] $[H_2O]$ = 2×10^{-4} mole l^{-1}

[b] $[H_2O]$ = 3×10^{-3} mole l^{-1}

[c] Hexadeuteriobenzene

Reactions carried out at $20^{\circ}C$ ($\pm 1^{\circ}$)

TABLE 2.11

VARIATION OF NITROPRODUCT RATIO

DURING THE COURSE OF A COMPETITION EXPERIMENT AT $20^{o}C(\pm 1^{o})$

A) Competing substrates; Toluene, Benzene

Substrate Concentration = 0.15 mole. 1^{-1}.

$Ti(NO_3)_4$ Concentration = 0.0326 mole.1^{-1}.

CONVERSION (%)	NITROPRODUCT RATIO TOLUENE:BENZENE
9	3.5
18	3.9
35	3.9
61	3.6
73	3.9
80	4.1
88	4.1
98	4.1

B) Competing Substrates; Toluene, Hexadeuteriobenzene

Substrate Concentration = 0.15 mole. 1^{-1}.

$Ti(NO_3)_4$ Concentration = 0.033 mole. 1^{-1}

CONVERSION (%)	NITROPRODUCT RATIO TOLUENE: C_6D_6
20	4.6
36	4.7
54	5.0
69	4.7
82	4.9
92	4.8
95	4.8
99	4.9

TABLE 2.12

RELATIVE REACTIVITY BY COMPETITION

Substrate	Rate
Mesitylene	20
o-Xylene	8
Toluene	5
t-Butylbenzene	1
Benzene	1
Hexadeuteriobenzene	1
Chlorobenzene	0.1
p-Dichlorobenzene	0.02

nitro compounds were observed. Indeed, an experiment showed that n-pentane (0.34 mole. l^{-1}) reacted with tetranitratotitanium (IV) (0.07 mole l^{-1}) in carbon tetrachloride to produce less than 1% yield of any product after twenty four hours.

2.2 DISCUSSION

The results obtained from studies of the reaction of benzene with tetranitratotitanium (IV) indicate a stoicheiometry involving one mole of benzene and one mole of the nitrato compound reacting to give one mole of nitrobenzene and a solid which has a Ti : NO_3^- ratio of approximately 1:3. The simplest formulation of this process can be represented by,

$$C_6H_6 + Ti(NO_3)_4 \longrightarrow C_6H_5NO_2 + Ti(OH)(NO_3)_3$$

although the precise nature of the inorganic product must remain uncertain owing to co-ordination of the aromatic species. The observation that up to 5% of dinitro products were produced in certain reactions however must indicate that some minor complications occur, although any further reaction of this sort must be slow by comparison with the main reaction.

In the reactions between tetranitratotitanium (IV) and benzene, the concentration dependence of the initial rate of reaction shows that the rate determining stage probably involves only tetranitratotitanium (IV). (Table 2.1). This deduction is compatible with the absence of a kinetic isotope effect and also the lack of effect of water concentration on the rate of reaction. Similar experiments carried out with toluene

and tetranitratotitanium (IV) produced similar results. The yields of mononitration products and the variation of rates with initial reactant concentrations, both indicated a reaction of the same stoicheiometry as mentioned above and also a reaction only involving the tetranitratotitanium (IV) in the rate limiting stage. The data obtained during the course of one reaction (Table 2.5) indicate that a simple reaction between one nitrating species and the substrate is proceeding throughout the reaction with no change of product isomer ratios.

The initial rates of reaction of benzene and toluene were found to be very similar to those of mesitylene, ethylbenzene, and t- butylbenzene under similar conditions and this confirms the previous indication of the absence of the substrate from the rate determining stage. However, both chlorobenzene and p-dichlorobenzene were found under similar conditions to react more slowly by an order of magnitude. It was thought that this effect was a result of the heterogeneity which is discussed later, or it may have been due to a change in the rate determing stage of the reaction. The results of the competition experiments (Tables 2.10-2.12) describe the selectivity of the nitrating species between the aromatic substrates. It is apparent that these data are so different from those observed from the direct rate measurements, that a different stage of reaction must be being studied, even when reasonable consideration is made of the effects of the heterogeneity of the medium.

It was concluded that the rate limiting stage involved the production of a reactive nitrating intermediate from

tetranitratotitanium (IV). The intra- and intermolecular selectivities observed in this work implied electrophilic rather than radical attack on the aromatic nucleus.

Various possible intermediates must be considered. Significant differences from the intra- molecular selectivity established for the nitronium ion were observed, the most studied example being that of toluene. The isomer ratios observed (Table 2.4) in this present work lie well outside the quite narrow range of values established in a wide range of conditions where the nitronium ion is known to be effective[32]. The reactive species in this case is in fact more selective than the nitronium ion between m- and p- positions[32]. The nitronium ion is also known to show a much greater intermolecular selectivity than that observed here. For nitronium ion nitrations in sulphuric acid, the rate ratio[147],

Benzene : Chlorobenzene : p- dichlorobenzene is

$$1 \quad : \quad 6 \times 10^{-2} \quad : \quad 6 \times 10^{-4}$$

whereas in this work, the observed ratio is,

$$1 \quad : \quad 1 \times 10^{-1} \quad : \quad 2 \times 10^{-2}$$

Similarly for nitronium ion nitrations in carbon tetrachloride, the rate ratio[34],

Benzene : Toluene is 1 : 17

whereas in this work it is 1 : 5.

Nitration via nitrosation was thought to be another possible pathway for reaction and the effects of urea on reaction rates were studied. However, even with the lack of any effect noticed, it is still dangerous to draw positive conclusions

because of the low solubility of urea in the reaction solutions. Reactions involving nitrosation should show a primary kinetic isotope effect[148] which was not the case.

Nitric acid is another possible intermediate, but in carbon tetrachloride, reactions are known to be too slow for it to be effective in this case[34]. For example, the time to produce 0.05 moles l^{-1} of nitromesitylene by nitric acid (0.1 mole l^{-1}) in carbon tetrachloride at 25°C is 2 months. Nitric acid also reacts through the intermediacy of the nitronium ion in this medium so that the inter- and intramolecular selectivities would be different from those observed in this work.

Both dinitrogen tetroxide and dinitrogen pentoxide could be considered as possible intermediates if equilibria such as the following were operating,

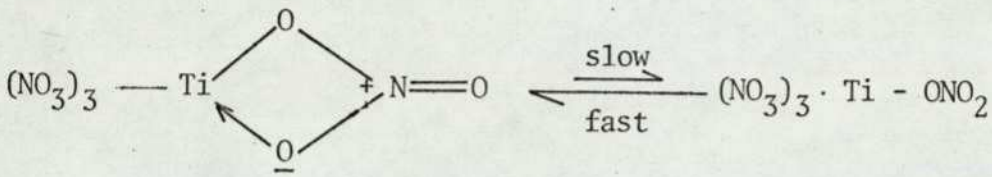
$$Ti(NO_3)_4 \rightleftharpoons TiO(NO_3)_2 + N_2O_5$$

$$Ti(NO_3)_4 \rightleftharpoons TiO_2(NO_3)_2 + N_2O_4$$

In an attempt to clarify this possibility, studies of the reactions of both dinitrogen pentoxide and dinitrogen tetroxide in carbon tetrachloride under conditions similar to those used for tetranitratotitanium (IV) were made. The results are presented and discussed in Chapters 4 and 5.

This work showed that dinitrogen pentoxide as an intermediate would involve intra- and intermolecular selectivities very different from those observed here. Dinitrogen tetroxide at suitable concentrations reacts with aromatic compounds much too slowly to be effective here.

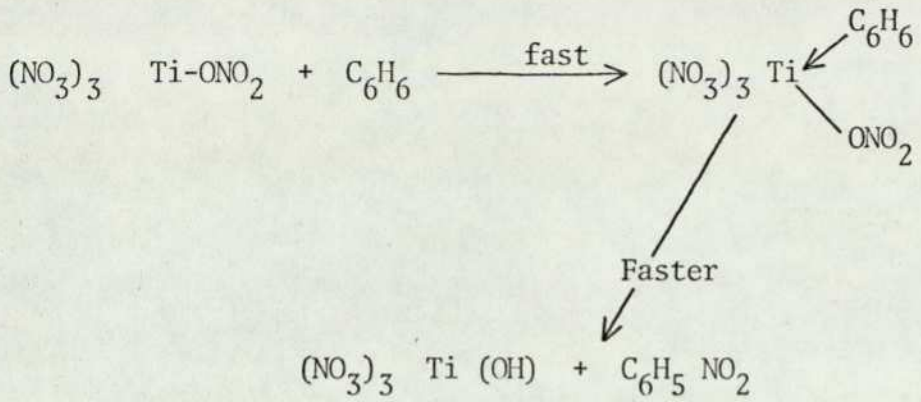
It is necessary to conclude therefore that some other intermediate is involved in the reactions of tetranitratotitanium (IV). One tentative suggestion is that the rate determining stage of the reactions might involve the production of a species from tetranitratotitanium (IV) with a unidentate nitrato ligand which thus presents an available co-ordination positon,



The relative reactivities of the aromatic molecules indicated for reaction with this intermediate by the competition experiments (Table 2.12) are in the sequence expected for reaction with an electrophile. The spread of rates however is less than that of any electrophilic substitution where proton loss is kinetically insignificant. It is difficult to see that any direct electrophilic nitration process could be so unselective, particularly in the absence of any evidence of a diffusion controlled reaction[32].

It is suggested therefore that a fast stage of the reaction involves a co-ordination from the π electrons of the aromatic molecules to the titanium nucleus, and that the complexes thus formed then undergoes a faster intramolecular electrophilic substitution.

The nature of the attack in the second faster stage is uncertain but it would be expected that a bidentate nitrato ligand is involved in the rearrangement process rather than the unreactive unidentate nitrato ligand[115].



The separation of stages of the reaction as described above is necessary to account for the anomalous combination of reactivity in this system. Low intermolecular selectivity outlined above was observed but the intramolecular selectivity is qualitatively similar to that of the nitronium ion, although for toluene, as has already been mentioned, there are significant differences in isomer ratios obtained. The normal ideas of selectivity in electrophilic substitution reactions need not apply during processes involving intra-molecular rearrangement, and it is unfortunate that the overall result of the reaction is to produce isomer distributions in general only slightly different from those observed in nitrations by the nitronium ion.

Certain other characteristics of the reactions however are not satisfied by the above mechanism. These include the curved rate plots often causing discrepencies in the rate results obtained, and the apparently random variation of the toluene isomer distributions over a narrow range. The most likely explanation of these points is that they are a consequence of the heterogeneous nature of the reactions caused by the precipitated solids. The observations that stirring had a negligible measured effect, and also that significant quantities of nitro compounds were found to be present in the precipitated solid suggests two

points. Firstly that the reaction is not surface catalysed, and secondly that there could well be equilibria operating at every stage of the reaction between the species in solution and those present in the precipitate. In such a case the species present would depend to a large extent on the nature of the substrate and also the initial concentrations of reactants. These factors may well have produced the secondary features observed.

The results obtained from the reactions of nitrobenzene, diphenyl and anisole also appear to be anomalous and do not fit the mechanism already described. In the case of nitrobenzene, the rate of nitration relative to benzene by nitronium ion[32] is found to be 6×10^{-8}. It is an indication of the very different nature of the mechanism of nitration in the present system that any appreciable yield of dinitrobenzene is obtained under conditions similar to those applicable to the nitration of benzene. The differences in rates and the low yields of products must be attributed to possible association of nitro-compounds with the precipitated solid which has already been observed in connection with the nitration of benzene. In the case of both anisole and biphenyl, nitration *via* nitrosation must be considered. Both substrates are very susceptible to nitrosation and several workers[37, 149] have observed anomalous data from them. It is sometimes possible to observe the presence of a nitrosating species reflected in a change in the isomer distribution from the aromatic substrate being studied, and indeed in this work low *o*-/*p*- ratios are observed which tend to support the possible intermediacy of nitrosation. The

presence of urea in several experiments did not significantly effect the ratio obtained although as has been previously mentioned, its solubility was very low. In the case of anisole, it is also possible that some by-products may have been formed by attack at carbon-oxygen bond. This may have occurred in anisole itself or in the nitroanisoles, and this could have produced the variations in isomer and rate data obtained. Some possible by-products which could have been detected were nitrobenzene, dinitrobenzene, nitrophenols, nitroaldehydes, and substituted biphenyls. However none of these were detected under the conditions used.

In conclusion it has been shown that tetranitratotitanium (IV) does exhibit a special mechanism of nitration of aromatic compounds. This mechanism however must be different from that by which it nitrates aliphatic compounds as typified by n-pentane. However the difficulties in its use and the relatively small differences in isomer proportions finally obtained suggest that there are only disadvantages in its use with simple aromatic compounds. The possibility of using other transition-metal nitrato compounds with the aim of observing variation of isomer distributions, and of nitrating usually unreactive heterocyclic compounds remains and the results obtained are discussed in subsequent chapters.

CHAPTER 3

THE REACTIONS OF TRANSITION-METAL NITRATO COMPOUNDS WITH AROMATIC AND HETERO-AROMATIC SYSTEMS

RESULTS

In view of the data compiled for tetranitratotitanium (IV), it was anticipated that similar experiments could be performed with other known transition-metal nitrato compounds, to obtain useful mechanistic information. It appeared that nitrosyl-tetranitrato iron (III), tetranitratozirconium (IV) and dinitratocopper (II) were most satisfactory both from their positions within the transition-metal series for comparative purposes, and also from their ease of preparation. However no suitable inert solvent could be found to maintain homogeneous conditions for mechanistic studies.

It was decided therefore to study the product distributions obtained from the three nitrato compounds mentioned in their reactions with aromatic substrates in the absence of solvent. Also reactions between the nitrato compounds of iron, zirconium and copper as well as titanium with heterocyclic compounds under non-acidic conditions were investigated.

3.1 AROMATIC COMPOUNDS

3.1.1 TETRANITRATOZIRCONIUM (IV)

The product isomer distributions and yields from the nitration of aromatic compounds with tetranitratozirconium (IV) are shown in Table 3.1.

In all cases solid residues were observed in the reaction flasks. The reaction was rapid, being complete in about 10 seconds after which the yield remained constant. No dinitroproducts were observed.

TABLE 3.1

AROMATIC NITRATION PRODUCTS OF TETRANITRATOZIRCONIUM (IV)

Substrate	Amount of Substrate /10^{-2} moles	Amount of $Zr(NO_3)_4$ /10^{-4} moles	Nitroproducts (%) 2-	3-	4	Yield a
Toluene	4.8	4.7	46.2	2.1	51.7	1.1
	2.8	7.5	45.8	2.0	52.2	1.5
Ethylbenzene	4.3	18.7	30.6	2.2	67.2	1.1
	3.5	4.2	31.0	2.2	66.8	1.2
t-Butylbenzene	4.5	6.5	8.0	4.0	88.0	1.4
	5.0	10.0	8.2	3.9	87.9	1.1
o-Xylene	2.2	3.5		35.3	64.7	1.2
m-Xylene	3.1	3.4	8.0		92.0	1.2
Nitrobenzene	6.0	15.0	6.7	93.2	0.1	*
	5.3	24.0	7.4	90.7	1.9	0.9
Chlorobenzene	4.1	16.0	26.9	b	73.1	1.0
Bromobenzene	6.2	4.5	30.4	b	69.6	0.96
Benzene	4.1	7.75	nitrobenzene			1.5

a moles of nitroproduct per mole of reagent

b % m- = less than 0.1%

* not determined.

Reactions performed at 20°C (± 1°)

3.1.2 NITROSYLTETRANITRATO IRON (III)

The product distributions and yields obtained from the reactions of aromatic compounds and nitrosyl-tetranitrato iron (III) are shown in Table 3.2. Brown solid residues were observed in all cases after reaction had terminated. Reaction was observed to be complete in about 10 seconds, after which the yield of nitro products remained constant. No dinitro-products were observed in any reaction.

3.1.3 DINITRATOCOPPER (II)

In the attempted reactions between aromatic compounds and dinitratocopper (II), no reaction was found to take place.

3.2 HETEROAROMATIC COMPOUNDS

Studies were confined to nitrogen heterocyclic compounds and product data were obtained from pyridine, quinoline and isoquinoline.

