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SINGLE AND TWO PHASE NITRATION
OF MONONITROTOLUENES

by

KEITH ANDREW FLEMING

A Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology, November, 1981.

Supervisor: Dr. A.N. Strachan

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TO MY WIFE AND PARENTS

ACKNOWLEDGEMENT

My sincere thanks are due to Dr. A.N. Strachan for his guidance, inspiration and friendship throughout the duration of the research described in this thesis.

I would also like to thank: my wife, without whose unwavering patience and encouragement this thesis may never have been completed; my fellow research workers, in the Chemistry Department, for their companionship; Professor R.F. Phillips for the provision of laboratory facilities; the technical staff of the Department for their help and advice; Air Products Incorporated for the provision of a research grant; and finally Mrs. A. Humphrey for typing this thesis.

SUMMARY

The homogeneous rates of nitration of ortho-, meta- and para-nitrotoluene in aqueous sulphuric acid have been determined over a range of temperatures. Some difficulties were experienced in measuring the rate of nitration of ortho-nitrotoluene because of competition between nitration of the latter and one or more side-reactions, the exact nature of which were not determined. Some possible explanations for this phenomenon are discussed. Combination of the experimental rate data with those published in the literature has enabled predictions to be made of values for the observed second order rate constant k_2 as a function of temperature and H_2SO_4 - H_2O composition.

The ratio of the dinitrotoluene isomers formed in the nitration of ortho-nitrotoluene has been determined as a function of temperature and H_2SO_4 - H_2O composition. The nitration rate and product distribution data have been combined with published data to predict the effect of changes in operating conditions on the products obtained from commercial toluene dinitration plants. Recommendations are made with regard to the optimisation of the operating conditions of these plants.

The effects of temperature and H_2SO_4 - H_2O

composition on the heterogeneous rates of nitration of ortho-nitrotoluene have been investigated for a low nitric acid concentration in a small stirred batch reactor and a small stirred cell.

Measurement of the solubility of ortho-nitrotoluene in aqueous sulphuric acid and the distribution of nitric acid between ortho-nitrotoluene and aqueous sulphuric acid has enabled an excellent correlation to be obtained between homogeneous rate data and the two phase rates of nitration in the stirred batch reactor for all conditions investigated. In this way kinetic control of the two phase rate of nitration of ortho-nitrotoluene in the stirred batch reactor has been demonstrated.

The two phase rate of nitration of ortho-nitrotoluene in the stirred cell has been shown to be mass transfer controlled under all conditions investigated. Three reaction regimes have been identified which are governed by the relative magnitudes of the mass transfer and kinetic rates. The observed rates in these regimes have been successfully interpreted in terms of Danckwerts' Surface Renewal Theory. Values for the diffusivity of ortho-nitrotoluene in mixed acid and for the overall mass transfer coefficient have been calculated from a Danckwerts plot. For runs at 25°C the calculated

mass transfer coefficient was lower than the values previously observed for toluene and chlorobenzene in a similar system. At higher temperatures the mass transfer coefficient was calculated using the Danckwerts equation and the results suggest that the mass transfer coefficient in the stirred cell under these conditions increases with temperature and k_2. This observation is discussed in terms of the effect of chemical reaction rate on the rate of surface renewal in the stirred cell.

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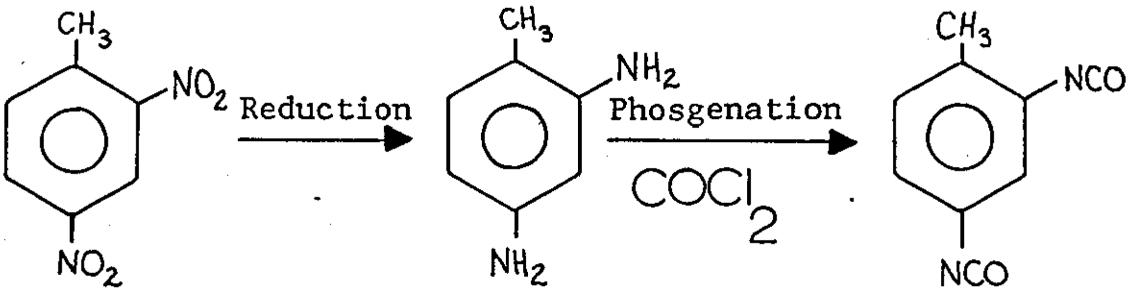
CHAPTER 1

INTRODUCTION

Nitration has been studied in great detail for many years. The main impetus for this intensive study, at least during the early part of this century, was the need for rapid and efficient production of nitrated compounds for military use as explosives and propellants. In addition, nitrated compounds, particularly nitroaromatics, have been used extensively as intermediates in the manufacture of dyestuffs, pharmaceuticals, synthetic adhesives and plastics.

Commercial nitration of mononitrotoluenes is usually carried out as the second stage of a two or three stage process. In the first stage, toluene is nitrated by contacting it with mixed aqueous nitric and sulphuric acids to produce a mixture of the three mononitrotoluene isomers. In the second stage, this mixture is further nitrated, usually without separation, to form a mixture of the six dinitrotoluene isomers. This in turn, in a third stage, may if desired, be further nitrated to form a mixture of trinitrotoluenes. The progressive introduction of nitro-groups into the aromatic ring deactivates the latter to further electrophilic attack and thus the above nitration stages require progressively more vigorous nitrating conditions, i.e. more concentrated acids and higher temperatures, to achieve successful nitration.

Dinitrotoluene is an important intermediate in the production of tolylene diisocyanates (more correctly called diisocyanatotoluenes) which are used in the manufacture of polyurethane foams and elastomers. A simplified reaction scheme for the conversion of 2, 4 - dinitrotoluene to 2, 4 - tolylene diisocyanate is shown below:



Tolylene diisocyanates, prepared using 2, 4 - dinitrotoluene as the starting compound, produce the highest quality polyurethanes, the quality of the polyurethanes deteriorating as the content of the other dinitrotoluene isomers in the starting material increase. A variety of methods for separating the 2, 4 - isomer from the dinitrotoluene mixture exist,but all of these are relatively expensive. An object of the work described in this thesis was to investigate the influence of reaction conditions on the rates and products of nitration of each of the mononitrotoluene isomers so that manufacturers of dinitrotoluenes can select the optimum conditions for operation of their dinitration reactors.

Commercial aromatic nitration plants employ two phase systems in which the reactant and its nitration products constitute one phase and the mixed acid the other. Since the phases are usually only slightly miscible the process involves mass transfer with simultaneous chemical reaction. In these systems the phases are stirred together rapidly to minimise mass transfer resistances. Many of the early investigators of heterogeneous nitration tried to overcome the complex problem of taking into account mass transfer resistances by using very rapidly stirred systems and thus tried to correlate the observed rates in terms of a simple kinetic model. However, this approach has recently been shown to be an oversimplication and mononitration of several aromatics, including toluene, has now been successfully correlated in terms of the current understanding of mass transfer with simultaneous chemical reaction (see Chapter 3). No correlations of this kind have been reported for the nitration of mononitrotoluenes. Therefore, it was one of the aims of the work described here to determine two phase rates of nitration of mononitrotoluenes and compare the results obtained with values predicted according to existing rate models.

THEORY AND LITERATURE

CHAPTER 2

HOMOGENEOUS AROMATIC NITRATION

The majority of early studies of aromatic nitration were carried out under homogeneous (one phase) conditions in which small quantities of aromatic compounds were dissolved in the nitrating medium. This technique has the advantage that rates can be measured under kinetically controlled conditions, the only limiting factor being the process of molecular diffusion and this only becomes rate determining for highly activated aromatic substrates.

2.1. THE MECHANISM OF HOMOGENEOUS AROMATIC NITRATION

The homogeneous nitration of aromatic compounds in various solvents has been studied extensively and has played a great part in the development of mechanistic organic chemistry. The nitronium ion is now established as the active entity in the nitration of aromatic compounds in many solvents including mixtures of aqueous sulphuric and nitric acid (Mixed Acid). The evidence leading to this conclusion is the subject of several excellent reviews (1-4) and therefore only a brief outline will be given here.

2.1.1. The Existence of the Nitronium Ion

Euler (5), in 1903, was the first to suggest the possible existence of the nitronium ion but confirmation was not obtained until the work of Ingold and co-workers (3) was published. These workers were able to prove the

existence of the nitronium ion in three ways, none of which depended on its behaviour as a nitrating agent.
These were as follows:-

(i) Hantzsch (6) had obtained an approximately three-fold depression of the freezing point of sulphuric acid by nitric acid. He had interpreted this in terms of formation of the ion $H_2NO_3^+$ by protonation of nitric acid. Ingold and co-workers (3), using an improved cryoscopic technique, were able to show that the freezing point depression was in fact four times that of an ideal solute. They claimed that this was "unmistakeable proof" that nitric acid in sulphuric acid is converted into the nitronium ion in accordance with equation 2.1

$HNO_3 + H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$...........2.1

(ii) Raman spectra of solutions of nitric acid in aqueous sulphuric acid displayed intense bands at 1400 cm^{-1} and 1050 cm^{-1}. These bands have been attributed to the nitronium ion and the bisulphate ion respectively, formed as indicated by equation 2.1. The bands were found to be very sensitive to the sulphuric acid - water composition.