3.2.1 TETRANITRATOTITANIUM (IV)

In all the reactions performed with tetranitratotitanium (IV), solid precipitates were observed. It was found that 3-nitropyridine was the predominant product obtained in the reaction of pyridine and tetranitratotitanium (IV) under a variety of initial reactant concentrations and reaction temperatures. The results are summarized in Table 3.3. The yield of nitropyridines varied between about 5 and 10% based on the release of one nitro group from each molecule of tetranitrato-titanium (IV).

TABLE 3.2

AROMATIC NITRATION PRODUCTS OF NITROSYLTETRANITRATOIRON (III)

Substrate	Amount of Substrate /10^{-2} moles	Amount of $Fe(NO_3)_4NO$ /10^{-4} moles	nitroproducts (%) 2-	3-	4-	Yield [a]
Toluene	3.9	3.5	42.9	2.0	55.1	2.0
	7.4	10.2	42.5	2.4	55.1	1.9
Ethylbenzene	5.1	13.5	30.4	2.4	67.2	1.6
t-Butylbenzene	11.9	5.8	6.7	4.2	89.1	1.8
o-Xylene	9.3	9.5	-	33.0	67.0	1.5
m-Xylene	5.8	4.0	10.2	-	89.8	1.9
Nitrobenzene	4.3	6.5	7.0	92.0	1.0	0.8
	4.2	4.0	7.3	91.8	0.9	0.9
Chlorobenzene	5.8	3.3	22.1	b	77.9	*
	2.3	10.3	22.9	b	77.1	1.7
Bromobenzene	6.2	7.0	24.6	0.2	75.2	1.4
Benzene	5.2	8.3	nitrobenzene			1.8

a moles of nitroproduct per mole of reagent

b % m- = less than 0.05%

* not determined

Reactions all performed at 20° (± 1°)C

TABLE 3.3

NITRATION OF PYRIDINE BY TETRANITRATOTITANIUM (IV) AT 20°C (±1°)

Amount of $Ti(NO_3)_4$ /10^{-4}moles	Amount of Pyridine /10^{-4}moles	nitropyridine product observed	yield of nitropyridines[c] /10^{-5}moles	% [a]
8.5	52.0	3-nitro [d]	2.46	3.0
3.5	16.8	3-nitro [d]	2.3	6.5
7.0 [b]	34.0	3-nitro= 92% 4-nitro= 8%	4.9	7.1
3.5	18.0	3-nitro [d]	1.8	5.3
7.1	35.0	3-nitro [d]	4.8	6.8
4.2	18.0	3-nitro [d]	3.7	8.8
12.9	12.9	3-nitro [d]	1.6	1.2
11.6	11.6	3-nitro [d]	1.6	0.9

Thanks are due to Mr. J. G. Golding for most of these results obtained during an undergraduate project.

[a] based on moles of nitroproduct per mole of reagent

[b] Under reflux at 78°C

[c] Analysis performed after 24 hrs. reaction

[d] Less than 1% 4-nitropyridine

The products obtained from reactions with quinoline and isoquinoline are shown in Table 3.4. The nature of the nitroquinoline products was determined by gas chromatography by comparison of retention times with authentic samples of the products. Further confirmation was achieved by gas chromatography - mass spectroscopy. Figure 3.1 shows the mass spectrum obtained for the major product produced during a typical experiment, which was thought to be 3-nitroquinoline. Figure 3.1 also shows the breakdown pattern expected from 3-nitroquinoline.

In all the reactions involving pyridine, quinoline and isoquinoline, production of nitro products was accompanied by much precipitation. In several experiments already described, the solid produced was isolated and analysed for the nitrate group and titanium. The results obtained are detailed in Table 3.5.

3.2.2 NITROSYLTETRANITRATO IRON (III) AND TETRANITRATOZIRCONIUM (IV)

Reactions between nitrosyltetranitrato iron (III) and tetranitratozirconium (IV) and heterocyclic compounds were carried out in the absence of solvent. The product data obtained from these reactions are listed in Table 3.6

The nitropyridine and nitroquinoline products were analysed by gas chromatography and retention times compared to those of authentic compounds. In addition the major products of the reactions with quinoline, were further studied by gas chromatography - mass spectroscopic techniques. The mass spectrum obtained from a typical experiment together with the breakdown pattern of 7-nitroquinoline is shown in Figure 3.2.

TABLE 3.4

NITRATION PRODUCTS OF QUINOLINE AND ISOQUINOLINE WITH TETRANITRATOTITANIUM (IV) AT 20°C (±1°)

Substrate	[Substrate] /10^{-2}mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2}mole l^{-1}	Nitroproducts (%)					Yield[a] %
			3-	5-	6-	7-	8	
Quinoline	51.0	6.9	83.3	<0.1	<0.1	3.0	13.7	39.3
	90.0 [b]	9.6	85.0	<0.1	<0.1	6.4	8.6	9.8
	90.0 [c]	9.6	85.0	<0.1	<0.1	6.3	8.7	21.0
	32.6	7.7	93.1	<0.1	<0.1	1.3	5.6	36.3
	8.5 [b]	6.0	86.2	<0.1	<0.1	5.0	8.8	4.6
	8.5 [c]	6.0	86.2	<0.1	<0.1	5.1	8.7	4.5
	7.6	7.6	78.9	<0.1	<0.1	8.7	12.4	6.1
Isoquinoline	60.0	2.1	-	75.3	-	-	24.7	0.5
	60.0	10.0	-	77.0	-	-	23.0	1.4

a Based on release of one nitrogroup from each molecule of reagent

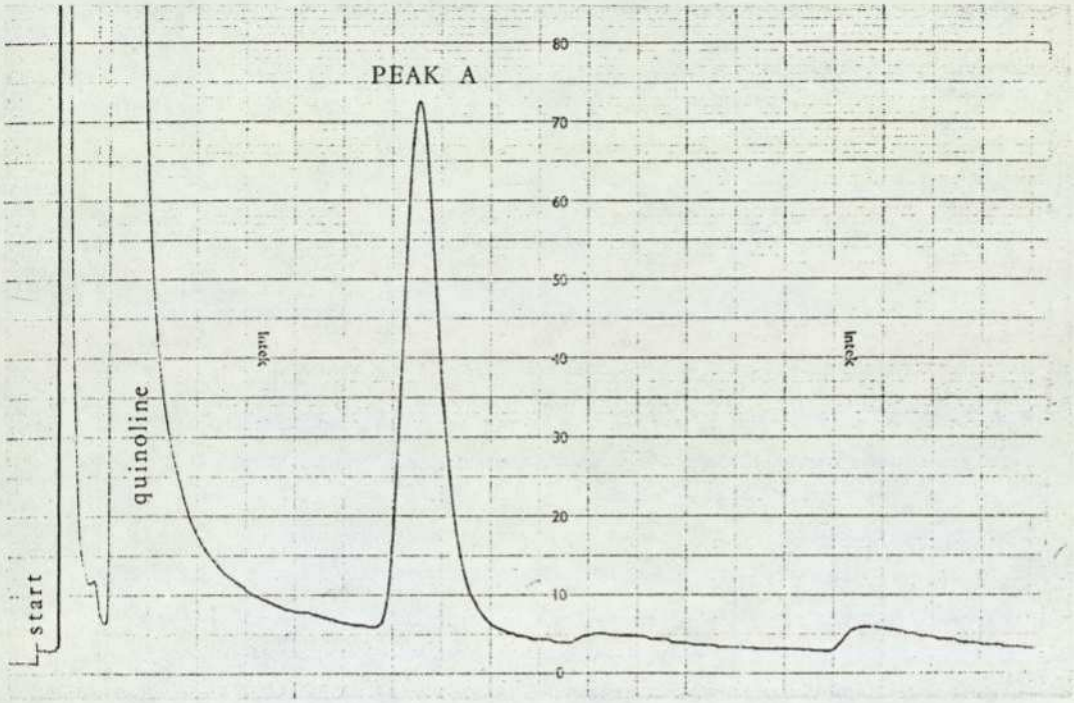
b Analysis after 1 hour

c Analysis after 24 hours when yield remained constant

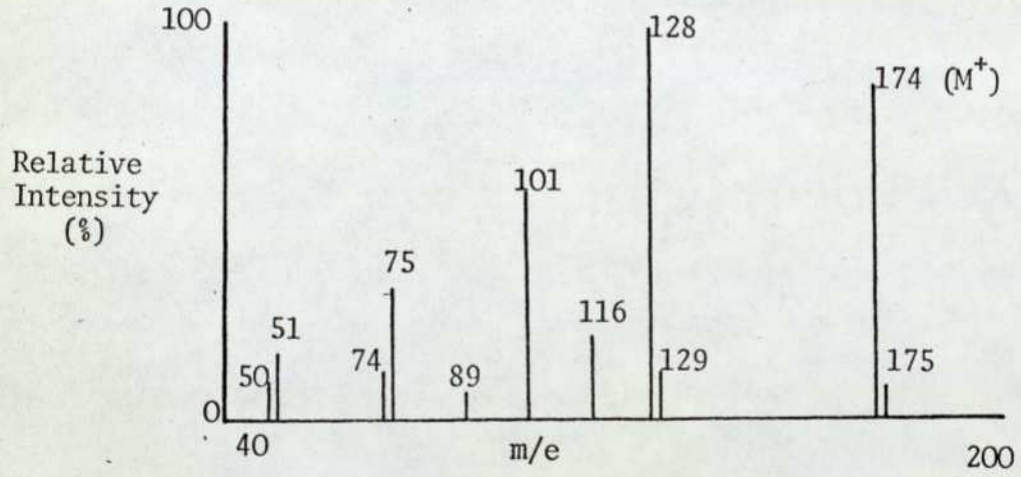
FIGURE 3.1

GAS CHROMATOGRAPHY / MASS SPECTRAL ANALYSIS OF MAJOR PRODUCT OBTAINED IN THE REACTION OF QUINOLINE AND $Ti(NO_3)_4$ IN CCl_4 at 20°C

A. GAS CHROMATOGRAPH OF REACTION MIXTURE



B. MASS SPECTRUM OF PEAK A



C. EXPECTED BREAKDOWN OF 3-NITROQUINOLINE

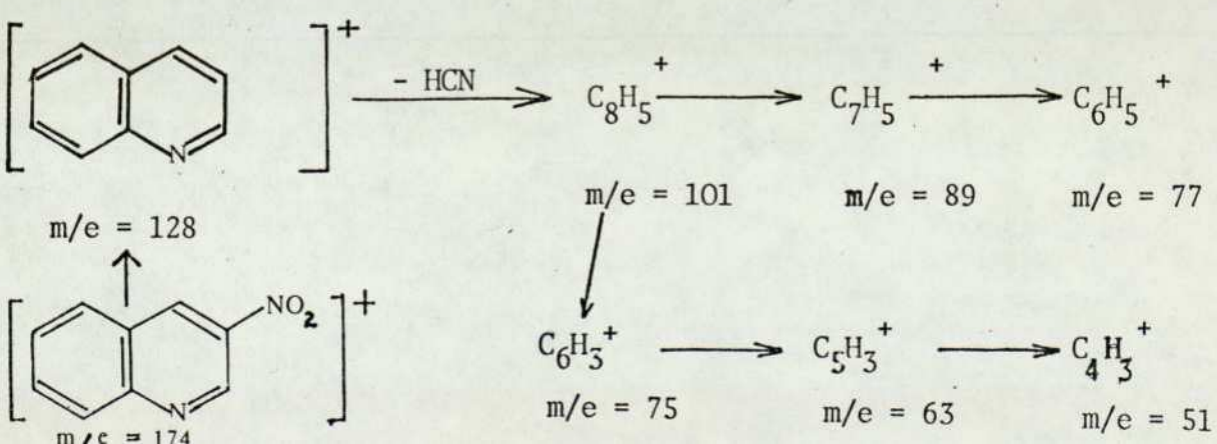


TABLE 3.5

ANALYSIS OF SOLID PRODUCED IN REACTIONS OF HETEROCYCLIC COMPOUNDS AND TETRANITRATOTITANIUM (IV)

Substrate	[Substrate] /10^{-2} mole l^{-1}	[$Ti(NO_3)_4$] /10^{-2} mole l^{-1}	Nitroproduct found on solid /10^{-3} mole l^{-1}	% Ti	% NO_3^-	NO_3^-:Ti Ratio
Pyridine	5.2 [a]	5.2	<0.1	8.26	41.4	3.9
	4.6 [b]	4.6	<0.1	8.8	42.4	3.7
Quinoline	7.6 [c]	7.6	4.7	9.4	46.7	3.85
	32.6 [d]	7.7	5.0	8.0	38.4	3.70

[a] Total yield of nitroproduct found to be 1.2%

[b] Total yield of nitroproduct found to be 0.9%

[c] Total yield of nitroproduct found to be 6.1%

[d] Total yield of nitroproduct found to be 36.3%

TABLE 3.6

REACTION PRODUCTS OBSERVED FROM HETEROCYCLIC COMPOUNDS AND NITRATO COMPOUNDS OF IRON AND ZIRCONIUM

a) Nitrosyltetranitrato iron (III) at 20°C (±1)

Substrate	Amount of Substrate /10^{-2} moles	Amount of $FeNO(NO_3)_4$ /10^{-3} moles	position of substitution % 2-	3-	4-	Yield % [a]
Pyridine	7.3	2.5	< 0.01	22.1	77.9	10.1
	6.6	3.9	< 0.01	33.0	67.0	4.4

			position of substitution					
			3-	5-	6-	7-	8-	
Quinoline	4.9	0.3	18.0	< 0.1	< 0.1	82.0	< 0.1	38.4
	6.1	2.5	17.0	< 0.1	< 0.1	83.0	< 0.1	25.0
Isoquinoline	1.0	1.5	b	86.1	b	b	13.9	1.4
	0.7	1.5	b	89.5	b	b	10.6	1.0

b) Tetranitratozirconium (IV) at 20°C (±1)

Substrate	Amount of Substrate /10^{-2} moles	Amount of $Zr(NO_3)_4$ /10^{-3} moles	position of substitution (%) 2-	3-	4	yield %[a]
Pyridine	13.7	1.95	<0.01	35.6	64.4	9.0
	10.8	0.66	<0.01	39.6	60.4	5.0

Quinoline			position of substitution 3-	5-	6-	7-	8-	
	5.9	2.5	2.7	<0.1	<0.1	97.3	<0.1	86.0
	6.5	3.0	5.0	<0.1	<0.1	95.0	<0.1	90.0
Isoquinoline	0.78	1.2	b	77.8	b	b	22.2	0.9
	0.87	1.7	b	77.3	b	b	22.7	0.7

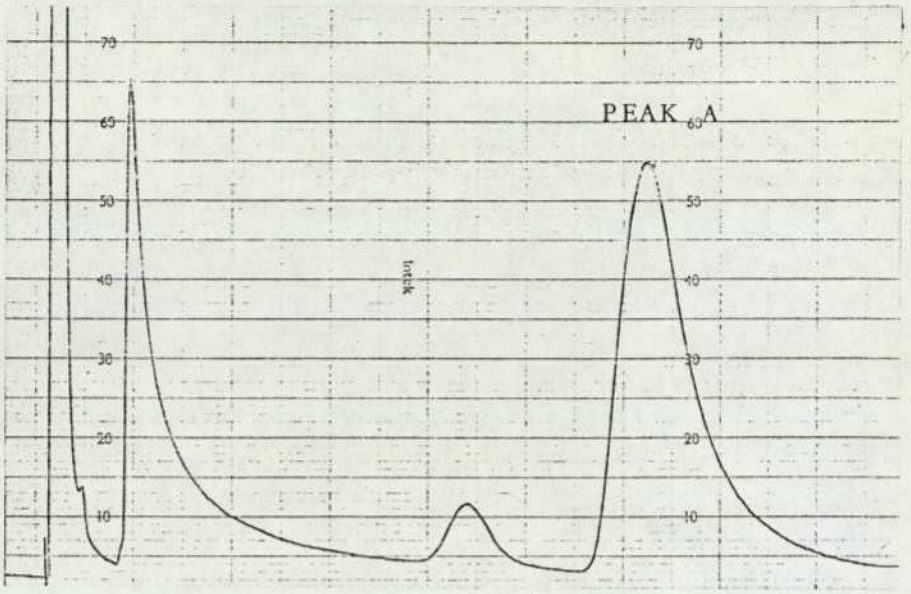
[a] based on moles of nitroproduct per mole of reagent

[b] unable to determine these products

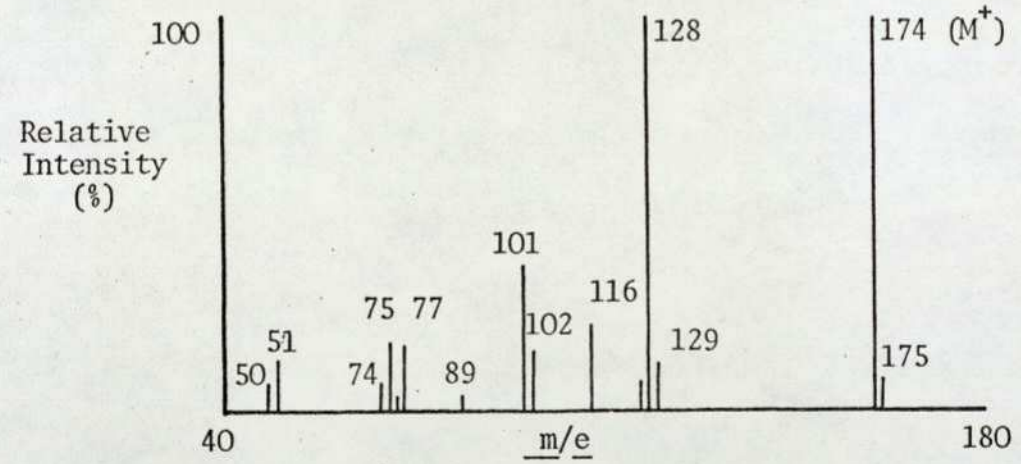
FIGURE 3.2

GAS CHROMATOGRAPHY / MASS SPECTRAL ANALYSIS OF PRODUCTS OF REACTION BETWEEN QUINOLINE AND $Zr(NO_3)_4$ AT 20°C

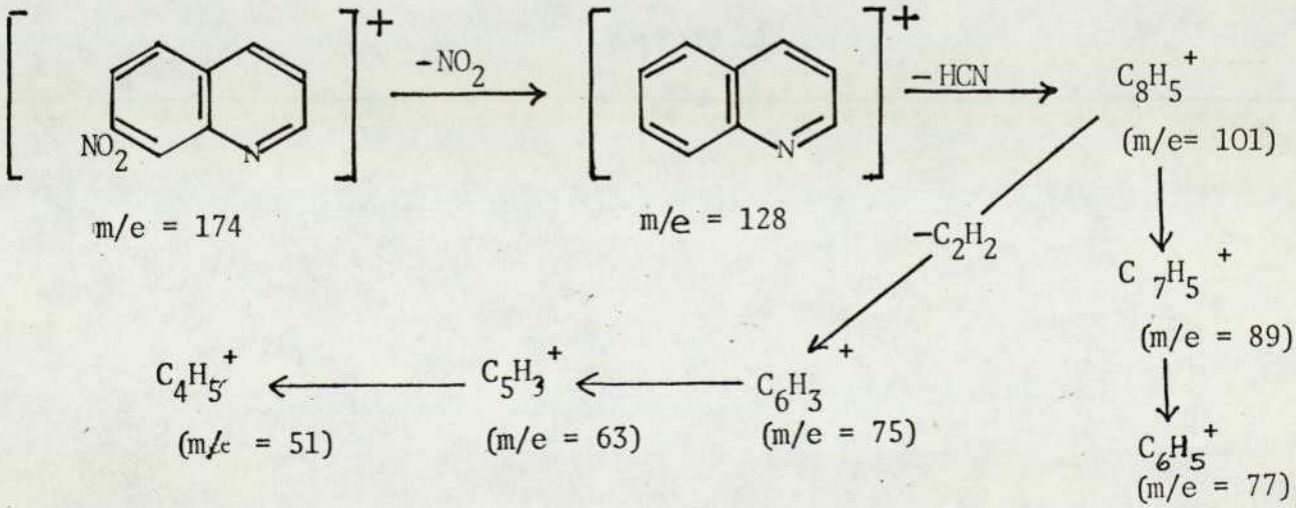
A. Chromatograph of Reaction Mixture



B. Mass Spectrum of Peak A



C. Expected Breakdown of 7-Nitroquinoline



For the analysis of the nitro-iso-quinoline products, a comparison was made with the reaction products obtained in the reaction of isoquinoline with nitric acid in sulphuric acid as performed by Dewar and Maitlis[136] (see experimental section for details). They analysed by spectroscopic techniques a mixture of 5- and 8-nitroisoquinolines formed in this mixed acid reaction. As the 5- nitroisoquinoline was available, conditions of separation and identification of the two nitro products were found by gas chromatography and the retention data used to identify the products obtained in reactions with the nitrato compounds.

In the mixed acid nitration of isoquinoline which was performed the percentage isomers observed were,

5 - nitroisoquinoline = 85.3%,

8 - nitroisoquinoline = 14.7%.

The values obtained by Dewar and Maitlis using spectroscopic techniques were,

5 - nitroisoquinoline = 84.8 (±1) %,

8 - nitroisoquinoline = 15.2 (±1) % at 100°C

and,

5 - nitroisoquinoline = 90.4 (±1) %,

8 - nitroisoquinoline = 9.6 (±1) % at 0°C.

Reactions between the nitrato compounds of iron and zirconium with the heterocyclic systems seemed to occur after several minutes. Maximum yields of nitro products were always obtained within the first 30 minutes of the reaction.

3.2.3 DINITRATO COPPER (II)

Although intense blue coloured solutions were observed on addition of dinitrato copper (II) to the heterocyclic systems studied, no nitropyridines, nitroquinolines or nitroisoquinolines were detected in any reaction.

3.3 DISCUSSION

The products formed from the nitration of aromatic compounds by the nitrato compounds of zirconium and iron (Tables 3.1 and 3.2) are very similar for the two reagents. They are also comparable to the data reported for tetranitratotitanium (IV) alone[123] and in carbon tetrachloride (Chapter 2). However, it is clear once again that the isomer values obtained with toluene are considerably different from those of conventional nitrations[32]. It is also noticable that the only significant difference between results from the nitrato compounds occurs with toluene. The percentage of m- nitro toluene varies from 0.8 (± 0.1)% in the case of tetranitratotitanium (IV) in carbon tetrachloride up to 2-5% with the other nitrato compounds in the absence of solvents.

The yields of mononitro products observed were once again very high. For tetranitratozirconium (IV) approximately one mole of nitro product is produced from one mole of reagent. Slight variations were probably due to heterogeneity. In the case of nitrosyltetranitratoiron (III), however, it appeared that much higher yields of nitro products were observed. It may be possible for more than one nitrato ligand to function as a

nitrating species in this case, but accurate mechanistic studies are needed to clarify this point.

The reactions of these nitrato compounds with pyridine and quinoline however showed some unusual results which may be of synthetic importance. In the case of pyridine yields of between 5 - 10% of almost exclusively 3 - nitro pyridine were obtained with tetranitratotitanium (IV) or mainly 4- nitropyridine with nitrosyltetranitrato iron (III) and tetranitratozirconium (IV). The normally vigorous conditions needed to nitrate pyridine have already been described (Chapter 1 Section 1.7.1), and the formation of N-nitropyridinium ion under non-acid conditions was also mentioned. The reactions with transition-metal nitrato compounds however lead at room temperature to 5 - 10% yields of nitro-pyridines.

The reactions with quinoline produce much better yields and once again the products obtained were found to vary with the metal nitrato compound chosen. Tetranitratotitanium (IV) gave mainly 3 - nitroquinoline whereas nitrosyltetranitrato iron (III) and tetranitratozirconium (IV) gave mainly 7-nitroquinoline. The 90% yield of almost pure 7-nitroquinoline is especially noteworthy.

In the previous chapter, it was suggested that in the nitration of aromatic compounds, the stage of reaction determining product formation may involve an intramolecular rearrangement of a co-ordination complex. In the case of heteroaromatic molecules, if a similar mode of reaction were to be envisaged, the likely co-ordination would take place between the titanium nucleus and

the heteroatom. Therefore, if an intramolecular rearrangement then takes place, it is probable that the major factor influencing the position of substitution would be the size and stereochemistry of the complex. It would therefore be possible to account for the complete change in isomer ratios on changing the reagent in the cases of pyridine and quinoline.

The solid produced during the reactions of heteroaromatic compounds with nitrato compounds was analysed in several experiments in an attempt to identify the structure of a co-ordination complex. However, the heterogeneous nature of the solid produced, caused analytical results to be variable. From the titanium and nitrate group analyses (Table 3.5), it is possible to envisage that complexes of the sort,

$Ti\ (NO_3)_4 \cdot x.\ (C_5H_5N)$ where $x = 2 - 3$. and

$Ti\ (NO_3)_4 \cdot y$ (Quinoline) where $y = 1.5 - 2$

might have been formed.

Complex formation between pyridine and quinoline and copper (II) salts is well described in the literature [150,151,152], and the complexes are known to be very stable compounds. It is probable therefore that in the reactions of dinitratocopper (II) and heteroaromatic systems, that complexes of the form $Cu\ (NO_3)_2 \cdot$ 2 py., and $Cu\ (NO_3)_2 \cdot$ 4 py. are produced and undergo no further reaction. This may be a consequence of change from bidentate to unidentate bonding of the nitrato ligand during co-ordination.

CHAPTER 4

THE NITRATION OF AROMATIC COMPOUNDS BY DINITROGEN PENTOXIDE IN CARBON TETRACHLORIDE SOLUTION

4.1 RESULTS

Initially a series of experiments was carried out using a crude form of dinitrogen pentoxide. This was obtained from the dehydration of fuming nitric acid using phosphorous pentoxide in the presence of air. Using this impure dinitrogen pentoxide in carbon tetrachloride, a series of reactions with toluene was performed as shown in Table 4.1.

Product analysis, which was performed after 12 hours, showed both a low yield of mononitrotoluenes and some unusual isomer ratios in the dilute solutions. It was thought that both were consequences of significant quantities of dinitrogen tetroxide present in the dinitrogen pentoxide. An estimate of the amounts of dinitrogen tetroxide present was obtained from nitrous acid determinations made on some of the reaction mixtures. Some results obtained are shown in Table 4.2, and they show that quite significant quantities of dinitrogen tetroxide must have been present in the impure dinitrogen pentoxide.

Pure samples of dinitrogen pentoxide were subsequently obtained by performing the dehydration of 'fuming' nitric acid and redistillation in an atmosphere of ozonised oxygen. As shown in Table 4.3, the yield of nitrotoluenes obtained was much greater, and the isomer proportions remained constant. However the suggestion that unusual isomer ratios of toluene as shown in Table 4.1 were a consequence of an unusual selectivity of dinitrogen tetroxide in carbon tetrachloride prompted further interest in the nitration characteristics of this reagent and these will be discussed in Chapter 5.

TABLE 4.1

NITRATION OF TOLUENE WITH CRUDE DINITROGEN PENTOXIDE AT 20°C

$[N_2O_5]$ /10^{-2} mole l^{-1}	[Toluene] /10^{-2} mole l^{-1}	Isomer Distribution %			Yield of nitrocompounds % [a]
		o-	m-	p-	
11	11	58	1	41	40
8	8	55	1	44	45
6	6	56	2	42	36
3	3	55	18	27	22
18	26	55	2	43	33
11	"	57	1	42	36
7	"	54	2	44	32
4	"	58	6	36	20
1.5	"	55	22	23	6
0.7	"	59	29	12	6
10	20	55	1	44	44
10 [b]	"	54	2	44	60
7	"	57	1	42	36
6 [b]	"	56	4	40	38
4	"	55	3	42	30
4 [b]	"	54	12	34	30
2	"	56	13	31	30
2 [b]	"	44	30	26	21
1	"	48	35	17	16
0.5	"	53	37	10	3
0.4 [b]	"	54	30	16	16

a Based on dinitrogen pentoxide concentration

b $[H_2O] = 2 \times 10^{-4}$ mole l^{-1}. In all other cases $[H_2O] = 2 \times 10^{-3}$ mole l^{-1}.

TABLE 4.2

DETERMINATION OF NITROUS ACID IN SOME REACTIONS OF TOLUENE WITH IMPURE DINITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT 20°C

$[N_2O_5]$ /10^{-2}mole l^{-1}	[Toluene] /10^{-2}mole l^{-1}	isomer distribution (%) o-	m-	p-	yield of nitrotoluenes % a b	Nitrous acid /10^{-2}mole l^{-1} b
18	26	55	2	43	33	5
11	26	57	1	42	36	4
7	26	54	2	44	32	3
4	26	58	6	36	20	1.5
1.5	26	55	22	23	6	0.5
0.7	26	59	29	12	6	0.2
18	-	-	-	-	-	5.5
0.7	-	-	-	-	-	0.2

a Based on dinitrogen pentoxide concentration.

b Analysis performed after 12 hrs.

TABLE 4.3

NITRATION OF TOLUENE WITH PURIFIED DINITROGEN PENTOXIDE AT 20°C

$[N_2O_5]$ $/10^{-2}$ mole l^{-1}	[Toluene] $/10^{-2}$ mole l^{-1}	isomer distribution %			Yield of nitrocompounds % [b]
		o-	m-	p-	
20	20	56	2	42	98 [c]
10	20	58	2	40	90
8	20	55	2	43	80
2	20	53	1	46	45
0.5	20	57	2	41	31 [d]
8 [a]	20	56	2	42	90
2 [a]	20	54	2	44	55

[a] Reaction carried out at 5°C (±2°)

[b] Based on dinitrogen pentoxide concentration

[c] $[HNO_2] = 5 \times 10^{-3}$ mole l^{-1}

[d] $[HNO_2] = 3 \times 10^{-4}$ mole l^{-1}

Studies of the intermolecular selectivity of dinitrogen pentoxide in carbon tetrachloride were performed by the competition method. It was decided to carry out the reactions at low temperatures to prevent further decomposition of dinitrogen pentoxide, although comparisons were made with some reactions performed at room temperature ($20^{o} \pm 1^{o}C$). The results obtained from the competitive studies are shown in Tables 4.4.1, 4.4.2, 4.4.3. It was observed that a certain variation in the nitroproduct ratios had occurred and there was a possibility that these may have been a consequence of imperfect mixing. The competition method should not be used when the rate of mixing of the two solutions is significant compared with the rate of nitration. It was necessary therefore to determine the rates of nitration of some aromatic compounds under similar conditions. The rates of nitration of both toluene and benzene by dinitrogen pentoxide in carbon tetrachloride were studied by quantitative gas-liquid chromatography. Good straight line first order plots were obtained from several reactions as shown in Figure 4.1, and indicated that the non-catalytic reaction was being studied. Table 4.5 shows some rate constants obtained for these reactions. The magnitudes of the rate constants obtained appear to suggest that the reactions had not occurred at a rate too fast for meaningful intermolecular selectivities to be determined by the competition method.