(iii) Ingold and co-workers (3) found that nitric acid and perchloric acid interact to form salt-like compounds. They showed that these solids were mixtures of nitronium and hydroxonium perchlorates. On crystallisation from nitromethane the pure nitronium salt $(NO_2)^+(C10_4)^-$ was obtained. This structure and that of other nitronium salts was confirmed both by Raman spectroscopy and X-ray analysis.

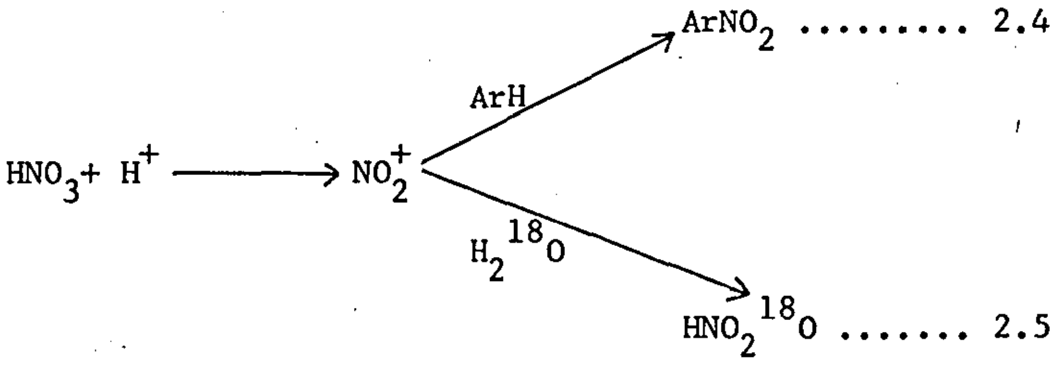
2.1.2. The Effectiveness of the Nitronium Ion

Strong evidence that the nitronium ion is the active entity in the nitration of aromatic compounds by nitric acid came from the work of Hughes, Ingold and Reed (7). They studied the nitration of a number of aromatic compounds in organic solvents. In each case the nitric acid was in constant excess over the aromatic compound. In such conditions,for aromatic compounds more reactive than benzene, the reaction is zeroth-order with respect to the aromatic compound. This clearly indicates that nitration proceeds through slow formation of a reactive intermediate. Ingold and co-workers (7) observed and interpreted the effect of addition of strong acids and ionised nitrates on the rates of these zeroth-order nitrations. They found that very small quantities of sulphuric acid accelerated the zeroth-order nitrations and very small quantities of nitrate ion retarded them without modifying the reaction order. This shows that the formation of nitronium ions must consist of two steps. The first step (equation 2.2), leading to the formation of nitrate ions, is easily reversible whereas the second (equation 2.3) is not reversible since the aromatic substrate traps the nitronium ions as soon as they are formed. These observations led to the proposal of the following mechanism for the formation of the nitronium ion in organic solvents.

$$2HNO_3 \underset{}{\overset{fast}{\rightleftharpoons}} H_2NO_3^+ + NO_3^- \quad \ldots\ldots\ldots\ldots\ldots\ 2.2$$

$$H_2NO_3^+ \xrightarrow{slow} H_2O + NO_2^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 2.3$$

Further confirmation of the existence and effectiveness of the nitronium ion, this time in aqueous media, was provided by the work of Bunton, Halevi and Steadman (8). They performed experiments in partly aqueous media in which the nitronium ion concentrations were too small to be detectable by techniques then available. Firstly, they measured the zeroth-order rates of nitration of some activated aromatic substrates. They then measured the rate of exchange of the oxygen isotope, ^{18}O, between water and nitric acid. The zeroth-order nitration rate and the ^{18}O exchange rate were found to be the same. Thus the reverse of the formation of the nitrating agent involves the transfer of one oxygen atom from water to nitric acid. The only reasonable interpretation of these observations involves the intermediate formation of the nitronium ion.



2.1.3. Nitration in Mixed Acid

In mixed acid the first step in the nitration of aromatic substrates is the protonation of nitric acid. The relationship between the concentrations of the nitronium ion and nitric acid is determined by the equilibrium:

$$HNO_3 + H^+ \rightleftharpoons H_2O + NO_2^+ \quad \ldots\ldots\ldots\ldots\ 2.6$$

The equilibrium constant, K, is given by equation 2.7.

$$K = \frac{(a_{NO_2^+})\cdot(a_{H_2O})}{(a_{HNO_3})\cdot(a_{H^+})} = \frac{[NO_2^+](\gamma_{NO_2^+})\cdot(a_{H_2O})}{[HNO_3]\,\gamma_{HNO_3}\cdot(a_{H^+})} \quad \ldots\ldots\ 2.7$$

where $a_{NO_2^+}$, a_{H_2O}, a_{HNO_3} and a_{H^+} are the activities of the nitronium ion, water, nitric acid and the hydrogen ion respectively and $\gamma_{NO_2^+}$ and γ_{HNO_3} are the activity coefficients of the nitronium ion and nitric acid respectively.

Then

$$R_e = \frac{[NO_2^+]}{[HNO_3]} = \frac{K\gamma_{HNO_3}\cdot(a_{H^+})}{\gamma_{NO_2^+}\cdot(a_{H_2O})} \quad \ldots\ldots\ldots\ 2.8$$

where R_e is a constant at a given temperature and a given H_2SO_4 - H_2O composition. R_e is thought to range from about 10^{-8} in 28 mole % H_2SO_4(9) to infinity in 62 mole % H_2SO_4 (nitric acid is fully ionised (10).

The rate of nitration of a given aromatic compound ArH is then as follows:

$$\text{Rate} = k_2' \left[NO_2^+\right] \left[ArH\right] \text{ .... } 2.9$$

where k_2' is the true second order rate constant. However, it is more convenient to define the rate as follows:

$$\text{Rate} = k_2 \left[HNO_3\right] \left[ArH\right] \text{ .... } 2.10$$

where k_2 is the observed rate constant given by

$$k_2 = k_2' R_e \text{ .... } 2.11$$

Martinsen (11) showed that k_2,for most aromatic nitro-compounds,passes through a maximum at about 62 mole% H_2SO_4. Later work (12) showed that the maximum k_2 value occurs at a definite acidity (defined by Hammett's (13) H_o function) rather than at a definite acid concentration i.e. the maximum acidity corresponds to a maximum value of R_e and hence a maximum k_2 value. For this reason, k_2 varies slightly with the concentration of nitric acid and the aromatic substrate since these modify the acidity of the medium.

The Effect of Molecular Diffusion

Further details of the mechanism of aromatic nitration in mixed acid were elucidated by Coombes, Moodie and Schofield (9). They found that for a series of sufficiently reactive aromatic substrates a limit is reached where the addition of further activating substituents does not lead to an increase in k_2. This limit is observed for activated aromatic substrates having a reactivity forty or more times that of benzene. Coombes, Moodie and Schofield interpreted this limiting rate of nitration in terms of the rate determining formation of an encounter pair $(\overline{NO_2^+.ArH})$ between the nitronium ion and the aromatic substrate. They calculated that the observed rate coefficients approached the theoretical diffusion limit. The following reaction scheme was proposed to account for their observations:

$$NO_2^+ + ArH \rightleftharpoons \overline{ArH.NO_2^+} \quad \ldots\ldots\ldots\ldots\ldots\ldots 2.12$$

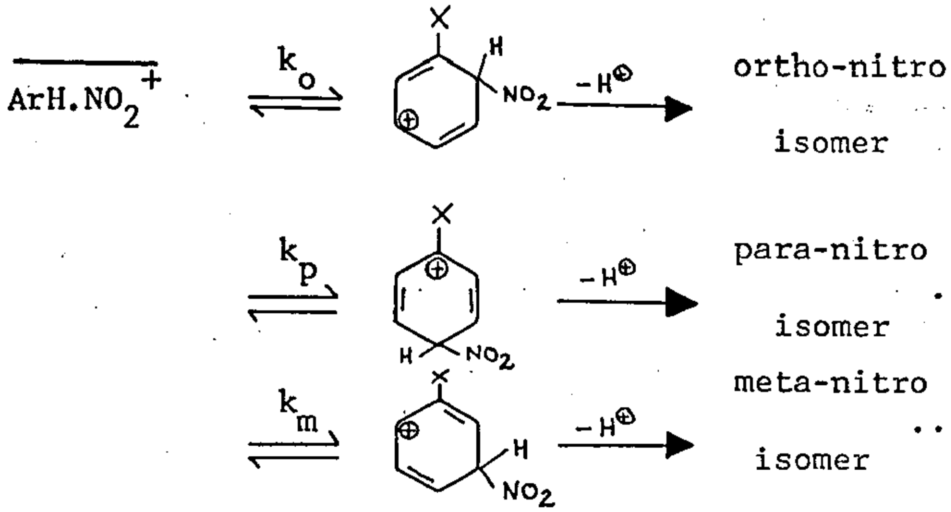
$$\overline{ArH.NO_2^+} \longrightarrow \text{products} \quad \ldots\ldots\ldots\ldots\ldots 2.13$$

Under diffusion controlled conditions reaction 2.12 is the rate determining step.