Studies of the effects of urea on the nitroproduct ratios were also performed but no significant variations were observed as shown in Tables 4.4.1, 4.4.2, and 4.4.3. Similarly

TABLE 4.4.1

COMPETITION OF AROMATIC COMPOUNDS FOR DINITROGEN PENTOXIDE AT 5°C (±2°)

Run No.	Substrate A	Substrate B	[A] /10^{-2} mole l^{-1}	[B] /10^{-2} mole l^{-1}	[N_2O_5] /10^{-2} mole l^{-1}	nitroproduct ratio A:B [e]
114	Toluene	Benzene	10	10	3.3 [b]	6
115	"	a	10	10	3.3 [b]	7
231	Toluene	Benzene	40	40	8.8	37
341	"	"	40	40	0.9	42
251	"	"	40	40	8.8	40 [c]
250	"	"	30	30	8.2	46
270	"	"	30	30	8.2	56 [d]
260	Toluene	Benzene	30	30	0.5	32
280	"	"	30	30	0.5	29 [d]
293	Toluene	Benzene	70	70	17	23
292	"	a	70	76	17	24 [c]
299	"	Benzene	20	230	15	26
304	"	"	20	230	0.3	28
305	"	a	95	70	0.3	17
302	"	Benzene	70	70	0.3	30
332	Toluene	a	50	60	8.6	47
334	"	Benzene	60	90	8.2	53
333	"	a	50	60	0.9	40
335	"	Benzene	60	90	0.9	39
400	Toluene	Benzene	130	135	5	45 [f]
401	"	"	130	135	5	38 [f]
600	"	"	130	135	5	41 [c]
601	"	"	130	135	5	34

a Hexadeuteriobenzene

b Crude dinitrogen pentoxide

c Reaction Temperature = 20°C (±1°C)

d [Urea] = 6×10^{-3} mole l^{-1}

e Results corrected for initial concentrations of substrates

f [H_2O] = 8×10^{-3} mole l^{-1}. In all other cases [H_2O] = 2×10^{-4} mole l^{-1}

TABLE 4.4.2

COMPETITION OF AROMATIC COMPOUNDS FOR DINITROGEN PENTOXIDE AT 5°C (±2°)

Run No.	Substrate A	Substrate B	[A] /10^{-2} mole l^{-1}	[B] /10^{-2} mole l^{-1}	[N_2O_5] /10^{-2} mole l^{-1}	nitro-product ratio A : B
16	Mesitylene	Benzene	10	10	3.3 [a]	24
32			40	40	9.0	260
42			40	40	0.9	250 [b]
52			30	30	8.2	370 [b]
62			30	30	0.5	340
94			70	70	16.0	380
03			70	70	0.3	310 [c]
95			70	70	16.0	330
36			86	90	8.0	360 [d]
02			86	90	5.0	150
03			86	90	5.0	270 [d]
04			86	90	5.0	192
05			86	90	5.0	240
52	Mesitylene	Toluene	30	30	8.2	7
61			30	30	0.5	9 [d]
02			90	130	5.0	16
56	Mesitylene	o-Xylene	30	30	8.2	5
66			30	30	0.5	6
34	o-xylene	Benzene	40	40	8.8	35 [c]
44			40	40	8.8	38 [b]
53			30	30	8.2	38
63			30	30	0.5	33
07			134	134	5.0	34 [d]
06			134	134	5.0	25
98	o-Xylene	Toluene	70	70	16.2	2.5 [c]
04	m-Xylene	Benzene	134	134	5.0	54 [d]
05			134	134	5.0	53

a Crude N_2O_5 used in this case

b Reactions carried out at 20°C (±1°)

c [Urea] = 6×10^{-3} mole l^{-1}

d [H_2O] = 8×10^{-3} mole l^{-1}

In all other cases [H_2O] = 2×10^{-4} mole l^{-1}

TABLE 4.4.3

COMPETITION OF AROMATIC COMPOUNDS FOR DINITROGEN PENTOXIDE AT 5°C (±2°)

Run No.	Substrate A	Substrate B	[A] /10^{-2} mole l^{-1}	[B] /10^{-2} mole l^{-1}	[N_2O_5] /10^{-2} mole l^{-1}	nitro product ratio A : B /10^{-2}
17	Chlorobenzene	Benzene	10	10	3.3 [a]	1
33			40	40	8.8	3
43			40	40	0.9	5
54			30	30	8.2	3
64			30	30	0.5	3
96			70	70	17.0	4
00			200	23	15.0	4 [b]
06			125	45	5.0	4 [b c]
07			125	45	5.0	3 [b]
08			125	45	5.0	5 [b c]
09			125	45	5.0	4 [b]
35	p-Dichlorobenzene	Benzene	40	40	8.8	0.1 [d]
45			40	40	0.9	0.1
55			30	30	8.2	0.5
65			30	30	0.5	0.5
97			70	70	15.2	0.4
01			136	26	16.2	0.6 [b]
06			136	26	0.3	0.3 [b]

[a] Crude dinitrogen pentoxide

[b] Corrected for substrate concentrations

[c] [H_2O] = 8×10^{-3} mole l^{-1}, in all other cases, [H_2O] = 2×10^{-4} mole l^{-1}

[d] Reaction performed at 20°C (±1°)

FIGURE 4.1

KINETIC PLOTS OBTAINED IN NITRATION OF TOLUENE AND BENZENE BY DINITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT 20° (±1°C)

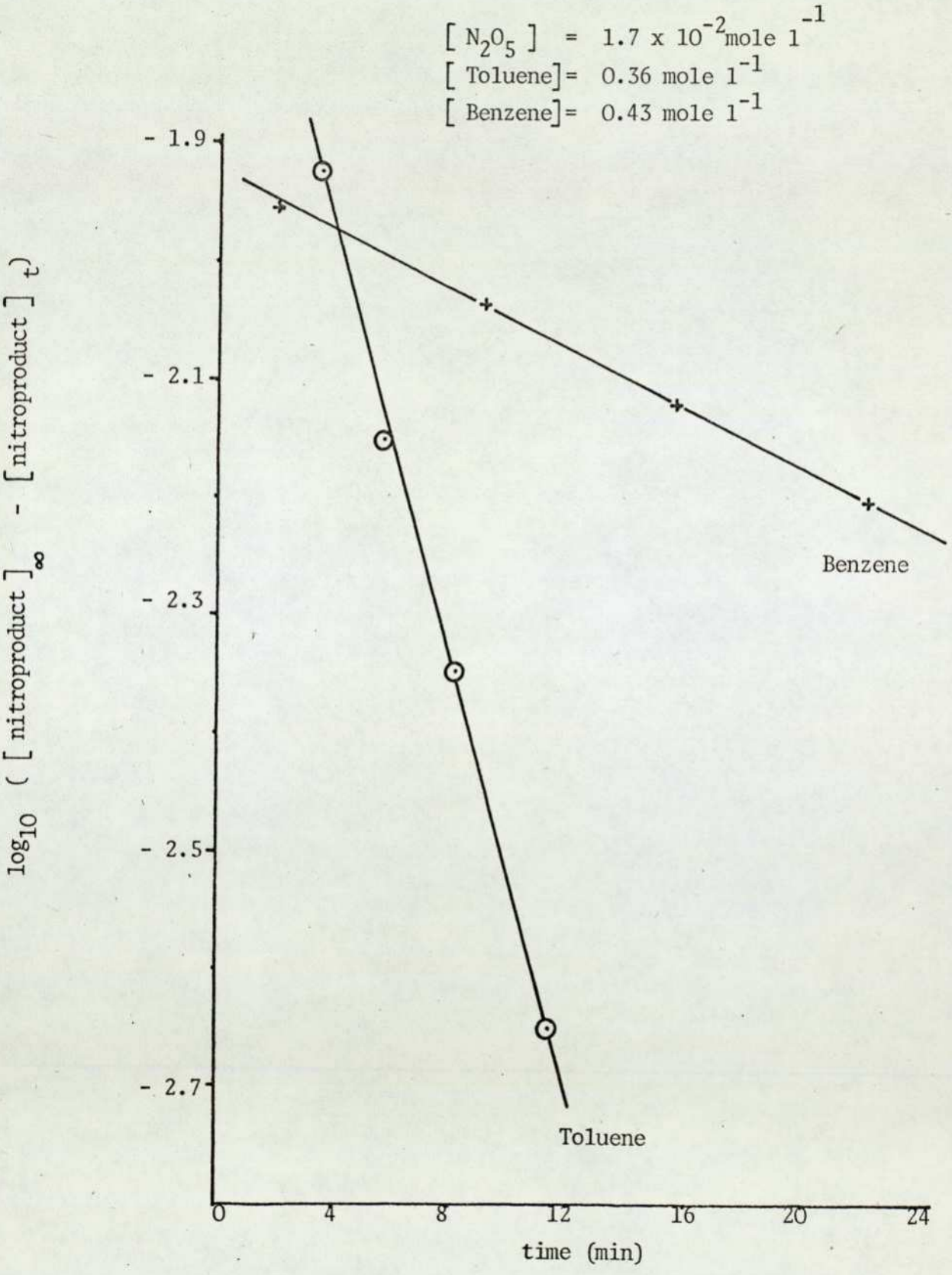


TABLE 4.5

FIRST AND SECOND ORDER RATE CONSTANTS FOR NITRATIONS OF TOLUENE AND BENZENE WITH DINITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT $20^{o}C (\pm 1^{o})$

A. TOLUENE

$[N_2O_5]$ /10^{-2}mole l^{-1}	[Toluene] /10^{-2}mole l^{-1}	k_1 /$10^{-3}s^{-1}$	k_2 /10^{-2}l mole$^{-1}s^{-1}$
5.3	36	22.3	42
1.7	36	3.6	21
0.5	36	0.9	18

B. BENZENE

$[N_2O_5]$ /10^{-2}mole l^{-1}	[Benzene] /10^{-2}mole l^{-1}	k_1 /$10^{-3}s^{-1}$	k_2 /10^{-2}l mole$^{-1}s^{-1}$
5.3	43	1.3	2.4
1.7	43	0.4	2.4
0.5	43	0.1	2.0

the presence of water dissolved in the solvent produced no significant variations in the nitroproduct ratios observed. Reactions performed at lower temperatures also appeared to yield very similar inter and intramolecular selectivities to those obtained at room temperature. This result suggested that effects due to decomposition of dinitrogen pentoxide were negligible. The isomer ratios obtained for some of the substrates studied are reported in Table 4.6. Those found for toluene using purified dinitrogen pentoxide are shown in Table 4.3.

From the results of the competition experiments, it was possible to construct an approximate series of reactivity relative to benzene and this is shown in Table 4.7. The results obtained for hexadeuteriobenzene shown in 4.4.1 indicated that there was no primary kinetic isotope effect in these reactions.

4.2 DISCUSSION

The results already described indicate that the inter and intramolecular selectivity behaviour of dinitrogen pentoxide in carbon tetrachloride is very similar to that observed for the nitronium ion. Several points are relevant. The isomer proportions of products from nitration of some aromatic compounds studied (Tables 4.3, 4.6) are very similar to those reported for the nitronium ion over a wide range of conditions[32]. Toluene which has been investigated most extensively here can be seen to give (%) o- 56, m- 2, p- 42 whereas nitration of toluene carried out using nitric acid in carbon tetrachloride gave (%) o- 53, m- 3, p- 44. A similar comparison can be made with isomer ratios

TABLE 4.6

PRODUCTS OF REACTIONS WITH AROMATIC COMPOUNDS

WITH DINITROGEN PENTOXIDE AT $5^{o}C$ ($\pm 2^{o}$)

Substrate	[Substrate] $/10^{-2}$ mole l^{-1}	$[N_2O_5]$ $/10^{-2}$ mole l^{-1}	Nitroproducts (%) 2-	3-	4-
o-Xylene	40	9	/	45	55
	40	1	/	43	57
	30	9	/	47	53
	30	0.5	/	41	59
	70	16 [a]	/	45	55
	134	5	/	40	60
m-Xylene	134	5	15	/	85
Chlorobenzene	40	9	28	<0.5	72
	40	1	30	<0.5	70 [b]
	30	8	26	<0.5	74
	30	0.5	28	<0.5	72
	70	17	30	<0.5	70

a [Urea] = 6×10^{-3} mole l^{-1}

b Reaction performed at $\sim 20^{o}C$

TABLE 4.7

RELATIVE REACTIVITY BY COMPETITION

Substrate	Rate
Mesitylene	350 (±50)
o-Xylene	55 (± 5)
m-Xylene	35 (± 5)
Toluene	35 (±10)
Benzene	1
Hexadeuteriobenzene	1
Chlorobenzene	0.04 (±0.01)
p-Dichlorobenzene	0.004 (±0.001)

$[N_2O_5]$ = 0.01 — 0.2 mole l^{-1}

[Substrate] = 0.4 − 1.5 mole l^{-1}

Reaction temperature range 5^{o} - 20^{o}C (± 2^{o})

observed in reactions of o- and m- xylenes[32,153] and chlorobenzene[32].

The intermolecular selectivities obtained from competition experiments as shown by Table 4.7 are in an order which is very similar to that expected for nitronium ion nitrations. This can be illustrated by a comparison of some recent results of relative reactivity obtained in some nitronium ion nitrations. These are shown in Table 4.8. The similarity of the present work and those data obtained from media in which the nitronium ion is known to be effective is apparent.

It was also noticable in the studies of inter and intramolecular selectivity of dinitrogen pentoxide in carbon tetrachloride, that the results obtained did not vary significantly over the temperature range employed i.e. 5 - 20°C. This fact suggested that the electrophile was not changing. Also it indicated that had any decomposition of the dinitrogen pentoxide into dinitrogen tetroxide, that this was minimal and did not affect the main reaction. The presence of small quantities of dinitrogen tetroxide or other possible nitrosating species were also shown to be relatively unimportant following the lack of effect of the addition of urea to the reaction mixtures. However, the possibility of nitrosation being an important factor in the reactions of reactive substrates i.e. mesitylene and the xylenes, cannot be completely ignored owing to the solubility problems known to exist with urea in carbon tetrachloride.

The main points already made appear to indicate that dinitrogen pentoxide in carbon tetrachloride operates through the intermediacy of the nitronium ion. It is therefore necessary to

TABLE 4.8

RELATIVE RATES OF NITRATION IN DIFFERENT NITRATING SYSTEMS AT 25°C

Substrate	NITRATING SYSTEM					
	7.5% aq. sulpholan + nitric acid [a]	15% aq. Nitromethane + nitric acid [a]	Nitric acid in carbon tetrachloride [b]	Nitric acid in acetic acid [c]	Nitric acid in 57.2% sulphuric acid [c]	Dinitrogen pentoxide in carbon tetrachloride This Work
Benzene	1	1	1	1	1	1
Toluene	20	25	17	23	17	35 (±5)
o-Xylene	61	139	-	-	-	35 (±5)
m-Xylene	100	146	-	136	95	55 (±5)
Mesitylene	350	400	-	355	150	350 (±50)
Chlorobenzene	-	0.03 [d]	-	-	0.06 [e]	0.04 (±0.01)
p-Dichlorobenzene	-	-	-	-	6×10^{-4} [e]	4×10^{-3}

a Reference no. 33

b Reference no. 34

c Reference no. 36

d Reference no. 154

e Reference no. 147

reconsider some of the conclusions reached by Ingold, Williams et. al.[73]. They postulated that under conditions where the concentration of dinitrogen pentoxide was low (0.03 - 0.1 mole l^{-1}), the aromatic substrate was in a large excess and the reaction temperature was 10 - 20°C, kinetic results together with observations of the effects of added species were indicative of the operation of the dinitrogen pentoxide molecule as the effective electrophile in the non-catalysed reaction. Under conditions where the concentrations of dinitrogen pentoxide were high (greater than 0.1 mole l^{-1} and at lower reaction temperatures (less than 10°C), nitration of aromatic compounds proceeded through the operation of the nitronium ion, the heterolysis of dinitrogen pentoxide being autocatalysed by nitric acid molecules.

In the present work, much of which was performed under conditions similar to those where the electrophile had been suggested to be dinitrogen pentoxide and in which the kinetic results indicated that no autocatalysis occurred, several points appear to exclude the possibility of a change in electrophile from the nitronium ion. The results of the intramolecular selectivity of chlorobenzene are particularly relevent here, as the change in o- / p- ratio with a change in reaction conditions as mentioned above was used to support the postulate that the effective electrophile had changed. In this work, the o- / p- ratio was accurately determined over a wide range of conditions (Table 4.4), and it was found to remain fairly constant and within the normal range expected for nitration by the nitronium ion[32].

The absence of a primary kinetic isotope effect was also noticed in some competition experiments performed with hexadeuteriobenzene (Table 4.4.1). This supports the result obtained by previous workers[74], and would therefore rule out the possibility of a cyclic transition state in the reactions of aromatic compounds and the dinitrogen pentoxide molecule (Section 1.5.1).

A more detailed study of the kinetic results quoted by Ingold, Williams et. al.[73] was performed by calculating the relative rates of nitration of the series of di-substituted halogenobenzenes and comparing the results with those obtained for the nitronium ion (Table 4.9). It is evident from these results that the relative rates of nitration for dinitrogen pentoxide in carbon tetrachloride are not consistent with an electrophile more selective than the nitronium ion. Indeed the results obtained for dinitrogen pentoxide in carbon tetrachloride are remarkably similar to those observed for nitric acid in acetic acid.

Two other points quoted by Ingold, Williams et al.[73] can also be discussed, namely the insensitivity of reaction rates of dinitrogen pentoxide to solvent polarity, and the catalysis observed on addition of nitrate to the reaction mixtures. The fact that added nitrate accelerates the rate suggests that the nitronium ion is not the electrophile. The major problem however encountered in studies of the effects of salts in non-polar solvents is the very low solubility in the media used. It may be therefore that in the studies made with dinitrogen pentoxide in carbon tetrachloride, the increases of rates found with the very small

TABLE 4.9

COMPARISON OF THE RELATIVE RATES OF NITRATION OF SOME POLYHALOGENOBENZENES

Compound	Relative rates of nitration		
	N_2O_5-CCl_4 15° [a]	HNO_3-H_2SO_4 25° [b]	HNO_3-AcOH 20° [c]
p-Dichlorobenzene	1.0	1.0	1.0
p-Dibromobenzene	1.1	1.9	-
o-Dichlorobenzene	1.6	2.0	1.3
m-Dichlorobenzene	2.2	5.6	2.5

a Reference no. 73

b Reference no. 147

c Reference no. 32

concentrations of added nitrate, are consequences of a salt-effect which might mask any effect on an equilibrium between dinitrogen pentoxide and the nitronium and nitrate ions or ion pairs;

$$N_2O_5 \rightleftharpoons (NO_2^+)\ (NO_3^-) \rightleftharpoons NO_2^+ + NO_3^-$$

Ingold, Williams et al.[73] supposed that the insensitivity of the rate to solvent polarity was inconsistent with the reaction being ionogenic. However, the facts that carbon tetrachloride is a faster solvent than nitromethane in nitration in solutions of nitric acid, and that the addition of acetonitrile or N,N-dimethyl formamide considerably retards N-nitration in solutions of nitric acid in carbon tetrachloride[155] suggest that the usual considerations of solvent polarity may break down. However this may only apply when molecular aggregates are involved which is not believed to be the case for the uncatalysed dinitrogen pentoxide reaction[73]. The effects on reaction rates when the solvent polarity is changed could be considered in terms of a replacement of ion-pairs by solvated ions and the effects of this might be uncertain.

From the work carried out on the inter and intramolecular selectivities of dinitrogen pentoxide in carbon tetrachloride, it is also possible to comment on the possibility of this reagent acting as the intermediate in the reactions of tetranitratotitanium (IV) as described in Chapter 2.

The results obtained for dinitrogen pentoxide and tetranitratotitanium (IV) in carbon tetrachloride differ from one another in several respects. The most important change is

that the intermolecular selectivities of the two nitrating agents are quite different. A comparison of Tables 4.7 and 2.12 shows that the intermolecular selectivity of tetranitratotitanium (IV) is very much less than that observed for dinitrogen pentoxide in carbon tetrachloride. However for tetranitratotitanium (IV), the diminished intermolecular selectivity is not accompanied with a loss of intramolecular selectivity. With the exception of toluene, the isomers produced for both dinitrogen pentoxide and tetranitratotitanium (IV) are quite similar and do not differ from those obtained from other methods of nitration [32]. For toluene however, the intramolecular selectivity from tetranitratotitanium (IV) (Table 2.4) is completely outside that observed for dinitrogen pentoxide (Table 4.3) for which the values closely resemble those of the nitronium ion[32].

It is therefore possible to conclude that dinitrogen pentoxide cannot be considered as a likely intermediate for the reactions of tetranitratotitanium (IV) in carbon tetrachloride.

CHAPTER 5

A STUDY OF THE REACTIONS OF DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE WITH SOME AROMATIC COMPOUNDS

5.1 RESULTS

A study of the inter and intramolecular selectivity of the reaction of dinitrogen tetroxide in carbon tetrachloride with a series of aromatic compounds of a wide range of expected reactivity was performed. Much of the initial work was carried out using toluene, a substrate which has already received extensive study both in previous chapters and elsewhere[32]. Table 5.1 shows the unusual mononitration isomer proportions obtained in a series of reactions of toluene and dinitrogen tetroxide in carbon tetrachloride. It was noticable however, that several other products were observed in the reaction mixtures. Analysis of these other products, by gas-liquid chromatography - mass spectrometry showed that they consisted mainly of side chain nitration and oxidation products of toluene e.g. benzyl alcohol, benzaldehyde and phenylnitromethane. Also, small amounts (ca. 1%) of dimethyldiphenyls were similarly detected. Table 5.2 illustrates the production of oxidation and side chain nitration products, compared to the nitration products during the course of a typical reaction. The presence of urea in the reaction solution did not prevent the formation of oxidation products but appeared to alter their relative proportions perhaps inhibiting the production of benzaldehyde from benzyl alcohol.

The mononitration products observed during the toluene reactions (Table 5.1) were also studied by gas chromatographic - mass spectrometric techniques to determine whether any other products produced during the course of the reaction with similar chromatographic retention times had caused the unusual isomer

TABLE 5.1

PRODUCTS OF REACTION OF DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE WITH TOLUENE AT 20°C (±1°C)

$[N_2O_4]$ /10^{-2} mole l^{-1}	[Toluene] /10^{-2} mole l^{-1}	Mononitration isomer distribution (%)			nitroproduct yield [a] %	time of analysis /hrs.
		o-	m-	p-		
24	19	19	46	35	0.3	20
14	19	15	48	37	0.7	20
9	19	24	44	32	0.7	20
5	19	22	51	27	3.0	20
2	19	27	46	27	5.0	20
1	19	33	49	18	9.0	20
20	75	31	15	54	9.0	150
10	38	19	24	57	4.3	150
4	38	30	37	33	9.0	150
120	350	45	6	49	1.0	0.5
"	"	47	4	49	2.0	2
"	"	48	3	49	4.0	120
2	38	31	53	16	3.0	1
"	"	36	48	16	3.5	2
"	"	36	46	17	4.0	22
"	"	39	44	17	6.0	45
25	200	30	50	20	0.1	1
"	"	37	40	23	1.5	40
"	"	39	27	34	3.3	60
"	"	47	18	35	4.2	140
"	"	47	18	35	11.0	360

[a] Yield based on dinitrogen tetroxide concentration.
$[H_2O]$ less than 2×10^{-4} mole l^{-1}

TABLE 5.2 a

REACTION PRODUCT COMPOSITIONS DURING DINITROGEN TETROXIDE-TOLUENE REACTIONS (AT 20°C (±1°))

No. 700

$[N_2O_4] = 0.25$ mole l^{-1}

[Toluene] = 2.0 mole l^{-1}

Time /Hrs.	PRODUCT COMPOSITION				Yield mono-nitrotoluenes %
	Benzaldehyde %	Benzyl alcohol %	Phenylnitro methane %	Mono nitro toluenes %	
0.25	3.0	-	1.5	95.5	0.1
0.5	4.0	-	1.5	94.5	0.1
2.0	5.0	3.0	2.0	90.0	1.0
40.0	10.0	10.0	23.0	57.0	2.5
60.0	10.0	6.0	24.0	60.0	3.3
140.0	11.0	6.0	24.0	59.0	4.2
360	12.1	6.0	25.0	56.9	11.0

TABLE 5.2b

Run No. 701

$[N_2O_4]$ = 0.25 mole l^{-1}

[Toluene] = 2.0 mole l^{-1}

[Urea] = 6×10^{-3} mole l^{-1}

Time/ Hrs.	PRODUCT COMPOSITION				Yield mono nitrotoluenes %
	Benzaldehyde %	Benzyl alcohol %	Phenylnitro methane %	Mononitro toluenes %	
0.3	2.2	-	-	97.8	0.1
0.5	2.0	1.0	2.0	95.0	0.2
2.0	5.0	4.8	10.0	80.2	1.0
40	2.0	12.0	28.0	58.0	3.2
60	2.0	20.0	35.0	43.0	6.0
140	2.0	20.0	36.0	42.0	6.5
360	1.0	20.0	35.0	44.0	7.3

distributions observed. This study confirmed however that the isomer distributions quoted in Table 5.1 were those for o-, m- and p- nitrotoluenes.

It was considered possible that mononitration products formed during a reaction with dinitrogen tetroxide in carbon tetrachloride might be diverted to other oxidation products e.g. to nitrobenzaldehydes. This was tested by adding a known mixture of nitrotoluenes to a solution of dinitrogen tetroxide in carbon tetrachloride and observing any change in the isomer proportions with time.

A mixture containing 60% o-, 5% m- and 35% p- nitrotoluenes was added to a solution of dinitrogen tetroxide in carbon tetrachloride (overall $[N_2O_4]$ = 0.35 mole l^{-1}, [nitrotoluenes] = 0.05 mole l^{-1}). Analysis of the mixture after 400 hours showed an isomer distribution of 61% o-, 6% m- and 33% p- nitrotoluenes.

The possibility of radical reactions between toluene and dinitrogen tetroxide was also investigated. The effect of an added radical trap (Topanol 345) on both reaction rate and isomer proportions was studied and some typical results are shown in Table 5.3. No significant effects were noticable from the addition of the radical trap to the reaction mixtures. Similarly, also shown in table 5.3, addition of urea produced no significant changes in either reaction rate or isomer distribution.

The isomer ratios for several other alkylbenzenes were determined and the results shown in Table 5.4. The results for ethylbenzene again demonstrate a high percentage of the m- nitro isomer, and those obtained with t- butylbenzene show an unusually

TABLE 5.3

EFFECTS OF ADDED UREA AND TOPANOL ON REACTION RATES AND PRODUCTS OF REACTION OF DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE WITH TOLUENE AT 20°C (±1°)

$[N_2O_4]$ /10^{-2}mole l^{-1}	[Toluene] /10^{-2}mole l^{-1}	Mononitration isomer distribution (%)			Nitroproduct yield % a	Time /hrs.
		o-	m-	p-		
2	38	31	53	16	3.0	1
"	"	36	48	16	3.5	2
"	"	36	46	17	4.0	22
"	"	39	44	17	6.0	45
2 b	38	38	49	13	2.0	1
"	"	33	53	14	3.0	2
"	"	38	47	15	4.0	22
"	"	40	44	16	6.0	45
25	200	32	55	13	0.1	0.3
"	"	30	54	16	0.1	0.5
"	"	30	50	19	1.15	2
"	"	37	40	23	2.5	40
"	"	39	27	34	3.3	60
"	"	47	18	35	4.2	140
"	"	47	18	35	11.0	360
25 c	200	32	44	24	0.1	0.3
"	"	32	43	25	0.2	0.5
"	"	35	40	25	1.0	2.0
"	"	44	22	34	3.2	40
"	"	45	17	38	6.0	60
"	"	50	17	33	6.5	140
"	"	50	17	33	7.3	360

a Yield based on dinitrogen tetroxide concentration.

b [Topanol] = 2×10^{-3} mole l^{-1}

c [Urea] = 6×10^{-3} mole l^{-1}

[H_2O] less than 2×10^{-4} mole l^{-1}

TABLE 5.4

NITRATION PRODUCTS IN REACTIONS OF SOME AROMATIC SUBSTRATES WITH DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE AT 20°C

Substrate	[Substrate] /mole l^{-1}	$[N_2O_4]$ /10^{-2}mole l^{-1}	Isomer Distribution (%) [b,c] 2-	3-	4-
Ethylbenzene	3.0	20.2	3.0	92.0	5.0
	0.6	22	5.0	90.0	5.0
t-Butylbenzene	3.0	20.2	30.1	13.9	56.0
	0.6	22	35.0	15.0	50.0
o-Xylene	3.0 [a]	20		42	58
	0.7	5		38	62
	1.5	3.3		30	70
	1.4 [a]	3.2		30	70
	0.4 [a]	3.3		35	65
Chlorobenzene	3.0 [a]	20	34	0.7	65.3
	0.8 [a]	5	30	0.5	69.5
	2.1 [a]	3	17	0.4	82.6
	0.4 [a]	2.3	20	0.6	79.4
	0.4	2.3	21	0.5	78.5

a $[\text{Urea}] = \sim 6 \times 10^{-3}$ mole l^{-1}

b All readings taken after 12 hours and were identical to readings taken after 120 hours.

c All product yields between 0.5 - 5% based on dinitrogen tetroxide concentration.

high percentage of the o- nitro isomer. The results obtained for o-xylene and chlorobenzene were in the range normally obtained in mixed acid nitrations[32].

A study of the intermolecular selectivity between aromatic substrates of dinitrogen tetroxide in carbon tetrachloride was performed by the competition method and the results obtained are shown in Tables 5.5.1 and 5.5.2. Several concentrations of dinitrogen tetroxide were used in these experiments. The unusual intramolecular selectivity associated with toluene was apparent during the competition experiments where low concentrations of dinitrogen tetroxide were used, and high percentages of the m-nitro isomer were observed (Table 5.5.1). No primary kinetic isotope effect was detected from the results obtained with hexadeuteriobenzene. The results obtained from these competition experiments enabled a series of reactivity relative to benzene to be constructed and this is shown in Table 5.6

5.2 DISCUSSION

In the reaction between toluene and dinitrogen tetroxide in carbon tetrachloride a remarkable intramolecular selectivity determined from the isomer distributions of mononitrotoluenes (Table 5.1) was observed. The values obtained are quite outside those normally obtained in the nitration of toluene by conventional nitrating agents over a wide range of conditions[32]. It was shown that the unusual data were a result of nitration by some species in the reaction solution and not of the diversion of mononitrotoluenes to oxidation products.

TABLE 5.5.1

COMPETITION OF AROMATIC COMPOUNDS FOR DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE AT 20°C (±1°)

A. TOLUENE AND BENZENE

[Toluene] /10^{-2}mole l^{-1}	[Benzene] /10^{-2}mole l^{-1}	[N_2O_4] /10^{-2}mole l^{-1}	Rate Ratio Toluene : Benzene	Nitrotoluene isomer proportions (%)		
				o-	m-	p-
300	300	20	32	50.4	9.2	40.4
80	95	5	27	55.4	16.1	28.5
80	95	5	25 [a]	50.0	14.4	35.6
80	95 [b]	5	22	54.8	18.9	26.3
105	170	3.4	48	46.7	31.8	21.5
105	170	3.4	47 [a]	43.7	27.2	29.1
105	85 [b]	3.4	50 [a]	48.2	26.2	25.6
38	45	2.3	44 [a]	33.5	48.0	18.5

a [Urea] ~ 6×10^{-3} mole l^{-1}

b Hexadeuteriobenzene

All measurements made between 100-150 hours after start of reaction

TABLE 5.5.2

COMPETITION OF AROMATIC COMPOUNDS FOR DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE AT 20°C (±1°)

B. OTHER AROMATIC SUBSTRATES

Substrate A	Substrate B	[A] /10^{-2} mole l^{-1}	[B] /10^{-2} mole l^{-1}	[N_2O_4] /10^{-2} mole l^{-1}	Rate Ratio A : B
Mesitylene	Benzene	300	300	20 [a]	266
		60	94	5	287
		60	94	5 [a]	355
		37	37	2.3	200
Mesitylene	Toluene	129	100	3.3	3.6
		129	100	3.3 [a]	4.0
		37	37	2.3	5.9
Mesitylene	o-Xylene	37	37	2.3	2.7
o-Xylene	Benzene	300	300	20	100
o-Xylene	Toluene	70	94	5	4.2
		140	155	3.2 [a]	3.2
		148	100	3.3 [a]	2.5
Chlorobenzene	Benzene	300	300	20 [a]	0.1
		82	94	5	0.2
		211	80	3.3 [a]	0.3
		211	80	3.3	0.2
		40	45	2.3	0.2
p-Dichloro-benzene	Benzene	300	300	20 [a]	0.01
		60	95	5	0.02
		211	80	3.3 [a]	0.04
		40	45	2.4	0.02
Chlorobenzene	p-Dichloro-benzene	40	40	2.3 [a]	8.0

a [Urea] ~ 6×10^{-3} mole l^{-1}

All measurements made between 100-150 hours after start of reactions

TABLE 5.6

RELATIVE REACTIVITY TO DINITROGEN TETROXIDE IN CARBON TETRACHLORIDE BY COMPETITION

Substrate	Rate
Mesitylene	280
O-Xylene	100
Toluene	40
Benzene	1
Hexadeuteriobenzene	1
Chlorobenzene	0.2
p-Dichlorobenzene	0.02

The rate of nitration of toluene with dinitrogen tetroxide in carbon tetrachloride was found to be extremely low (Table 5.1) under the conditions used. The production of some oxidation and side chain nitration products occurs at a rate lower than that of the production of nitrotoluenes. It appears that toluene was particularly susceptible to oxidation under the conditions employed, and this appears to have been the case for the other alkylbenzenes studied where oxidation product formation was also observed. Toluene, however, was usually in a large excess over the dinitrogen tetroxide so that, unless some of the oxidation products were inhibiting the nitration reaction, the rates and isomer data obtained were a true consequence of nitration of toluene by dinitrogen tetroxide.