Formation of the Benzenonium Ion

The conversion of the encounter pair to the final products involves the formation of one or more benzenonium ions:

for example



...2.14

....2.15

.... 2.16

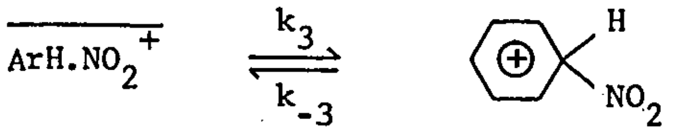
The formation of the benzenonium ions may be the rate determining step. The relative magnitude of the rate constants k_o, k_m and k_p will then determine the relative proportions of the products formed. Melander (14) has shown, using labelled solvents, that the loss of the proton is not usually kinetically significant.

Summary of the Mechanism of Aromatic Nitration in Mixed Acid

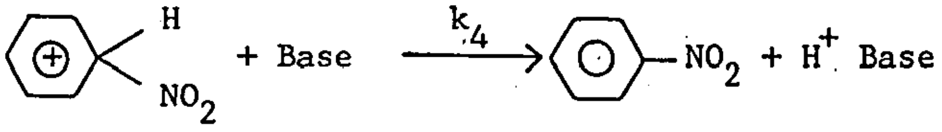
The reaction path for aromatic nitration by mixed acid is now considered (15) to involve four possible rate determining steps of which the last is only rate determining in special structural situations. The steps are as follows:

$$HNO_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + NO_2^+ \qquad \text{..........} \quad (2.6)$$

$$NO_2^+ + ArH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overline{ArH.NO_2^+} \qquad \text{..........} \quad (2.12)$$



....(2.14 -2.16)



.. 2.17

By applying steady state approximations the following rate law may be derived:

$$\text{Rate} = \frac{k_1 k_2 k_3 \; [\text{ArH}] \; [\text{HNO}_3] \; a_{\text{H}^+}}{k_{-1} a_{\text{H}_2\text{O}} \, (k_3 + k_{-2}) + k_2 k_3 [\text{ArH}]} \quad \ldots\ldots \; 2.18$$

from which the second order nitration rate is

$$\text{Rate} = k_{\text{observed}} \; [\text{HNO}_3] \; [\text{ArH}] \quad \ldots\ldots\ldots\ldots \; 2.19$$

for which the condition is

$$k_{-1} a_{\text{H}_2\text{O}} \gg k_2 k_3 \; [\text{ArH}] \; /(k_3 + k_{-2}) \text{ with } k_3 \ll k_{-2}.$$

2.2. NITRATION OF MONONITROTOLUENES

Some of the data reviewed in this section were obtained by two phase nitration experiments. These are included in this section rather than in Chapter 3, so that all literature concerning the nitration of mononitrotoluenes can be considered together.

2.2.1. Physical Properties of Mononitrotoluenes

Three isomers of mononitrotoluene exist. They are ortho-, meta- and para-nitrotoluene.

Some physical properties of these three isomers are compared in Table 2.1.

Table 2.1

Physical Properties of Mononitrotoluenes (16)

	ortho-	meta-	para-
Melting Point/^{o}C	-10.5 (α form) -4.1 (β form)	16	54.5
Boiling Point/^{o}C	220.4^{a}	232.6^{a}	238.3^{a}
Density/gcm $^{-3}$	1.1629^{b}	1.1571^{b}	1.103^{c}

Notes

a - boiling point at a pressure of 760 mm of Mercury.

b - density at a temperature of 20^{o}C.

c - density at a temperature of 75^{o}C.

2.2.2. Nitrotoluene Isomer Distribution obtained from Nitration of Toluene.

If toluene is nitrated in mixed acid a mixture of the three mononitrotoluenes will be obtained. The relative proportions of each isomer in this mixture depend on the reaction temperature and the mixed acid composition used, as shown in Table 2.2.

Table 2.2

Effect of Temperature and Acid Composition on Nitrotoluene Isomer Distribution

Acid Composition /mole %			Temperature /°C	Nitrotoluene Isomer Distribution / Weight %			Reference
H_2SO_4	HNO_3	H_2O		ortho	meta	para	
27.2	26.7	46.1	30	52.5	3.5	44.0	17
30.7	19.4	49.9	0	61.1	4.5	34.4	18
"	"	"	20	61.9	4.5	33.6	18
"	"	"	40	63.6	4.2	32.2	18
"	"	"	50	62.2	4.3	33.5	18
31.4	10.4	58.2	0	60.5	3.3	36.2	18
"	"	"	40	62.7	3.9	33.4	18
35.6	4.2	58.4*	30	58.5	4.4	37.2	19
40.5	51.3	8.2	25	56.0	2.4	41.6	20

*This mixed acid contained 1.8 mole % HNO_2

It may be seen that a great variety of conditions have been used to obtain these mononitrotoluene isomer distributions. Therefore it is difficult to assess the variables which affect the isomer distribution. The only variable whose effect is clearly discernible is temperature.

For a given acid composition, increasing the temperature increases the ortho/para ratio. There is also some evidence to indicate that increasing the temperature increases the percentage of meta-nitrotoluene.

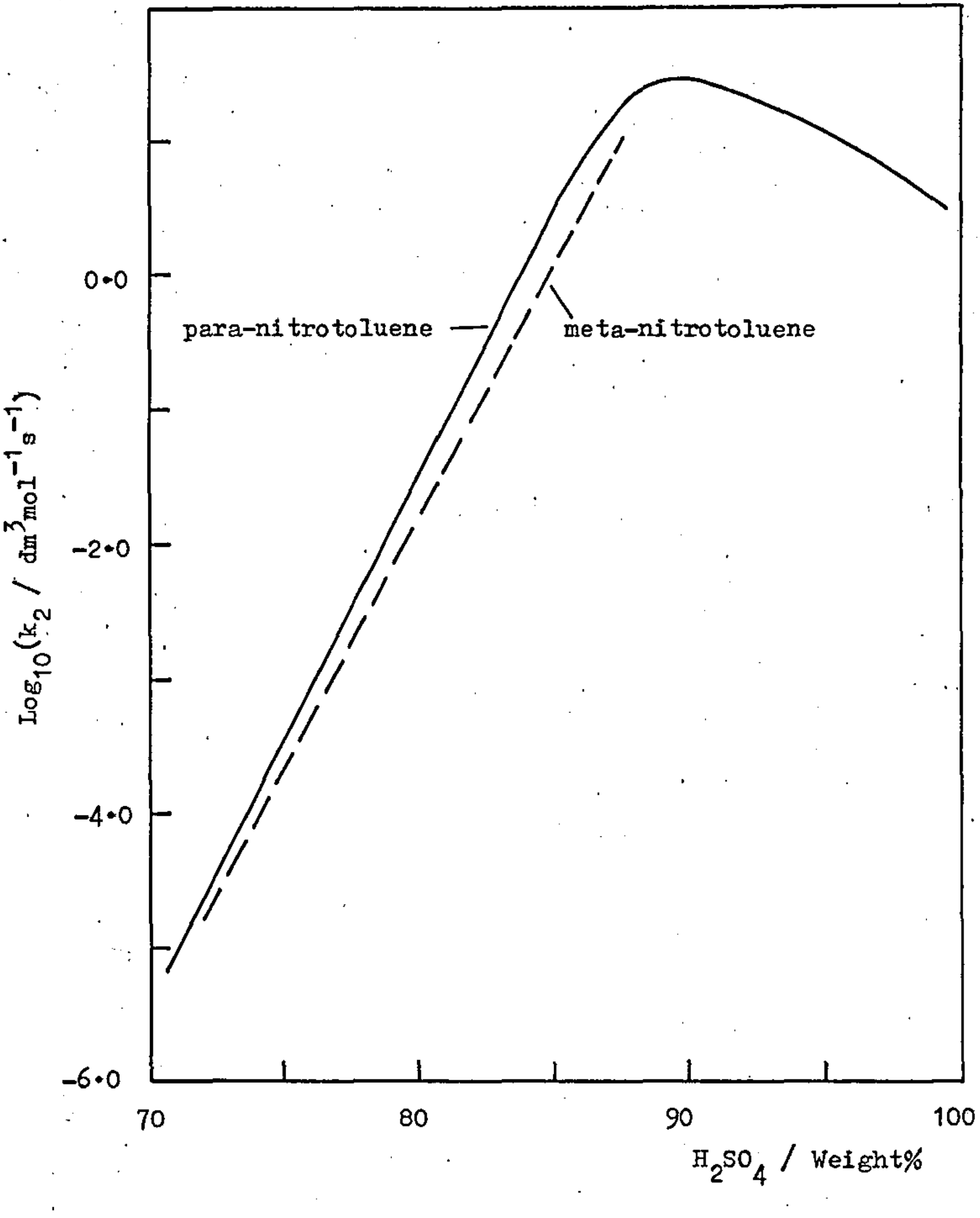
2.2.3. Effect of H_2SO_4-H_2O Composition on k_2

Published literature (21) indicates that k_2 for mononitrotoluenes increases with mole % H_2SO_4 to a maximum value at about 62 mole % H_2SO_4. This observation is in line with the foregoing discussion of the mechanism of aromatic nitration in mixed acid (section 2.1.3).

Tillett (22) studied the variation of the second order nitration rate constant, k_2, for meta-nitrotoluene at 25°C over the range 72-87 weight % H_2SO_4 (about 32-55 mole % H_2SO_4) and Vinnik, Grabovskaya and Arzamaskova (21) studied k_2 for para-nitrotoluene at the same temperature over the range 71-99 weight % H_2SO_4 (about 31-95 mole % H_2SO_4). The results obtained by the above workers are compared in Figure 2.1. The value of k_2, for both isomers, increases linearly with weight % H_2SO_4 for compositions in the range 70-86 weight % H_2SO_4 (30-53 mole % H_2SO_4). Over this range of compositions the k_2 values for the meta- and para-isomers at a given composition are quite similar although k_2 for para-nitrotoluene is always greater than k_2 for meta-nitrotoluene.

No rate data of this kind have been published for

Figure 2.1 **Log$_{10}$k$_2$ for Nitration of Mononitrotoluenes as a Function of H_2SO_4-H_2O Composition at 25°C.**



ortho-nitrotoluene.

2.2.4. Effect of Temperature on k_2

The only work published in the open literature on the effect of temperature on the rate of nitration of mononitrotoluenes is that by Vinnik, Grabovskaya and Arzamaskova (21). They studied the variation of k_2 with temperature for the nitration of para-nitrotoluene in 30.8 mole % H_2SO_4 and obtained an activation energy, E_2, of 90.4 kJ mol^{-1} from their data. Unfortunately, these workers did not study the effect of temperature on k_2 for the nitration of para-nitrotoluene in other H_2SO_4 - H_2O compositions. However, the variation of E_2 with H_2SO_4-H_2O composition has been studied for several other aromatics (23-25) and consideration of this work may enable estimates to be made of the effect of temperature on k_2 for mononitrotoluenes as a function of H_2SO_4-H_2O composition. The value of E_2 is determined by the sum of two activation terms

$$E_2 = E_2' + \Delta H_{form}$$

where E_2' is the activation energy for the attack of the nitronium ion on a given aromatic substrate and ΔH_{form} is the heat of formation of nitronium ions from nitric acid in a particular H_2SO_4-H_2O composition. The value of E_2' varies with each aromatic whereas ΔH_{form} is independent of the substrate. The major contribution to the value of

E_2 is from ΔH_{form} which decreases with increasing % H_2SO_4. The extent to which ΔH_{form}, and hence E_2, decreases is independent of the aromatic substrate. Chapman and Strachan (26) compared the rate of decrease of E_2 with increasing weight % H_2SO_4 for several aromatics and pointed out that, on average, E_2 for these aromatics decreased by 2.80 kJ mol $^{-1}$ for each weight % increase in H_2SO_4.

2.2.5. Relative Rates of Nitration

Tillett (22) determined the relative rates of nitration of the three mononitrotoluenes by competitive nitration in 86 mole % H_2SO_4 at 25°C. He found that the ortho: meta: para: nitration rates were in the ratio 2.23:1.00:1.14 respectively. These ratios are in good agreement with those (2.3: 1.0: 1.2 respectively) determined by direct nitration in 46.4 mole % H_2SO_4 at 25°C by Westheimer and Kharasch (12). Shutov and co-workers (27) obtained relative rate data for para- and meta-nitrotoluene by competitive nitration in 78 mole% H_2SO_4 at 16°C. They found that para: meta rates were on average in the ratio 1.76: 1 - rather different from the relative rates discussed above.

2.2.6. Products of Nitration of Mononitrotoluenes.

Nitration of mono-nitrotoluene leads to the formation of dinitrotoluene. Six dinitrotoluene isomers exist. Their names and melting points are listed in Table 2.3.

Table 2.3

Melting Points of Dinitrotoluenes (28)

Name	Melting Point /°C
2,3- dinitrotoluene	63
2,4- dinitrotoluene	71
2,5- dinitrotoluene	52.5
2,6- dinitrotoluene	65.5
3,4- dinitrotoluene	60
3,5- dinitrotoluene	91

The products of nitration of mononitrotoluene depend on the mononitro-isomer nitrated as shown below.

(i) Nitration of Para-nitrotoluene

Gibson, Duckham and Fairburn (18) reported that nitration of para-nitrotoluene yields exclusively 2,4-dinitrotoluene. Roberts, Watkins and Kobe (29) confirmed this observation using an isotopic dilution method.

(ii) Nitration of Ortho-nitrotoluene

Gibson, Duckham and Fairburn (18) found that nitration of ortho-nitrotoluene yields mixtures of 2,4- dinitrotoluene and 2,6- dinitrotoluene in the ratio 2:1. Roberts, Browder and Kobe (30) confirmed this observation by isotopic dilution, finding less than 0.4% of the 2,3-isomer in the product mixture. On the basis of only a few results, Shutov and co-workers (27) claimed that the proportion of

2,6- dinitrotoluene formed is only slightly affected by temperature but is increased by using lower H_2SO_4 concentrations.

(iii) Nitration of Meta-nitrotoluene

Both Gibson and co-workers (18) and Tillett (22) have identified the relative proportions of the products formed in the nitration of meta-nitrotoluene. Their findings are compared in Table 2.4.

Table 2.4

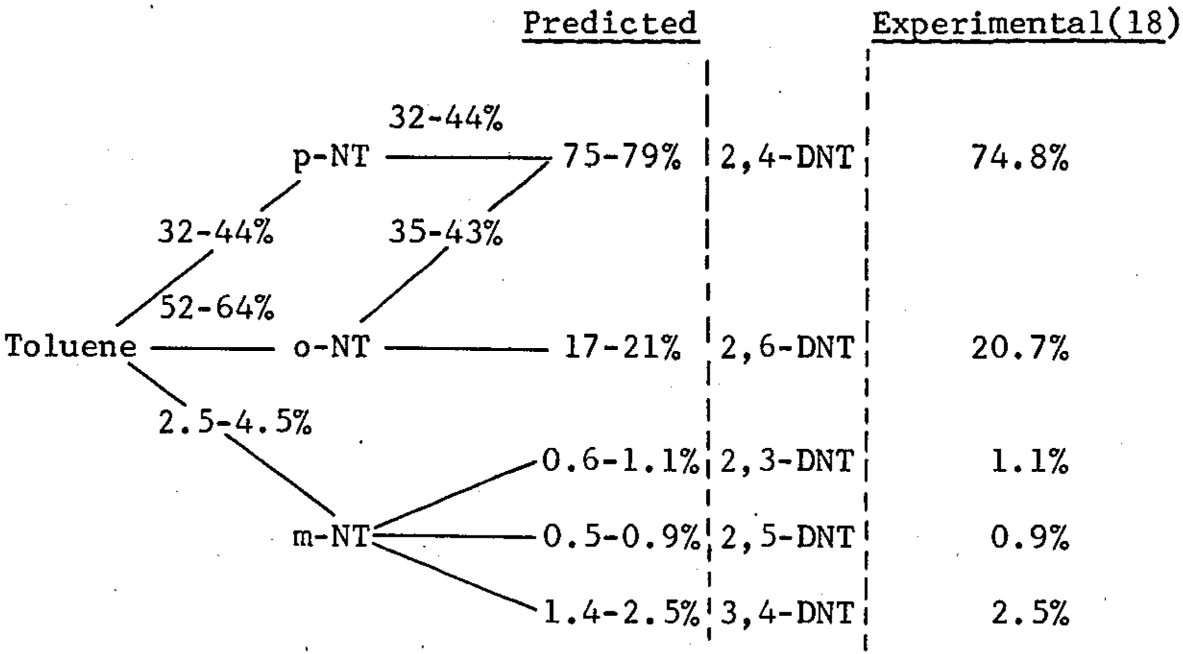
Nitration Products of Meta-nitrotoluene

Dinitrotoluene isomer	Percentage of Total Product	
	Gibson et al (18)	Tillett (22)
2,3-	25	25
2,5-	20	18.6
3,4	55	55
3,5	—	1.4

It is not possible, using available published data, to estimate the effect of temperature and mixed acid composition on the ratio of products formed from the nitration of the mononitrotoluene isomers.

2.3. NITRATION OF TOLUENE DIRECT TO DINITROTOLUENE

In industrial processes dinitrotoluene is often manufactured by a two stage process. In the first stage, toluene is nitrated under relatively mild conditions to form a mixture of mononitrotoluenes. In the second stage, this mixture of mononitrotoluenes is nitrated, without being separated into its components, under more severe conditions to form a mixture of dinitrotoluenes. Consideration of the data already shown allows a prediction to be made of the percentage of each dinitrotoluene isomer formed in such a process. This prediction and the way in which it was obtained is shown below:



The above prediction is in good agreement with the experimental findings given by Gibson et al (18) shown at the right hand side above. The 2,4/2,6 dinitrotoluene ratio given by the above predicted and experimental percentages is in the range 3.6-4.4. Harris (31) reported recently that, under manufacturing conditions, the nitration of toluene, with a mixture containing 41 mole % H_2SO_4, 27 mole % HNO_3 and 32 mole % water, gives a reaction product with a 2,4/2,6 dinitrotoluene isomer ratio of 4.0. When dinitrotoluene is used for diisocyanate production a dinitrotoluene mixture with this ratio of 2,4/2,6 dinitrotoluenes is usually required. However, it is considered desirable (see Introduction) to increase the 2,4/2,6 dinitrotoluene isomer ratio and decrease the proportion of 2,3-, 2,5- and 3,4- dinitrotoluene isomers in the product mixture, if this can be achieved economically (32). The desired change in isomer ratios could be achieved, although perhaps not at a sufficiently low cost, by lowering the reaction temperature since at the mononitration stage the ortho- to para- ratio will tend to decrease and the percentage of meta-nitrotoluene formed will also tend to decrease (see Section 2.2.2). Hence, the proportion of the 2,4- dinitrotoluene isomer should increase and the proportions of the remaining isomers should decrease. This is confirmed by some experimental data reported by Coon, McDonald and Hill (33) in a United States patent. In this work the nitration mixture was 77 mole % H_2SO_4, 8 mole % HNO_3 and 15 mole % H_2O with a mole ratio HNO_3:toluene of 4:1. The results are shown in Table 2.5