For toluene, there appear to be two distinct types of reaction. At low concentrations of dinitrogen tetroxide (less than 0.2 mole l^{-1}), the isomer distributions characterised by a high percentage of m- nitrotoluene were observed. When higher concentrations of dinitrogen tetroxide were used, the isomer data showed initially a high percentage of m- nitrotoluene but as the reaction proceeded, the ratio began to resemble an isomer distribution expected for electrophilic attack[32]. At even higher dinitrogen tetroxide concentrations (ca. 1 mole l^{-1}.) the isomer distributions show a low percentage of the m- nitro isomer and would appear to indicate the operation of an electrophilic mechanism (Table 5.1). The rates of reaction at the high dinitrogen tetroxide concentrations are still very slow and reactions are characterised by low yields of nitrotoluenes.

For reactions occurring with low concentrations of dinitrogen tetroxide, the isomer data obtained suggested that a radical rather than an electrophilic process had taken place although the presence of radical traps appeared to have no effect both on the initial rate of nitration or on the isomer distribution obtained. Some recent studies by Suehiro et al.[156] showed the isomer distribution of mononitrotoluenes obtained from a radical nitration of toluene. Using nitrogen dioxide in the presence of benzoyl peroxide at elevated temperatures they reported 4-15% yields of nitrotoluenes in the following isomeric proportions,

o- nitrotoluene	=	6-25%
m- nitrotoluene	=	75-91%
p- nitrotoluene	=	0-3%

The very high percentages of m- nitrotoluene observed were considered a consequence of a radical mechanism of nitration occurring in this case. Although the conditions employed by these workers were quite different from those used in the present work the similarity of the isomer ratios obtained (i.e. high m- nitrotoluene percentages) appear to indicate that a similar radical mechanism may also have occurred in the latter case. The other alkylbenzene substrates studied under similar conditions to those of toluene also appear to give unusual isomeric proportions with the low concentrations of dinitrogen tetroxide. Ethylbenzene in particular (Table 5.4) yields almost exclusively the m- nitro isomer.

The possibility of nitration via nitrosation for dinitrogen tetroxide in carbon tetrachloride with some reactive

substrates has already been reported[35]. However in this work, the absence of a primary kinetic isotope effect and the negligible effects of urea on reaction rates and isomeric data appear to rule out nitrosation as a likely mechanism.

The intermolecular selectivities between aromatic substrates of dinitrogen tetroxide in carbon tetrachloride were also of interest. The toluene : benzene rate ratio for dinitrogen tetroxide in carbon tetrachloride in the present work (Table 5.6) remained fairly constant over the range of concentrations where the change of selectivity between positions in toluene had already been observed. At low dinitrogen tetroxide concentrations, the effective species associates a selectivity between benzene and toluene approaching that of the nitronium ion (1:17-30) with almost an absence of intramolecular selectivity. The values of relative reactivity of the alkylbenzenes studied compared to benzene (Table 5.6) are those expected for an electrophile of comparable selectivity to the nitronium ion, but for the halogenobenzenes the values obtained are those for an electrophile less selective than the nitronium ion. A comparison can be made here of some results obtained for nitronium ion reactions, reported relative rates of nitration of dinitrogen tetroxide in other inert organic solvents and also the results obtained in the present work. These are shown in Table 5.7. The values reported in the present work for substrates more reactive than benzene agree reasonably with those obtained for nitrations in which the nitronium ion is effective. There appear however to be some differences between the data obtained for dinitrogen tetroxide in nitromethane[91] and the present

TABLE 5.7

RELATIVE RATES OF NITRATION IN DIFFERENT NITRATING SYSTEMS AT 25°C

Substrate	NITRATING SYSTEM					
	Nitric acid in 57.2% sulphuric acid [a]	Nitric acid in aq. nitromethane [b]	Nitric acid in aq. sulpholan [b]	Nitric acid in carbon tetrachloride [c]	N_2O_4 in Nitromethane [d]	N_2O_4 in carbon tetrachloride This Work
Benzene	1	1	1	1	1	1
Toluene	17	25	20	17	19 *	40
o-Xylene	-	139	61	-	48	100
m-Xylene	95	146	100	-	57	-
Mesitylene	150	400	350	-	8.7×10^3	280
Chlorobenzene	0.06	0.03 [f]	-	-	-	0.2
p-Dichlorobenzene	6×10^{-4} [e]	-	-	-	-	0.02

a Reference 36
b Reference 33
c Reference 34
d Reference 91
e Reference 147
f Reference 154
* No isomer ratios for toluene are reported in this work.

work. Although the order of reactivity of substrates is the same in both cases, the values obtained for mesitylene for example appear to be quite different. It would be expected however that fortuitous nitrosation would assume increasing importance for the more reactive substrates and this may possibly explain the differences in the values obtained.

From the studies carried out on the reactions of aromatic substrates with dinitrogen tetroxide in carbon tetrachloride, it is possible to comment on this reagent acting as the intermediate in the reactions of tetranitratotitanium (IV) as described in Chapter 2. The most important difference between the results obtained for tetranitratotitanium (IV) and dinitrogen tetroxide in carbon tetrachloride is that the rates of nitration observed for the latter reagent are much too low for it to be effective as a feasible intermediate in the reactions of the nitrato compound. Also the intermolecular selectivity between more reactive substrates for dinitrogen tetroxide in carbon tetrachloride (Table 5.6) is much larger than that observed for tetranitratotitanium (IV) in carbon tetrachloride under comparable conditions (Table 2.12).

It is therefore possible to conclude that dinitrogen tetroxide is not an intermediate in the reactions of tetranitrato-titanium (IV) in carbon tetrachloride.

SECTION III

CHAPTER 6

EXPERIMENTAL

6.1 PREPARATION OF ANHYDROUS TRANSITION-METAL NITRATO COMPOUNDS AND OXIDES OF NITROGEN

6.1.1 TETRANITRATOTITANIUM (IV)

Anhydrous tetranitratotitanium (IV) was prepared by a method similar to that of Field and Hardy[3]. The hydrated hydroxide was obtained by precipitation with aqueous sodium hydroxide from titanium tetrachloride, filtered and dried *in vacuo* at 100°C for several hours. An excess of dinitrogen pentoxide, prepared by dehydrating fuming nitric acid with phosphorous pentoxide, was distilled on to the solid hydrated hydroxide cooled by liquid nitrogen. The mixture was warmed to approximately 30°C to melt the dinitrogen pentoxide, after which reaction was observed. After about 12 hours there were two layers and most of the product had dissolved to form a straw coloured liquid lower layer. The excess of dinitrogen pentoxide was removed *in vacuo*, and the yellow solid which remained eventually lost its coordinated oxides of nitrogen (*ca.* 1-2 hours) to leave a white residue. The pure tetranitratotitanium (IV) was obtained from the residue by vacuum sublimation at 70-80°C and 1×10^{-3} mm. Hg. The white, transparent crystalline tetranitratotitanium (IV) was extremely hygroscopic, and subsequent manipulation was performed under anhydrous conditions in a nitrogen filled dry-box. Purification was performed by resublimation.

ANALYSIS

The product contained 15.9% of titanium (as determined by atomic absorption spectroscopy) and 83.3%(±1.0) of nitrate groups (determined with nitron[157] after hydrolysis in water).

Tetranitratotitanium (IV) required 16.2% of titanium and 83.8% nitrate.

6.1.2 TETRANITRATOZIRCONIUM (IV)

Anhydrous tetranitratozirconium (IV) was prepared by a method similar to that of Field and Hardy[104, 122]. Hydrated zirconyl nitrate was treated with an excess of dinitrogen pentoxide and allowed to react for 12 hours. The excess of dinitrogen pentoxide was removed in vacuo to leave a yellow solid which eventually lost its coordinated nitrogen oxides to leave a white residue. The product was obtained by vacuum sublimation at 100°C and 1×10^{-3} mm. Hg, and purification was performed by resublimation. The colourless crystalline product was extremely hygroscopic and subsequent manipulations were performed in a nitrogen filled dry box.

ANALYSIS

The product contained 73.1% (±1.0) of nitrate (as determined with nitron[157] after hydrolysis in water). Tetranitratozirconium (IV) requires 73.1% nitrate.

6.1.3 NITROSYLTETRANITRATOIRON (III)

Anhydrous nitrosyltetranitratoiron (III) was prepared by a method similar to that of Field and Hardy[104]. Dinitrogen pentoxide was distilled into a liquid nitrogen cooled reaction tube containing clean iron wire. The mixture was warmed to 30°C to melt the dinitrogen pentoxide after which a rapid reaction was observed. After 12 hours, the excess of dinitrogen pentoxide was removed in vacuo and a brown residue remained. The pure nitrosyltetranitratoiron (III) was obtained from this residue by sublimation at 120° (±5°) and 1×10^{-3} mm. Hg. The dark brown crystalline product was very hygroscopic and

subsequent manipulations were performed in a nitrogen filled dry box.

ANALYSIS

The product contained 16.4% iron (as determined by atomic absorption) and 75.3%(±) nitrate (as determined by nitron[157] after hydrolysis in water). Nitrosyltetranitratoiron (III) requires 16.7% iron and 74.2% of nitrate.

It has been reported by Addison and his co-workers[118] that on prolonged heating, the sublimed product becomes $[Fe(NO_3)_4]^- NO_2^+$. This structure however would require a nitrate analysis of 88.7%.

6.1.4 DINITRATOCOPPER (II)

Anhydrous dinitratocopper (II) was prepared by a method similar to that of Field and Hardy[104]. Cleaned copper gauze placed in a reaction tube and cooled with liquid nitrogen was treated with dinitrogen pentoxide. After allowing the reaction mixture to reach room temperature, a rapid reaction was observed which was allowed to proceed for 12 hours. The excess of dinitrogen pentoxide was removed in vacuo and a blue-green solid residue was observed. Vacuum sublimation of this residue at 150° and $1x10^{-3}$ mm Hg produced the pale blue crystalline dinitratocopper (II).

ANALYSIS

The product contained 34.0%(±0.5) of copper (as determined by α-benzoinoxime[157] and atomic absorption spectroscopy) and 65.8%(±1.0) of nitrate (as determined by nitron[157] after hydrolysis in water). Dinitratocopper (II) requires 33.8% copper and 66.2% of nitrate.

6.1.5 DINITROGEN PENTOXIDE

This was prepared in an all glass apparatus by the dehydration of fuming nitric acid with phosphorous pentoxide. Some preliminary experiments were performed using a 'crude' form of the dinitrogen

pentoxide but subsequent work in competition experiments required a pure form of the pentoxide. It was necessary to prepare dinitrogen pentoxide in ozone as described below.

Nitric acid (d = 1·5) was slowly added to phosphorous pentoxide (30-50 g) in a three necked flask through which a continuous stream of ozonised oxygen was passing. The dinitrogen pentoxide was collected in a receiver cooled with solid carbon dioxide. Resublimation of the collected sample was then performed in a stream of ozonised oxygen yielding a colourless crystalline solid. The product was stored in an atmosphere of ozonised oxygen at -80° until required.

6.1.6 DINITROGEN TETROXIDE

Dinitrogen tetroxide was obtained from Matheson Gas Products Ltd. (99.5% pure) and was normally used without further purification.

6.2 MATERIALS

Carbon tetrachloride (Analar) was dried over Type 4A molecular sieves (1/16" pellets) and stored in a dry box. Water content (usually $\sim 2 \times 10^{-4}$) was monitored by measuring the absorption at 5300 cm^{-1} [158]. Fuming nitric acid and phosphorous pentoxide used to generate dinitrogen pentoxide were both Analar reagents.

6.2.1 AROMATIC COMPOUNDS

Benzene, toluene and nitrobenzene were AnalaR reagents. Mesitylene, the xylenes, ethylbenzene, t-butylbenzene and anisole were all laboratory grade reagents purified by distillation. All these reagents were dried over Type 4A molecular sieves (1/16" pellets). Biphenyl was recrystallized from aqueous ethanol. Hexadeuteriobenzene and pentadeuterionitrobenzene were commercially available spectroscopic grade reagents and were used without further purification.

Nitromesitylene, nitrotoluenes, nitroxylenes, nitroethylbenzenes, nitro-t-butylbenzenes, nitrochlorobenzenes, nitrobromobenzenes, nitrobiphenyls and nitroanisoles were all suitably purified commercial reagents.

6.2.2 HETEROAROMATIC COMPOUNDS

Pyridine was Analar grade and dried over Type 4A (1/16" pellets). Quinoline and isoquinoline were redistilled laboratory grade reagents.

6.2.2.1 NITROPYRIDINES

2-, 3- and 4- nitropyridines were prepared by a method similar to that of Kirpal and Bohem[159].

2.5 g of the corresponding amino pyridine in 12.5 ml of concentrated sulphuric acid was added to a cooled mixture of 50 ml of fuming sulphuric acid (S.G.1.93) and 25 ml of hydrogen peroxide. After 24 hours , the reaction mixture was added to 200 ml of distilled water, and neutralised with sodium bicarbonate.

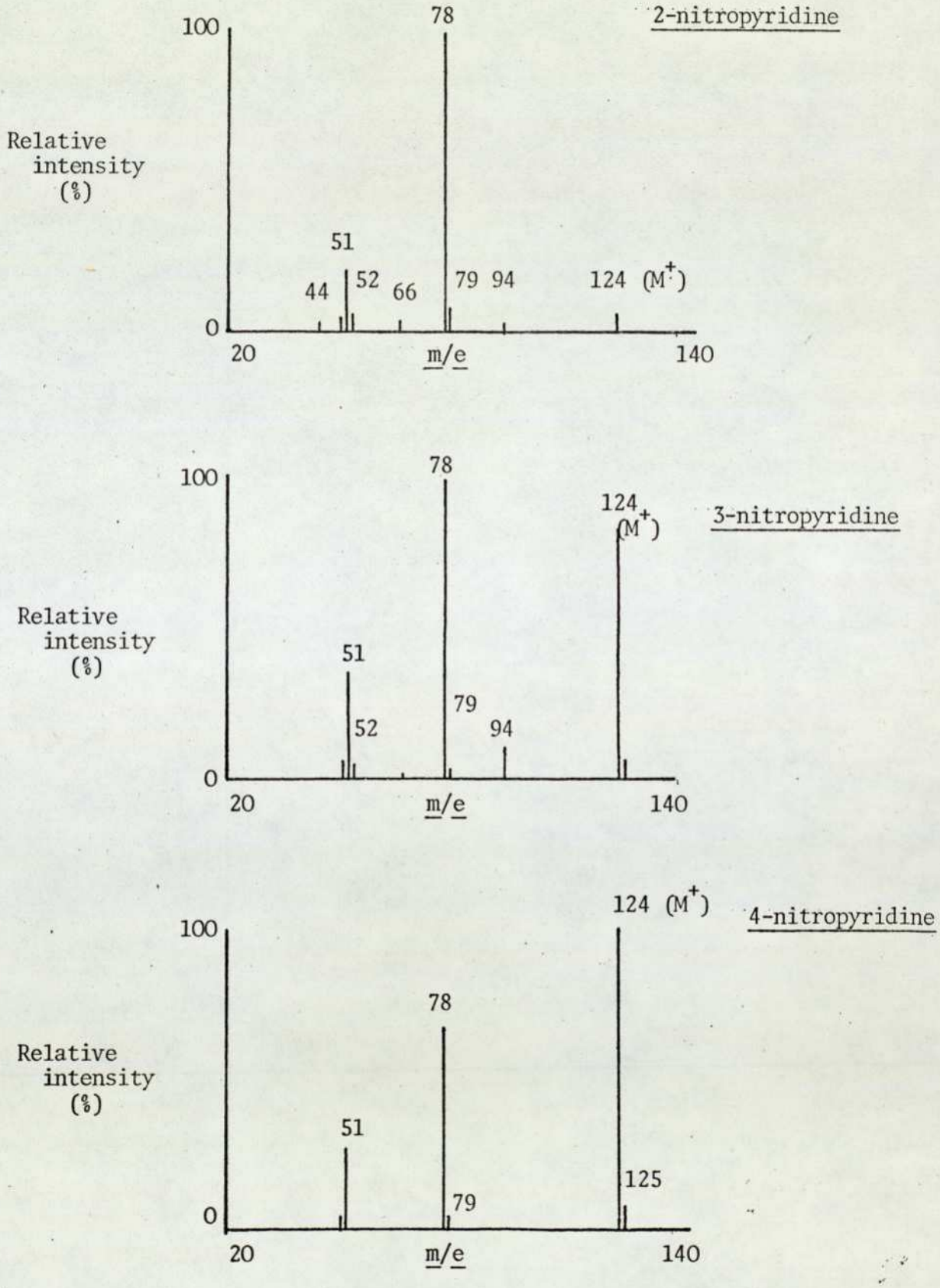
The reaction solution was extracted with chloroform (5x50 ml) and after evaporation, yellow crystalline solids were obtained. The produce was recrystallized twice from an ethanol-water solvent pair (50/50) and dried in vacuo. Product purity was determined by gas-liquid chromatography. The identity of the nitropyridine was confirmed by a comparison of melting points with those previously reported and also by mass spectrometry (6.5).