Table 2.5

Effect of Temperature on Toluene Dinitration Products (33)

Temperature /°C	Percentage of Dinitrotoluene Isomers			
	2,4-	2,6-	3,4-	2,3- + 2,5-
-5	84.48	13.46	1.41	0.65
-15	85.34	12.83	1.29	0.53
-25	86.47	11.77	1.26	0.50
-35	88.98	9.62	1.07	0.33

CHAPTER 3

HETEROGENEOUS AROMATIC NITRATION

Large scale industrial nitration of aromatic compounds is performed using a two phase system in which the aromatic substrate and its nitroproducts constitute one phase and mixed nitric and sulphuric acids (Mixed Acid) the other. Nitroaromatics may be prepared either in batch reactors or in a series of constant flow stirred tank reactors (CFSTR*s*). In either case the organic phase is dispersed in the acid phase by rapid stirring.

The majority of published work on heterogeneous aromatic nitration is concerned with the mononitration of toluene and chlorobenzene in CFSTR*s*. An account of this work will be included here since the general principles which arise also apply to the nitration of mononitrotoluenes in a batch reactor.

3.1 MACROKINETICS OF TWO PHASE AROMATIC NITRATION

An important consideration among early workers in this field was to determine whether reaction occurs in both phases or merely in the aqueous phase. Some workers (34, 35) claimed that reaction occurs in both phases but the majority have assumed that reaction occurs predominantly in the acid phase. The process of two phase nitration involves the following major steps:

(i) Diffusion of the aromatic substrate from the bulk of the organic phase to the interface between the phases.

(ii) Diffusion of the aromatic substrate from the interface to the bulk of the aqueous phase.

(iii) During step (ii) chemical reaction occurs between the aromatic substrate and the nitronium ion.

(iv) Diffusion of the nitrated aromatic to the interface and migration of the water formed (or its ions) away from the reaction zone.

(v) Migration of the nitrated aromatic from the interface to the bulk of the organic phase.

Since only reaction in the aqueous phase is considered to be significant, step (ii) or step (iii) are likely to be rate determining under most circumstances.

The following material balance may be applied to this system (36):

$$\begin{bmatrix}\text{Net Rate of transfer}\\ \text{of aromatic to}\\ \text{aqueous phase.}\\ \\ \end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{reaction in}\\ \text{acid phase}\\ \\ \end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of aromatic in}\\ \text{acid phase.}\end{bmatrix} \ldots 3.1$$

Under steady state conditions the rate of accumulation may be neglected. The following equation then applies:

$$a'K_L(X_{ArH}[ArH]_a^s - [ArH]_a) = k_2[HNO_3]_a\,[ArH]_a \quad \ldots 3.2$$

where a' is the interfacial area per unit volume of acid phase; K_L is the overall mass transfer coefficient;

$[ArH]_a^s$ and $[ArH]_a$ are the saturation and steady state concentrations respectively in the acid phase; k_2 is the observed second order rate constant and $[HNO_3]_a$ is the concentration of nitric acid in the acid phase. X_{ArH} is the mole fraction of the aromatic substrate in the organic phase.

Rearranging equation 3.2 we have

$$[ArH]_a = \frac{a'K_L X_{ArH} [ArH]_a^s}{k_2 [HNO_3]_a + a'K_L} \quad \ldots\ldots\; 3.3$$

The rate at which nitric acid is consumed is then given by:

$$\frac{-d[HNO_3]_a}{dt} = k_2 [HNO_3]_a [ArH]_a = \frac{k_2 [HNO_3]_a a'K_L X_{ArH} [ArH]_a^s}{k_2 [HNO_3]_a + a'K_L} \quad \ldots 3.4$$

If $a'K_L \gg k_2 [HNO_3]_a$ the rate will be kinetically controlled and given by $k_2 [HNO_3]_a X_{ArH} [ArH]_a^s$. If initial rates are measured $X_{ArH} \approx 1$ and therefore the rate will be given by $k_2 [HNO_3]_a [ArH]_a^s$.

If $a'K_L \ll k_2 [HNO_3]_a$ the rate will be mass transfer controlled and given by $a'K_L X_{ArH} [ArH]_a^s$. As above, if initial rates are measured, the rate will be given by $a'K_L [ArH]_a^s$.

3.1.1. Attempts to Eliminate Mass Transfer Resistances

Early investigators of the rates of two phase nitration concentrated solely on establishing conditions under which the rate was kinetically controlled, since methods of measuring a' and K_L, and therefore predicting rates under mass transfer controlled conditions, were not then available. The rate of nitration was considered to be kinetically controlled (mass transfer resistances were said to have been overcome) if the following criteria were satisfied:

(i) The nitration rate remained constant as the agitation rate was increased.

(ii) The nitration rate increased by a factor of about two for a 10°C rise in temperature.

McKinley and White (37) measured the variation of the rate of nitration of toluene with agitation rate in a CFSTR. They found that at low agitation rates the rate of nitration increased rapidly with agitation rate. However, a transition point was reached above which further increases in agitation rate resulted in negligible increases in agitation rate. In addition, for agitation rates above the transition point, the nitration rate was found to increase by a factor of 2.2 for a 10°C temperature rise. Lewis and Suen (34) had earlier found that, for the two phase nitration of benzene, the rate increased by a factor of two for a 10°C temperature rise. Hence, these workers claimed that they had eliminated mass transfer resistances at high agitation rates and that the observed rates were kinetically controlled. A series of papers (38-41) followed, in all of which, it was claimed that mass transfer resistances had been eliminated by the use of high agitation rates.

3.1.2. Evidence for Mass Transfer Control

Severe criticism of the assumptions made by previous workers was made in a series of reviews by Albright and Hanson (36,42,43). Hanson and co-workers re-examined, and in some cases extended, the work performed by earlier workers. Presented below are some of the arguments in favour of the suggestion that early workers in this field had not been successful in eliminating mass transfer resistances.

The Effect of Variations in Agitation Rate

Agitation influences mass transfer both by its effect on the interfacial area and by determining the degree of turbulence in each phase. The overall rate will be kinetically controlled only if the chemical reaction rate is appreciably slower than the rate of mass transfer across the interface.

Albright and Hanson (43) argued that, although an increase in agitation rate initally increases the interfacial area and the rate of surface renewal, this effect does not extend to very high agitation rates. They explained that when the size of drops of dispersed phase falls below a critical value internal circulation is suppressed. Each drop then behaves as a rigid sphere in which mass transfer depends on molecular diffusion,which is a relatively slow process. In addition,interaction between droplets of dispersed phase, which is thought to increase mass transfer, is suppressed. Hence,the levelling of nitration rates at high agitation rates does not provide conclusive proof that mass transfer resistances have been eliminated.

Hanson, Marsland and Wilson (44) studied the effect of variations in agitation on the rate of nitration of toluene in a CFSTR similar to that used by McKinley and White (37). They employed agitation rates up to 8000 r.p.m. but were still able to detect slight increases in nitration rate. Hanson, Marsland and Naz (45) used the same reactor to nitrate chlorobenzene and observed similar effects to those for toluene. Hence,the claim of earlier workers to have eliminated mass transfer resistances by using high agitation rates appears to be unfounded.

The Effect of Variations in Temperature

Albright and Hanson (43) have pointed out that each of the constants in equation 3.2 is temperature dependent. They concluded, therefore, that the effect of temperature on two phase nitration is very complex and is consequently of little value in elucidating the rate controlling step unless the effect of temperature on each constant is known accurately.

Hanson, Marsland and Wilson (44) measured two phase rates of nitration of toluene in a CFSTR at several temperatures. To try to resolve doubts about the claims of earlier workers to have eliminated mass transfer resistances they attempted to correlate their results using equation 3.5,i.e. assuming that the rate of reaction was in each case kinetically controlled.

$$R_A = k[T]_o[HNO_3]_a \qquad \ldots\ldots\ldots \; 3.5$$

where R_A is the rate of nitration of toluene per unit volume of acid phase, $[T]_o$ is the concentration of toluene in the organic phase and $[HNO_3]_a$ is the concentration of nitric acid in the aqueous phase. The constant k is a composite incorporating both the true velocity constant k' and the distribution coefficient $\emptyset$ where:

$$\emptyset = \frac{[T]_o}{[T]_a} \quad \text{and } k = \frac{k'}{\emptyset}$$

Hanson, Marsland and Wilson found that,even for rises in temperature of 12°C,the rate never increased by more than a factor of 1.74, in contradiction of earlier workers who claimed to observe temperature coefficients of two for 10°C increases. They found that the "12°C temperature coefficient" decreased as the temperature range increased. They suggested that this might be due,in part,to the fact that mass transfer resistances tend to become more prominent as the temperature is raised,since the temperature coefficient for mass transfer is considerably less than that for chemical reactions.

In addition, temperature changes will affect the distribution of the reactants between the phases (and hence their concentrations in each phase) and the concentration of the nitrating species. These workers, therefore, questioned the validity of using the overall temperature coefficient as a criterion for determining whether two phase rates of reaction are mass transfer or kinetically controlled.

The Effects of Variations in Phase Ratio

Some investigators have reported that the two phase rate of nitration depends on the phase ratio. Both Lewis and Suen (34) and White and Biggs (35) explained this by proposing that nitration occurs in both phases at different rates.

Hanson and co-workers (45,46) examined the effect of the phase ratio on the rate of nitration of toluene and chlorobenzene. They found that it was not possible to correlate their results in terms of a simple kinetic model. Hanson, Marsland and Naz (45) reported that the rate of nitration of chlorobenzene in a CFSTR showed considerable dependence on phase ratio. They varied the latter from 1:2 to 2:1 and found that the smallest change in rate was 50%. They argued that although this effect could be explained by assuming that reaction takes place in both phases at different rates it could equally well reflect the existence of a significant mass transfer resistance since a variation in the phase ratio would produce a variation in the interfacial area.

Hanson and co-workers (45,46) also studied the effect of space time and phase inversion on the rate of two phase nitration. The results of these investigations, like those already described, indicated that mass transfer resistances played some part in determining the rate of nitration of various aromatics in CFSTRs. The work of Albright, Hanson and co-workers therefore made an important contribution to the understanding of two phase nitration, since they showed that the exclusive use of a kinetic model for the interpretation of data from two phase nitrations was an oversimplification.

In a recent paper, Strachan (47) reviewed the published work on the two phase nitration of toluene in CFSTRs. He opposed the contention of Albright and Hanson (43) that the two phase nitration of toluene had been mass transfer controlled under all conditions previously investigated. To lend support to this argument Strachan cited his own work with Cox (24, 48) which proved that the rate of nitration of toluene in a batch reactor was kinetically controlled under certain conditions. He re-examined the data of several workers, notably McKinley and White (37) and Barduhn and Kobe (39), in the light of recent advances in the understanding of the theories of mass transfer with chemical reaction (see section 3.1.4). He reached the conclusion that, at least in some of the runs performed by these workers, the rate of nitration was kinetically controlled.

3.1.3. Mass Transfer at the Liquid - Liquid Interface

A number of models of mass transfer processes have been proposed in an attempt to rationalise observed phenomena. These models, which are described below, are based on gas-liquid systems but they are applicable to liquid-liquid systems such as those employed for two phase aromatic nitration.

The Film Theory

This theory was first proposed by Whitman(49) in 1923. It is based on the assumption that there exists,close to any fluid interface,a stagnant film of thickness d' through which transport processes take place by molecular diffusion. From Fick's first law equation the absorption rate per unit surface $\overline{V}$ is given by

$$\overline{V} = -D\left(\frac{\partial C}{\partial x}\right)_{x=0} + (u_x C)_{x = 0} \qquad \ldots\ldots\ 3.6.$$

where C is the concentration of the absorbing component in the liquid phase; x is the distance from the interface; D is the molecular diffusivity of the solute in the continuous phase and u_x is the velocity component normal to the interface. A further assumption is made that a given surface element behaves as a rigid body during its time at the interface. The velocity component u_x then becomes equal to zero. The concentration gradient on the continuous phase side of the interface is given by equation 3.7.

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{C_i - C_o}{d'} \qquad \text{........ } 3.7$$

where C_i and C_o are the concentrations of the solute at the interface and in the bulk of the continuous phase respectively.

From equations 3.6 and 3.7 we have, assuming u = 0,

$$\bar{V} = \frac{-D(C_i - C_o)}{d'} \qquad \text{......... } 3.8$$

Hence, the individual mass transfer coefficient K_L' for the continuous phase is defined as

$$K_L' = \frac{D}{d'} \qquad \text{......... } 3.9$$

and

$$\bar{V} = K_L' (C_i - C_o) \text{ ...... } 3.10$$

Since it is not possible in practice to measure the concentration C_i at the interface, the overall mass transfer coefficient, K_L, is defined such that the overall rate of mass transfer is given by

$$\bar{V} = K_L(C^* - C_o) \text{ .... } 3.11$$

and hence

$$K_L = \frac{D}{d} \qquad \text{........ } 3.12$$

where C^* is the saturation concentration of solute in the continuous phase, and d is the distance between the bulk of the continuous phase and the region in which the continuous phase solute concentration is C^*. The value of d is not measurable in practice but this theory enables a prediction to be made for the relationship between K_L and D. Experimentally K_L has been found to be proportional to $D^{\frac{1}{2}}$ (50). The discrepancy between this relation and that predicted by the film theory has been attributed by Danckwerts (51) to the simplifying assumption that a "stagnant film" exists. He elaborated the film theory by supposing that, for the absorption of a gas into a stirred liquid, the turbulence that exists in the main body of liquid is damped out near the gas-liquid interface just as it would be close to a rigid surface. The film theory can then be interpreted by supposing that the scale of turbulence and the magnitude of the eddy diffusivity become progressively smaller, as the surface is approached, until transport by eddies becomes of negligible importance. Conversely, transport by eddy diffusion becomes increasingly important with increasing depth, the concentration of the bulk of the liquid being kept virtually uniform by large scale turbulence.

The Penetration Theory

(a) Higbie's Model

The penetration theory was first proposed by Higbie (52).

It rejects the hypothesis that a stagnant film exists at the interface and likewise rejects Danckwerts's more elaborate interpretation of the film theory that the scale of turbulence diminishes as the interface is approached. Instead,it proposes that the turbulence extends to the interface and that eddies constantly bring fresh liquid from the bulk to the interface. The assumption is made that each element of liquid remains at the interface for the same, finite, length of time before being replaced. The theory further supposes that, during the lifetime of given element, solute will be absorbed into that element at the same rate as a stagnant liquid of infinite depth, exposed to the surface for the same length of time. Each element becomes increasingly saturated during its time at the surface of the liquid and the absorption rate therefore decreases. Hence the surface consists of a large number of elements of different "ages", elements of each "age" having a different absorption rate.

The unsteady state molecular diffusion within each element is governed by Fick's second law equation:

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad \ldots\ldots\ldots 3.13$$

where t is the instantaneous age of each element.

The boundary conditions applicable to this equation are: $t = 0, \quad C = C_o$

$x = 0, \quad C = C_i$

$x \longrightarrow \infty, \quad C = C_o$

where C_o and C_i are the concentrations of the solute in the bulk continuous phase and at the interface respectively. The solution (53) of equation 3.13 leads to the following expression for the instantaneous absorption rate V' in a given element having an "age" t:

$$V' = -D\left(\frac{\partial C}{\partial x}\right)_{x=0} = (C_i - C_o)\sqrt{\frac{D}{\pi t}} \quad \ldots\ldots\ldots\ldots 3.14$$

The average absorption rate $\overline{V}$, over the whole time t^* that an element remains at the surface, is then given by equations 3.15 and 3.16.

$$\overline{V} = \frac{1}{t^*}\int_o^{t^*} V'dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.15$$

$$\therefore \quad \overline{V} = 2(C_i - C_o)\sqrt{\frac{D}{\pi t^*}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.16$$

As for the film theory, C_i cannot be measured in practice but can be replaced by C^* if it is assumed that the surface of the liquid is saturated constantly with solute.

Hence

$$\overline{V} = 2\,(C^* - C_o)\sqrt{\frac{D}{\pi t^*}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.17$$

and combining equation 3.11 and 3.17 we have:

$$K_L = 2\sqrt{\frac{D}{\pi t^*}} \qquad \ldots\ldots\ 3.18$$

Higbie's version of the penetration theory is therefore successful in predicting the observed proportionality between K_L and $D^{\frac{1}{2}}$.

(b) Danckwerts' Surface Renewal Model

Danckwerts (54) rejected Higbie's hypothesis that all surface elements have an equal lifetime. He considered that a liquid in turbulent motion consists of a mass of eddies which incessantly change their positions and shapes. These eddies continually expose fresh surface to the solute and mix the surface elements into the bulk of the liquid. If the surface of the liquid is constantly saturated with solute the rate of absorption of solute into each element during an exposure time, t, can, as for Higbie's model, be obtained from the solution of equation 3.13.

Hence

$$V' = (C^* - C_o)\sqrt{\frac{D}{\pi t}} \qquad \ldots.\ 3.19$$

Each element is only considered to be stagnant for the finite time, t, that it remains exposed to the surface. The rate of mass transfer is therefore governed by the "age" of each surface element and not the motion of the liquid beneath the surface.

The average rate of mass transfer is then given by

$$\bar{V} = \int_0^\infty \sqrt{\frac{D}{\pi t}}\,(C^* - C_o)\,\phi(t).dt \;.......3.20$$

where $\phi(t).dt$ is the fraction of total surface composed of elements whose "age" is between t and dt. The total area of surface which is exposed to the gas is taken as unity.