The melting points are shown below:

Nitropyridine	Observed M.Pt(^{o}C)	Literature M.Pt(^{o}C)	Ref.
2-nitro	69 70^{o}	71^{o}	160
3-nitro	36^{o}	41^{o}	160
4-nitro	46 - 48^{o}	50^{o}	160

The mass spectral breakdown patterns for the three nitropyridines are shown in Fig. 6.1 The molecular weight of the nitropyridines prepared was also obtained by mass spectrometry. The measured

Figure 6.1 Mass Spectra of 2-, 3-, and 4- Nitro Pyridines



value for each of the products was found to be 124.0272, and the calculated molecular weight was 124.0273.

6.2.2.2 NITROQUINOLINES

Samples of 3- and 7-nitroquinolines were kindly supplied by Professor K. Schofield (Exeter University). Samples of 5-, 6- and 8-nitroquinolines were commercial samples recrystallised from ethanol.

6.2.2.3 NITROISOQUINOLINES

A sample of 5-nitroisoquinoline was kindly supplied by Professor K. Schofield. 8-Nitroisoquinoline was known to be produced as a reaction product (together with 5-nitroisoquinoline) in a mixed acid nitration of isoquinoline by the method of Dewar and Maitlis[136], and the reaction was therefore repeated in this present work to enable gas chromatography data to be obtained for this isomer.

2g of fuming nitric acid (d = 1.5) dissolved in 5 ml of sulphuric acid (d = 1.84) was gradually added to a solution containing 3g of isoquinoline dissolved in 10 ml of sulphuric acid at room temperature. After 30 minutes the mixture was poured onto ice. The mononitro fraction was separated by partial basification (pH 2·5) with sodium hydroxide solution followed by chloroform extraction (5x50 ml). The solution was shaken with magnesium sulphate, filtered and the total volume reduced to about 10 ml by evaporation. This solution was then analysed by gas-liquid chromatography (Section 6.4). Two products were obtained, from which the 5-nitro isomer could be identified by comparison with the authentic sample. The second product was assumed to be the 8-nitroisoquinoline. The isomer proportions observed were as follows,

5-nitroisoquinoline = 85.3% (±2.0)

8-nitroisoquinoline = 14.7% (±2.0)

6.2.3 ALIPHATIC COMPOUNDS

n-Pentane was a commercially available spectroscopic-grade reagent suitably distilled before use.

6.2.4 OTHER COMPOUNDS

Urea and tetraethylammonium nitrate were commercially available compounds used without further purification. Topanol 354 (2, 6-di-t-butyl-4-methoxyphenol) was a commercially available reagent (I.C.I. Ltd. 99% pure) and was used without further purification.

6.3 KINETIC AND PRODUCT MEASUREMENTS

6.3.1 Tetranitratotitanium (IV)

A solution of tetranitratotitanium (IV) in carbon tetrachloride (25 ml) was thermostatted inside a drybox, and the required amount of substrate was added by pipette or microsyringe. In the competition experiments, usually equimolar mixtures of substrates were taken and added to the reagent solution. All reactions were carried out at $20^{\circ}C(\pm 1^{\circ})$.

The mixtures were briefly shaken, or in some cases stirred throughout the course of the reaction. The reaction was followed by removal of small samples (0.5 ml) at suitable times. These were then treated with water to prevent further reaction, and the organic layer was analysed after addition of a suitable internal standard, by quantitative gas-liquid chromatography (See section 6.4).

Similar procedures were adopted for reactions of this reagent with heteroaromatic compounds. Owing to the solubility in water of some of the nitroproducts however, analysis was normally performed without its addition to the small samples removed from the reaction mxiture.

Each reaction was accompanied by the production of a solid

precipitate, and this fact prevented any meaningful spectroscopic kinetic analyses to be made. Attempts to find alternative solvents in which the solid would not be precipitated proved unsuccessful.

For some reactions, the solid produced was filtered off in the dry box, washed with carbon tetrachloride (100 ml) and dried in vacuo for several hours. Analysis of this residue consisted of estimation of titanium content by atomic absorption measurements, and the determination of nitrate content by the nitron method.

6.3.2 NITRATO COMPOUNDS OF ZIRCONIUM, IRON AND COPPER

Samples of aromatic and heteroaromatic substrates (5-10 ml) were shaken with weighed amounts (0.1-0.5 g) of the nitrato compound at room temperature ($20^{o}(\pm 1^{o})$). Most reactions appeared to occur in about 10 seconds (heteroaromatics after approximately 1 minute), although the solutions were usually left for about 30 minutes before analysis. After the addition of a known amount of an internal standard, the products were analysed quantitatively by gas-liquid chromatography (Section 6.4).

Identification of the nitroproducts was carried out by comparison of retention times with those of authentic samples. In the case of nitroquinoline, the identity of the products was confirmed by gas-chromatography-mass spectrometry techniques.

6.3.3 DINITROGEN PENTOXIDE

Standard solutions of dinitrogen pentoxide in carbon tetrachloride (20-25 ml) were kept at the appropriate temperatures (5^{o}-20^{o}C), and the required amount of substrate, or in the competition experiments, equimolar amounts of the substrates, were added to the reagent solution. The mixtures were briefly shaken throughout the reaction.

Some reactions were followed by removal of small samples (0.5 ml) at suitable times. These were washed with water and the organic

layer was analysed by quantitative gas-liquid chromatography (See section 6.4).

6.3.3.1 NITROUS ACID DETERMINATION

A 1 ml sample from the nitrating solution was added to 1 ml of a 1% ($^{W}/_{V}$) aqueous solution of sulphanilic acid, and 10 ml of water. After 10 minutes, 1 ml of a saturated solution of α-naphthol (1 g in 100 ml water) was added, and the whole solution made up to 25 ml with 0.880 ammonia solution. The optical density of this solution was then determined at 523 nm. in a 1 cm. cell using water as a blank. By comparison with a calibration chart of standard solutions of sodium nitrite, it was found that an optical density of 0.15 at this wavelength indicates that the concentration of nitrous acid in the original solution was 1.0×10^{-4} mole l^{-1}

6.3.4 DINITROGEN TETROXIDE

Standard solutions of dinitrogen tetroxide (0.01-1.2 mole l^{-1}) in carbon tetrachloride (25 ml) were thermostatted inside a dry box. Suitable quantities of the substrate, or in competition experiments, equimolar mixtures of the substrates, were added to the reagent solution. All reactions were carried out at ~20°C. The mixtures were briefly shaken at 5 minute intervals. In some cases, the reaction was followed by removal of small quantities (0.5 ml) at suitable times. All samples were washed with water and after addition of a suitable internal standard the organic layer was analysed by quantitative gas-liquid chromatography, and product identity confirmed by mass spectrometry.

6.4 GAS CHROMATOGRAPHY

All gas chromatography was performed on a Pye 104 Chromatograph fitted with a flame ionisation detector which used hydrogen (15 p.s.i. inlet pressure) in an atmosphere of compressed air (10 p.s.i. inlet pressure). Nitrogen was used as the carrier gas at a flow rate of 45

or 60 ml/min. The columns retention times and internal standards used for analysis of particular nitrocompounds are shown in Tables 6.1, 6.2 and 6.3.

The yields of nitroproducts were calculated by a method based on relative response factors. The relative response factors of the nitroproducts were measured with respect to a given internal standard which was added to the sample prior to analysis.

The area (Ap) of a given peak is proportional to the concentration (Cp) of the respective solute, i.e.

$$A = fp.\ Cp$$

where f_p is a constant, and depends on the chemical characteristics of component p. Therefore, using this relationship, it is possible to obtain expressions for two peaks of components s and x, where s is a standard, and x is to be determined.

$$A_x = fs.Cs \quad \text{and}$$

$$A_x = fx.Cx$$

Rearranging, it is possible to write

$$\frac{Cx}{Cs} = \frac{Ax}{As} \times \frac{fs}{fx} \qquad - \quad (1)$$

The constants ratio $\left[{}^{fs}/_{fx} \right]$ can be obtained from standard solutions of both internal standard and the nitroproduct.

In the present work, the internal standards were chosen such that the factor fs/fx was approximately 1.0, so that the concentration of the nitroproduct in a reaction (Cx) could be easily obtained from application of equation (1).

Peak areas were either cut out and weighed or measured directly (by height x width at half height).

6.5 MASS SPECTROMETRY

Accurate mass measurements and fragmentation spectra were obtained from the Physico-Chemical Measurements Unit, using an A.E.1 MS 902 spectrometer. The electron energy was 70eV.

6.6 ATOMIC ABSORPTION SPECTROSCOPY

Analyses of titanium, iron and copper in the anhydrous nitrate compounds prepared were made on a Perkin-Elmer 290B spectrophotometer.

6.7 INFRA-RED SPECTROSCOPY

Spectra of solutions of tetranitratotitanium (IV) in carbon tetrachloride were obtained on a Perkin-Elmer 457 spectrometer. The most convenient cells for this work were disposable silver chloride infra-red cells (Research and Industrial Instruments Company, Ltd.). The cell lengths varied from 0.1mm - 0.5 mm. These cells could be filled by syringe inside a drybox and then sealed efficiently.

FIGURE 6.1

KEY TO COLUMNS USED IN FIGURES 6.2, 6.3

No.	Columns
A	- 5ft. x ¼", (1½%) OV225 Silicone on universal support (60-80 mesh)
B	- 5ft. x ¼", (10%) SE30 Silicone on universal support (60-85 mesh)
C	- 5ft. x ¼", (15%) Polyethylene glycol (20 M) on universal support (60-85 mesh)
D	- 1½ ft. x ¼", SE30 Silicone on universal support (60-85 mesh)

FIGURE 6.2

SEPARATION CONDITIONS FOR AROMATIC NITROPRODUCTS

NITROPRODUCT	Column a	Column Temp. °C	Carrier Gas Flow Rate $ml\ min^{-1}$	Retention Time min	INTERNAL STANDARD
Nitrobenzene $C_6D_5NO_2$	A	115°	40	7.3	m-Nitrotoluene
o-Nitrotoluene				10.0	
m- "	A	115°	40	12.5	Nitrobenzene
p- "				14.0	
o-Ethylnitrobenzene				6.8	
m- "	A	130°	60	9.5	Nitrobenzene
p- "				11.5	
o-t-Butylnitrobenzene				8.0	
m- "	A	130°	60	11.5	Nitrobenzene
p- "				15.0	
3-Nitro-o-Xylene	A	150°	60	6.5	m-Nitrotoluene
4-Nitro-o-Xylene				9.2	
2-Nitro-m-Xylene	A	150°	60	3.5	m-Nitrotoluene
4-Nitro-m-Xylene				5.5	
Nitromesitylene	A	130°	60	10.5	m-Nitrotoluene
2-Nitroanisole	B	165°	60	7.5	Nitrobenzene
4-Nitroanisole				9.0	
2-Nitrobiphenyl	B	175°	60	14.5	Nitrobenzene
4-Nitrobiphenyl				27.0	
o-Chloronitrobenzene				14.0	
m- "	C	178°	60	12.3	Nitrobenzene
p- "				11.5	
o-Bromonitrobenzene				25.5	
m- "	C	150°	60	22.0	Nitrobenzene
p- "				20.0	
2,5-Dichloronitro-benzene	C	185°	60	21.0	m-Nitrotoluene

a - See Figure For Column Key

FIGURE 6.3

SEPARATION CONDITIONS OF HETEROAROMATIC NITROPRODUCTS

Nitroproduct	column a	column temp ^{o}C	carrier gas flow rate ml. min^{-1}	retention time min	internal standard
2-nitropyridine				50	
3- "	C	160°	60	18.6	nitrobenzene
4- "				7.4	
3-nitroquinoline				3.0	
5- "				2.5	yields
6- "	D	148°	60	3.5	calculated by
7- "				4.0	calibration
8- "				6.0	of chromatograph with product.
5-nitroisoquinoline	A	160°	40	23	
8- "				26	

a - see figure for column key

REFERENCES

1. a) A. F. Holleman, Die direckte Einführung von Substituenten in den Benzolkern, 1910, Liepzig : Veit.

   b) A. F. Holleman, Chem. Rev., 1925, 1, 187.

2. C. C. Addison and N. Logan, "Advances in Inorganic Chemistry and Radiochemistry," 1964, Vol 6, p.72 -142, Academic Press.

3. B. O. Field and C. J. Hardy, J. Chem. Soc., 1963, 5278.

4. H. von Euler, Annalen, 1903, 330, 296.

5. a) E. D. Hughes, C. K. Ingold and R. I. Reed, Nature, 1946, 158, 448.

   b) R. J. Gillespie and D. J. Millen, Quart. Rev. Chem. Soc., 1948, 2, 227.

6. a) S. Féneánt and J. Chédin, C. r. Lebd. Séanc. Acad. Sci., 1947, 224, 1008, Paris.

   b) W. R. Angus and A. H. Leckie, Proc. Roy. Soc. Lond., 1935, A149, 327.

   c) O. Redlich and L. E. Nielsen, J. Amer. Chem. Soc., 1943, 65, 654.

7. R. A. Marcus and J. M. Frescoe, J. Chem. Phys., 1957, 27, 564.

8. a) R. J. Gillespie, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1950, 2552.

   b) T. J. Lewis, Ph.D. Thesis, University of London, 1954.

9. W. H. Lee and D. J. Millen, J. Chem. Soc., 1956, 4463.

10. E. D. Hughes, C. K. Ingold and R. I. Reed, J. Chem. Soc., 1950, 2400.

11. a) C. A. Bunton, E. A. Halevi and D. R. Llewellyn, J. Chem. Soc., 1952, 4913.

b) C. A. Bunton and E. A. Halevi, J. Chem. Soc., 1952, 4917.

c) C. A. Bunton and G. Stedman, J. Chem. Soc., 1958, 2420.

12. A. Hantzsch, Z. Phys. Chem., 1908, 65, 41.

13. R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold and E. R. A. Peeling, J. Chem. Soc., 1950, 2504.

14. a) A. Saposchnikow, Z. Phys. Chem., 1904, 49, 677. ibid, 1905, 51, 609; ibid, 1905, 53, 225.

b) F. Bergius, Z. Phys. Chem., 1910, 72, 338.

15. R. J. Gillespie and S. Wasif, J. Chem. Soc., 1953, 221.

16. a) D. J. Millen, J. Chem. Soc., 1950, 2600.

b) C. K. Ingold, D. J. Millen and H. G. Poole, J. Chem. Soc., 1950, 2576.

17. a) A. Hantzsch, Ber., 1925, 58, 958.

b) A. Hantzsch, and K. Berger, Ber., 1928, 61, 1328.

c) D. R. Goddard, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1950, 2559.