Hence

$$\int_0^\infty \phi(t).dt = 1 \qquad ....3.21$$

Integration of equation 3.21 necessitates the adoption of a specific form for the age distribution function $\phi(t)$. Danckwerts achieved this by assuming that the probability for an element to disappear from the surface in a given time is independent of its age. The mean rate of production of fresh surface, S, will be a constant, dependent on the hydrodynamic conditions. The rate of disappearance of surface elements of any given age is then proportional to the number of elements of that age which are present and hence:

$$-\frac{d\phi(t)}{dt} = S\phi(t) \;................ 3.22$$

On integration this yields

$$\phi(t) = Se^{-St}.................... 3.23$$

Equation 3.20 then becomes

$$\bar{V} = \sqrt{\frac{D}{\pi}}\,(C^{*} - C_{o})\,S\int_{o}^{\infty}\frac{e^{-St}}{\sqrt{t}}\,dt \quad \text{...........3.24}$$

for which the Laplace transform is

$$\bar{V} = \sqrt{DS}\,(C^{*} - C_{o}) \quad \text{..................... 3.25}$$

and from equation 3.11

$$K_{L} = \sqrt{DS} \quad \text{............................ 3.26}$$

Astarita (55) has suggested that the function 1/S should be called the equivalent diffusion time t_D, which then represents the average life of a given surface element.

As for Higbie's model the surface renewal theory leads to a relationship between K_L and $D^{\frac{1}{2}}$ in agreement with experimental evidence (50). In practice, however, the precision of results obtained from large scale gas absorption experiments are such that it is difficult to firmly establish whether the film theory or the penetration theory applies. Since the equations derived from the film theory are easier to use, the latter is often employed in design calculations. However, when mass transfer with chemical reaction is being considered the penetration theory, and in particular Danckwerts' surface renewal model, become important.

3.1.4. Mass Transfer with Pseudo-First-Order Chemical Reaction.

When two phases, which are not at chemical equilibrium with each other, are brought into contact the phenomenon which takes place is referred to as mass transfer with chemical reaction. Chemical reaction is thought to occur in a zone adjacent to the interface (55). The steps involved in this mechanism have been discussed already.

Mass transfer accompanied by pseudo-first-order chemical reaction may be treated mathematically by modifying Fick's second law equation:

$$D\left(\frac{\partial^2 C}{\partial x^2}\right) = \frac{\partial C}{\partial t} + k_1 C \quad \ldots\ldots\ldots\ldots\ldots 3.27$$

where k_1 is the pseudo-first-order rate constant for which the following boundary conditions apply:

$C = C_i \quad x = 0 \quad t > 0$

$C = C_o \quad x > 0 \quad t = 0$

$C = 0 \quad x = \infty \quad t > 0$

Equation 3.27 has been solved by Danckwerts (53) and this solution leads to the following expression for the instantaneous rate of mass transfer, per unit area of surface, of the liquid that has been stagnant at the interface for a time t:

$$V' = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = C_i \sqrt{Dk_1}\left[\operatorname{erf}\sqrt{k_1 t} + \frac{e^{-k_1 t}}{\sqrt{\pi k t}}\right] \ldots\ldots 3.28$$

To obtain an expression for the mean rate of mass transfer per unit area of an agitated liquid, V' must be integrated over the life of each surface element (since the rate of mass transfer decreases with the time that each element remains at the interface). The contributions from all the elements are then added together. In Higbie's model each element is assumed to have an equal life but in the more realistic Danckwerts model a distribution of life-times is assumed, the age distribution function $\phi(t)$ being used (equation 3.23). The mean rate of mass transfer per unit area $\bar{V}$ is given by equation 3.29.

$$\bar{V} = \int_0^{\infty} Se^{-St} V' dt \quad \ldots\ldots\ldots\ldots\ldots 3.29$$

This expression has also been solved by Danckwerts (54) and leads to

$$\bar{V} = C_i \sqrt{D(S+k_1)} \quad \ldots\ldots\ldots\ldots\ldots 3.30$$

The overall rate of reaction R_a is then

$$R_a = \bar{V}a' = a'C_i \sqrt{D(S+k_1)} \quad \ldots 3.31$$

Where a' is the interfacial area per unit volume. This is known as the Danckwerts equation. It is often used in an alternative form which is obtained by substituting for DS from equation 3.26. Then

$$R_a = a' C_i \sqrt{K_L^2 + Dk_1} \quad \ldots\ldots\ldots 3.32$$

This equation is of great importance to designers of contacting devices, in which mass transfer accompanies chemical reaction, since under certain conditions it enables value of a' and K_L to be obtained separately. A plot of $(R_a/C_i)^2$ versus k_1 (known as a Danckwerts plot) should be linear and should have a slope equal to $(a')^2D$ and an intercept equal to $(a'K_L)^2$. If a' is known, both D and K_L can be calculated from this plot.

Danckwerts, Kennedy and Roberts (56) successfully applied the Danckwerts equation to the absorption of carbon dioxide by alkaline solutions in a packed column. Sharma and co-workers (57) extended the use of the Danckwerts equation to liquid-liquid systems. It was found that the fast pseudo-first-order alkaline hydrolysis of formate esters in a wide variety of agitated batch and continuous flow stirred tank reactors obeyed this equation. A comprehensive review of work in this field has been published by Sharma and Danckwerts (58).

The two asymptotes of equation 3.32 can easily be calculated and these lead to further interesting equations.

If $K_L^2 \gg Dk_1$

$$R_a = a'K_LC_i \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3.33$$

and if $K_L^2 \ll Dk_1$

$$R_a = a'C_i\sqrt{Dk_1} \quad \ldots\ldots\ldots\ldots\ldots \quad 3.34$$

With the aid of these relationships Astarita (55) has defined a number of regimes which, together with the kinetic regime apply to systems in which mass transfer accompanies chemical reaction.

Cox (59) investigated these regimes, which are described below, by measuring initial rates of nitration of chlorobenzene and toluene in a stirred batch reactor as a function of the aqueous phase acid composition. A plot of some of the results obtained is shown in Figure 3.1. It can be seen that the various regimes are well defined for toluene but less so for chlorobenzene.

The Kinetic Regime

The rate of reaction in this regime is so slow in comparison with the diffusion rate that the concentration of aromatic substrate is maintained throughout the continuous phase at its equilibrium value i.e. the saturation concentration of aromatic in this phase.

The concentration profile for this regime is shown in Figure 3.2(a). If second order kinetics apply, the overall rate of nitration of a given aromatic is

$$R_a = k_2 [HNO_3]_a [ArH]_a \quad \text{.........} \; 3.35$$

where R_a is the number of moles of aromatic substrate nitrated per unit volume of the acid phase, per unit time; k_2 is the observed second order homogeneous nitration rate constant for the aromatic; and $[HNO_3]_a$ and $[ArH]_a$ are the aqueous phase concentrations of nitric acid and aromatic respectively.

Figure 3.1 Initial Rate of Nitration versus % H_2SO_4 for Toluene and Chlorobenzene in the Stirred Reactor (after Cox(59)).