18. M. Schmeisser and S. Elischer, Z. Naturforsch., 1952, 7b, 583.

19. S. J. Kuhn and G. A. Olah, J. Amer. Chem. Soc., 1961, 83, 4570.

20. F. G. Cox, G. A. Jeffery and M. R. Truter, Nature, 1948, 162, 259.

21. D. J. Millen, J. Chem. Soc., 1950, 2606.

22. a) H. Martinsen, Z. Phys. Chem., 1905, 50, 385.

b) H. Martinsen, Z. Phys. Chem., 1907, 59, 605.

23. R. Vandoni, Mem. Services Chim. État, 1944, 31, 83, 87.

24. N. S. Bayliss and D. W. Watts, Aust. J. Chem., 1963, 16, 943.

25. A. M. Lowen, M. A. Murray and G. Williams, J. Chem. Soc., 1950, 3318.

26. a) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, J. Amer. Chem. Soc., 1955, 77, 3044.

b) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, J. Amer. Chem. Soc., 1959, 81, 2344.

27. L. P. Hammett and A. J. Deyrup, J. Amer. Chem. Soc., 1932, 54, 2721.

28. F. H. Westheimer and M. S. Kharasch, J. Amer. Chem. Soc., 1946, 68, 1871.

29. R. G. Coombes, R. B. Moodie and K. Schofield, J. Chem. Soc. (B), 1968, 800.

30. a) I. M. Koltoff and A. Willman, J. Amer. Chem. Soc., 1934, 56, 1007.

b) E. Susz, B. Briner and P. Favarger, Helv. Chim. Acta., 1935, 18, 375.

c) E. G. Taylor and A. G. Follows, Can. J. Chem., 1951, 29, 461.

31. G. Benfold and C. K. Ingold, J. Chem. Soc., 1938, 929.

32. J. G. Hoggett, R. B. Moodie, J. R. Penton and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, 1971.

33. J. G. Hoggett, R. B. Moodie and K. Schofield, J. Chem. Soc. B, 1969, 1.

34. R. G. Coombes, J. Chem. Soc. B, 1969, 1256.

35. a) T. G. Bonner, R. A. Hancock, G. Yousif and (in part) F. R. Rolle, J. Chem. Soc. B, 1969, 1237.

b) T. G. Bonner, R. A. Hancock and F. R. Rolle, Tetrahedron Letters, 1968, 1665.

36. S. R. Hartshorn, R. B. Moodie, K. Schofield and M. J. Thompson, J. Chem. Soc. B, 1971, 2447.

37. J. G. Hoggett, R. B. Moodie and K. Schofield, Chem. Commun., 1969, 605.

38. S. R. Hartshorn and K. Schofield, Prog. Org. Chem., 1973, 8, 278.

39. A. Fischer, A. J. Read and J. Vaughan, J. Chem. Soc., 1964, 3691.

40. a) R. O. C. Norman and G. K. Radda, J. Chem. Soc., 1961, 3030.

b) J. R. Knowles and R. O. C. Norman, J. Chem. Soc., 1961, 3888.

41. M. A. Paul, J. Amer. Chem. Soc., 1958, 80, 5329.

42. J. H. Ridd, 'Studies on Chemical Structure and Reactivity,' Metheun, London, 1966, 133.

43. S. R. Hartshorn, J. G. Hoggett, R. B. Moodie, K. Schofield and M. J. Thompson, J. Chem. Soc. B, 1971, 2461.

44. a) N. C. Marziano, J. H. Rees and J. H. Ridd, Paper presented at Inaugural Meeting of Organic Reaction Mechanisms Group of the Chemical Society, University of Kent at Canterbury, 1973.

b) J. Chem. Soc. Perkin II, 1974, 600.

45. A. Hantzsch, Z. Phys. Chem., 1930, 1961.

46. G. A. Olah and S. J. Kuhn, 'Friedel Crafts and Related Reactions,' Interscience, New York, 1964, vol III, part 2, p. 1393.

47. G. A. Olah, S. H. Flood and J. C. Evans, J. Amer. Chem. Soc., 1962, 84, 3687.

48. a) J. Jones and J. Jones, Tetrahedron Letters, 1964, 2117.

b) G. A. Olah, J. A. Olah and N. A. Overchuk, J. Org. Chem., 1965, 30, 3373.

49. G. A. Olah, S. J. Kuhn and S. H. Flood, J. Amer. Chem. Soc., 1961, 83, 4571.

50. G. A. Olah, S. J. Kuhn and S. H. Flood, J. Amer. Chem. Soc., 1961, 83, 4581.

51. A. W. Francis, J. Amer. Chem. Soc., 1926, 48, 655.

52. W. S. Tolgyesi, Can. J. Chem., 1965, 43, 343.

53. a) J. H. Ridd, Accts. Chem. Res., 1971, 4, 248.

b) P. F. Christy, J. H. Ridd and N. D. Stears, J. Chem. Soc. B., 1970, 797.

54. H. Zollinger, In 'Advances in Physical Organic Chemistry,' 1964 vol. 2, ed. V. Gold, Academic Press, London.

55. L. Melander (a) 'Isotope effects on reaction rates,' 1960, New York, Ronald Press.

b) Ark. Kemi., 1950, 2, 211.

56. a) C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, J. G. Minkoff and R. I. Reed, J. Chem. Soc., 1950, 2628.

57. N. S. Bayliss, R. Dingle, D. W. Watts and R. J. Wilkie, Aust. J. Chem., 1963, 16, 933.

58. a) J. D. S. Goulden and D. J. Millen, J. Chem. Soc., 1950, 2620.

b) D. J. Millen and D. Watson, J. Chem. Soc. 1957, 1369.

59. a) J. Chédin, C.r. hebd. Séanc. Acd. Sci., Paris, 1935, 200, 1397.; ibid, 1935, 201, 552.

b) J. Chédin and J. C. Pradier, C. r. hebd. Séanc. Acad. Sci., 1936, 203, 722.

60. a) F. Daniels, J. Amer. Chem. Soc., 1925, 47, 2856.

b) C. K. Ingold and D. J. Millen. J. Chem. Soc., 1950, 2612.

61. P. E. Grison, K. Ericks and J. L. de Vries, Acta Cryst., 1950, 3, 290.

62. a) E. Spreckels, Ber., 1919, 52B, 315.

b) K. E. Cooper and C. K. Ingold, J. Chem. Soc., 1927, 836.

63. G. E. Gibson, Proc. Roy. Soc. Edin., 1908, 28, 705.

64. Lothar Meyer, Ber., 1818, 22, 23.

65. E. Bamberger, Ber., 1894, 27, 584.

66. E. Hoff, Annalen, 1900, 311, 91.

67. F. Russ and E. Pokorny, Monatsh, 1913, 34, 1051.

68. F. Daniels and A. C. Bright, J. Amer. Chem. Soc., 1920, 42, 1131.

69. L. B. Haines and H. Adkins, J. Amer. Chem. Soc., 1925, 47, 1419.

70. E. Spreckels, Ber., 1919, 52B, 315.

71. A. Klemenc and A. Schüller, Z. anorg. allg. Chem., 1924, 141, 321.

72. V. Gold. Ph.D. Thesis, Univ. London 1945.

73. V. Gold, E. D. Hughes, C. K. Ingold and G. H. Williams, J. Chem. Soc., 1950, 2452.

74. K. Halvarson and L. Melander, Ark. Kemi, 1957, 11, 77.

75. V. Gold, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1950, 2467.

76. M. E. Kurz, L. T. A. Yang, E. P. Zahora and R. C. Adams, J. Org. Chem., 1973, 38, 2271.

77. J. S. Broadley and J. M. Robertson, Nature, 1949, 164, 915.

78. A. G. Whittaker, J. Chem. Phys., 1956, 24, 780.

79. a) R. G. Snyder and I. C. Hisatsune, J. Mol. Spectroscopy, 1957, 1, 139.

b) R. N. Wiener and E. R. Nixon, J. Chem. Phys., 1957, 26, 906.

80. G. Jander, H. Spandau and C. C. Addison in "Chemistry in Non-aqueous ionizing solvents" Pergamon, 1967. Vol. III.

81. A. Hasenbach, J. Prakt. Chem., 1871, 4, 17.

82. A.Leeds, Ber., 1880, 13, 1993.

83. H. Wieland, Ber., 1921, 54, 1776.

84. a) A. Schaarschmidt and E. Smolla, Ber., 1924, 57, 32.

b) A. Schaarschmidt, H. Balzerkewicz and J. Gante, Ber.,1925, 58, 499.

85. A. V. Topchiev, 'Nitration of hydrocarbons and other organic compounds,' Pergamon Press, 1959.

86. L. A. Pinck, J. Amer. Chem. Soc., 1927, 49, 2536.

87. M. Battegay, Bull. Soc. Chim., 1928, 43, 109.

88. A. Schaarschmidt, Ber., 1924, 57, 2065.

89. A. I. Titov, Zh. obshch. Khim., 1937, 7, 667.

90. J. C. Evans, H. W. Rinn, S. J. Kuhn and G. A. Olah, Inorg. Chem., 1964, 3, 837.

91. G. R. Underwood, R. S. Silverman and A. Vanderwalde, J. Chem. Soc. Perkin II, 1973, 1177.

92. A. I. Titov, Tetrahedron, 1963, 19, 557.

93. M. Schmeisser and K. Brandle, Angew. Chem., 1961, 73, 388.

94. C. C. Addison and B. J. Hathaway, Proc. Chem. Soc., 1957, 19.

95. C. C. Addison and B. M. Gatehouse, J. Chem. Soc., 1960, 613.

96. C. C. Addison and A. Walker, J. Chem. Soc., 1963, 1220.

97. C. C. Addison, J. Lewis and R. Thompson, J. Chem. Soc., 1951, 2829.

98. C. C. Addison, H. A. J. Champ, N. Hodge and A. H Norbury, J. Chem. Soc., 1964, 2354.

99. C. C. Addison and A. Walker, Proc. Chem. Soc., 1961, 242.

100. C. C. Addison, B. J. Hathaway and N. Logan, Proc. Chem. Soc., 1958, 51.

101. C. C. Addison, 'Advances in Chemistry,' Amer. Chem. Soc., Special Publication, No. 14, 1962, 131.

102. A. Guntz and F. Martin, Bull. Soc. Chim. France, 1909, 5, 1004.

103. M. Schmeisser, Angew, Chem., 1955, 67, 493.

104. B. O. Field and C. J. Hardy, J. Chem. Soc., 1964, 4428.

105. C. C. Addison and D. J. Chapman, J. Chem. Soc., 1964, 539.

106. C. C. Addison, P. M. Boorman and N. Logan, J. Chem. Soc. A, 1966, (10), 1434.

107. C. C. Addison and B. G. Ward, Chem. Commun., 1966, 22, 819.

108. C. C. Addison and W. B. Simpson, J. Chem. Soc., 1965, 598.

109. C. C. Addison, G. S. Brownlee and N. Logan, J. Chem. Soc. Dalton, 1972, 1440.

110. L. N. Komissarova, G. Pustikina, N. P. Kharameeva and V. I. Spitzyn, Z. Anorg. Allgem. Chem., 1966, 344, (1-2), 76.

111. D. W. Johnson and D. Sutton, Can. J. Chem., 1972, 50, 3326.

112. R. J. Fereday, N. Logan and D. Sutton, Chem. Commun.,1968, 271.

113. C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, Quart. Rev. Chem. Soc., 1971, 25(2), 289.

114. C. D. Garner and S. C. Wallwork, J. Chem. Soc. A, 1966, 1496.

115. C. C. Addison, Coord. Chem. Rev., 1966, 1, 58.

116. S. C. Wallwork, Proc. Chem. Soc., 1959, 311.

117. B. Duffin and S. C. Wallwork, Acta. Cryst., 1963, 16, A33.

118. C. C. Addison, P. M. Boorman and N. Logan, J. Chem. Soc., 1965, 4978.

119. J. B. Menke, Rec. Trav. Chim., 1925, 44, 141, 269.

120. G. Bacharach, J. Amer. Chem. Soc., 1927, 49, 1552.

121. W. Davey and J. R. Gwilt, J. Chem. Soc., 1950, 204.

122. B. O. Field and C. J. Hardy, Proc. Chem. Soc., 1962, 76.

123. D. W. Amos, D. A. Baines and G. W. Flewett, Tetrahedron Letters, 1973, 3191.

124. C. C. Addison, D. W. Amos, D. Sutton and W. H. H. Hoyle, J. Chem. Soc., A, 1967, 808.

125. C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' G. Bell and Sons, London, 2nd Edition, 1969, 335.

126. F. Friedl, Ber., 1912, 45, 428.

127. F. Friedl, Chem. Ztg., 1913, 36, 589. and Monatsh., 1913, 34, 759.

128. E. Murmann, Osterr. Chem. Ztg., 1923, 26, 141.

129. A. Kirpal and E. Reiter, Ber., 1925, 58, 699.

130. H. J. Den Hertog and J. Overhoff, Rec. Trav. Chim., 1930, 49, 552.

131. P. P. Shorygin and A. V. Topchiev, Ber., 1936, 69, 1874.

132. D. A. Davenport, H. J. Buckhart and H. H. Sisler, J. Amer. Chem. Soc., 1953, 75, 4175.

133. P. W. Foster, Ph.D. Thesis, Univ. of London, 1954.

134. M. J. S. Dewar and P. M. Maitlis, Chem. and Ind., 1955, 685.

135. L. F. Fieser and E. B. Hershberg, J. Amer. Chem. Soc., 1940, 62, 1640.

136. M. J. S. Dewar and P. M. Maitlis, J. Chem. Soc., 1957, 2521.

137. D. H. G. Crout, J. R. Penton and K. Schofield, J. Chem. Soc.,(B), 1971, 1254.

138. M. W. Austin and J. H. Ridd, J. Chem. Soc., 1963, 4204.

139. R. B. Moodie, K. Schofield and M. J. Williamson, 'Nitro Compounds', (Proceedings of the International Symposium, Warsaw, 1963), Pergamon, London, 1964, p. 89.

140. G. Bacharach, A. H. Haut, and L. Caroline, Rec. Trav. Chim., 1933, 52, 413.

141. P. P. Schorygin and A. V. Topchiev, Ber., 1936, 69, 1874.

142. J. R. Laville and W. A. Waters, J. Chem. Soc., 1954, 400.

143. M. J. S. Dewar and P. M. Maitlis, J. Chem. Soc., 1957, 944.

144. J. H. Ridd, 'Physical Methods in Heterocyclic Chemistry,' (ed. A. R. Katritzky). Academic Press, New York, 1963.

145. K. Schofield, Quart. Rev. Chem. Soc., 1950, 4, 382.

146. E. Ochiai, J. Pharm. Soc. Japan, 1945, 65, 73;
ibid, 1951, 71, 1385.
ibid, 1953, 73, 660.

147. R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie and K. Schofield, J. Chem. Soc., B, 1970, 347.

148. B. C. Challis, R. J. Higgins and A. J. Lawson, J. Chem. Soc. Perkin II, 1972, 1831.

149. R. Taylor, Tetrahedron Letters, 1972, 1755.

150. M. Choca, J. R. Ferraro, and K. Nakamoto, J. Chem. Soc. Dalton, 1972, 2297.

151. R. V. Biagetti, W. G. Bottjer and H. M. Haendler, Inorg. Chem., 1966, 5, 379.

152. N. Logan and W. B. Simpson, Spectrochem. Acta., 1965, 21, 857.

153. R. G. Coombes and L. W. Russell, J. Chem. Soc. B, 1971, 2443.

154. M. L. Bird and C. K. Ingold, J. Chem. Soc., 1938, 918.

155. T. G. Bonner and R. A. Hancock, J. Chem. Soc. B, 1966, 972.

156. T. Suehiro, M. Hirai and T. Kaneko, Bull. Chem. Soc. Japan., 1971, 44 (5), 1402.

157. A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd Edition, Longmans Press.

158. a) B. D. Pearson, J. E. Ollerenshaw, Chem. and Ind., 1966, 370.

b) R. L. Meeker, F. Critchfield and E. T. Bishop, Analyt. Chem., 1962, 34, 1510.

159. A. Kirpal and W. Bohem, Ber., 1937, 64, 767.

160. I. Heilbron and H. M. Bunbury, "Dictonary of Organic Compounds," Eyre and Spottiswoode, London, 1953.