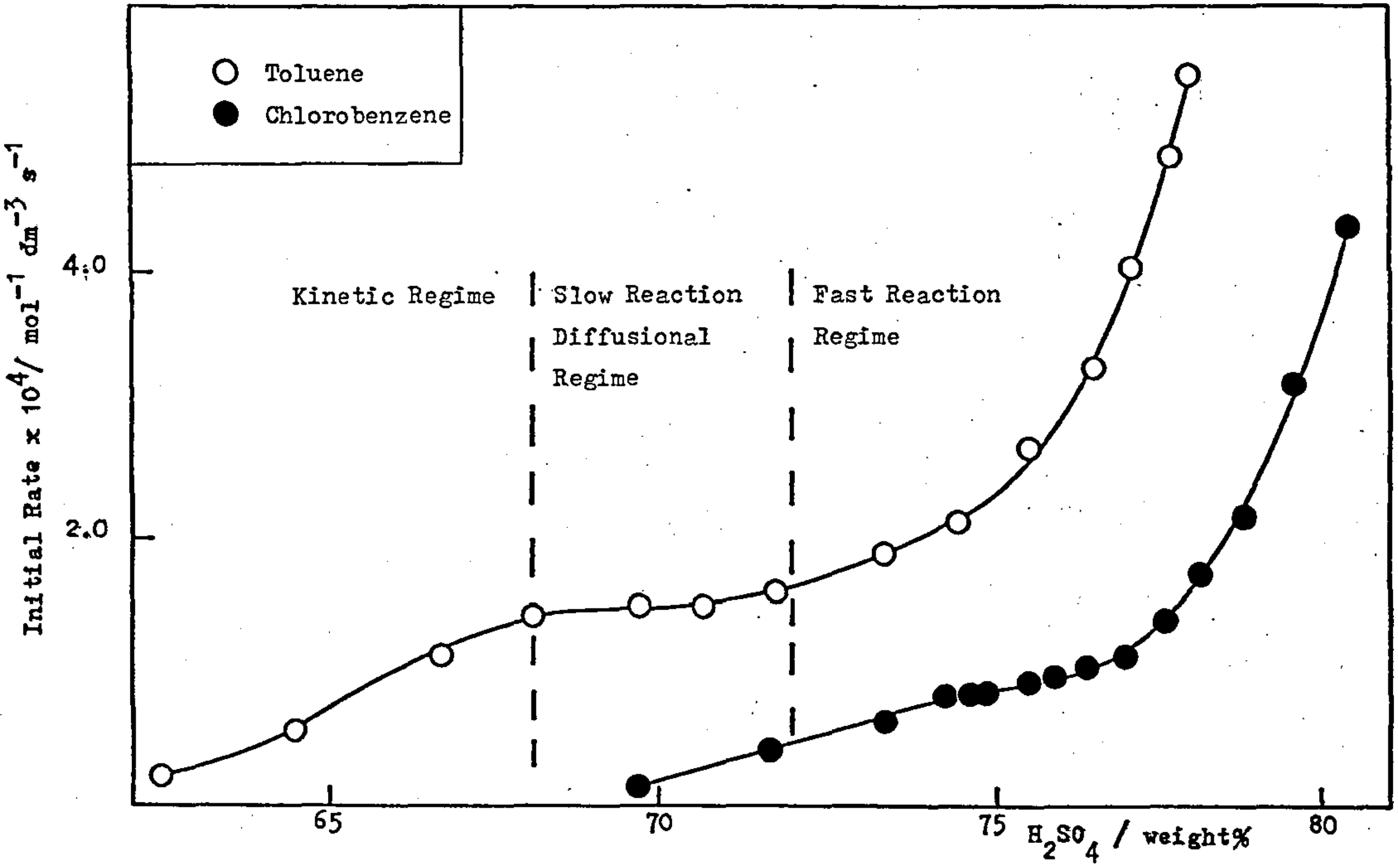
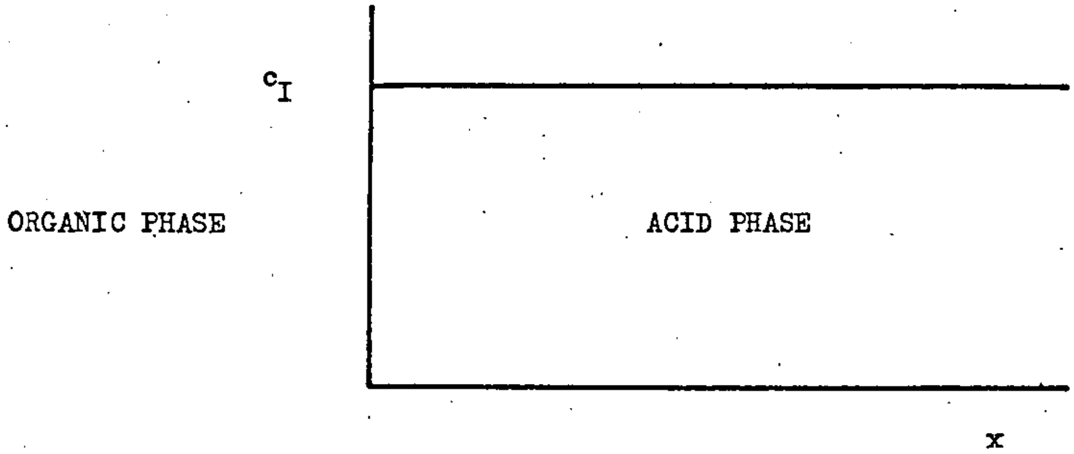
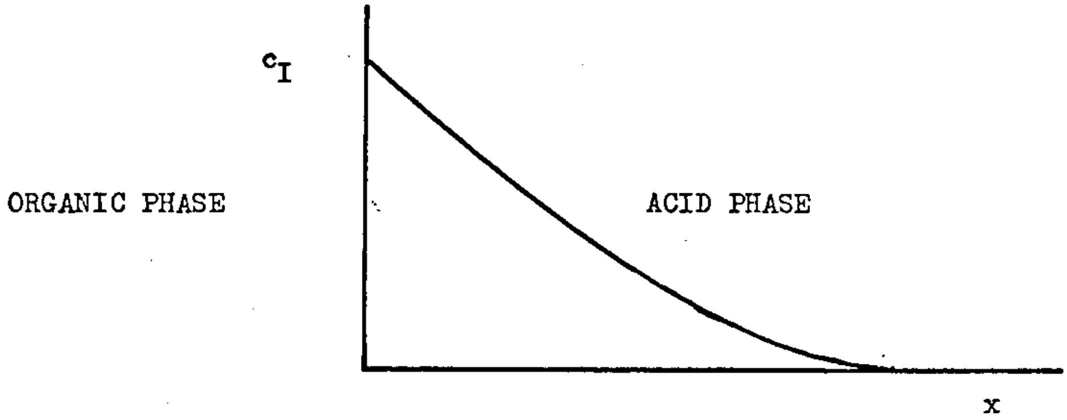


FIGURE 3.2 CONCENTRATION PROFILES FOR REACTION REGIMES.

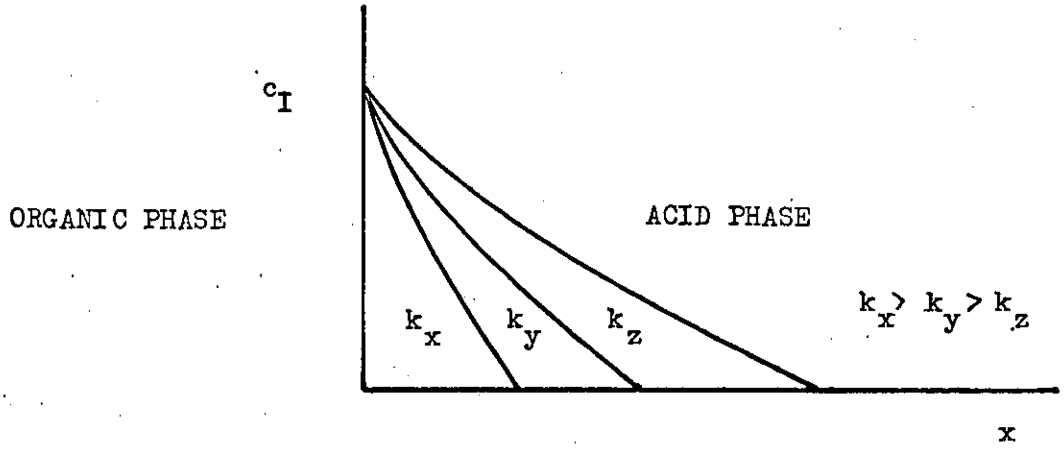
(a) The Kinetic Regime.



(b) The Slow Reaction Diffusional Regime.



(c) The Fast Reaction Regime.



To a good approximation $[ArH]_a = X_{ArH} [ArH]_a^s$ where X_{ArH} is the mole fraction of the reactant in the organic phase and $[ArH]_a^s$ is its saturation concentration in the aqueous phase. Therefore if the reaction is kinetically controlled

$$\frac{R_a}{X_{ArH}} = k_2 [HNO_3]_a [ArH]_a^s \quad .... \quad 3.36$$

Cox and Strachan (60) have shown that the initial rate of nitration of chlorobenzene in a stirred batch reactor, using 30.2 mole % H_2SO_4 and a low nitric acid concentration (0.032 mol dm^{-3}), is kinetically controlled.

The Slow Reaction Diffusional Regime

In this regime, the chemical reaction rate is fast enough to keep the concentration of the aromatic in the bulk of the continuous phase down to zero but too slow to prevent accumulation of the aromatic substrate at the interface. The equation governing reactions in this regime is derived from the Danckwerts equation (3.31 + 3.32) for the case where $K_L^2 \gg Dk_1 = Dk_2 [HNO_3]$ as shown in equation 3.33. This can be re-written as

$$R_a/X_{ArH} = a'K_L [ArH]_a^s \quad .... \quad 3.37$$

The concentration profile for this regime is shown in Figure 3.2(b). The slope of this profile is independent of the kinetic rate constant (and therefore sulphuric and nitric acid concentrations) and hence this regime is easily recognised because it corresponds to a plateau in a plot of $R_a / [ArH]_a^s$ versus $H_2SO_4 - H_2O$ composition (see Figure 3.1). Since the reaction rate is insufficient to prevent accumulation of aromatic at the interface, elements of the continuous phase become increasingly saturated during their residence at the interface. The overall rate of reaction in this regime is dependent on the hydrodynamic conditions, since the average rate of renewal, S, (which is proportional to K_L) is dependent on the degree of turbulence.

The Fast Reaction Diffusional Regime

The rate of chemical reaction in this regime is so fast that the aromatic substrate is consumed as fast as it is transferred to the aqueous phase. In contrast to behaviour in the slow reaction diffusional regime, accumulation of the aromatic substrate at the interface does not occur. The equation governing the overall two phase rate of reaction in this regime is derived from the Danckwerts equation (3.31 + 3.32) for the case $K_L^2 \ll Dk_1 = Dk_2 [HNO_3]$ when the rate of nitration of a given aromatic is given by equation 3.38.

$$R_a/X_{ArH} = a' [ArH]_a^s \sqrt{Dk_2 [HNO_3]_a} \quad \ldots\ldots 3.38$$

The slope of the concentration profile (Figure 3.2(c)) is dependent on the chemical reaction rate constant, k_2. The greater k_2, the steeper the slope of the concentration profile, and the greater the overall rate of reaction. Hence, a rapid increase in rate occurs as the sulphuric acid concentration is increased (see Figure 3.1). Since accumulation at the interface does not occur, the rate of nitration per unit area, R_a/a' is independent of hydrodynamic conditions.

Chapman and Strachan (26) nitrated chlorobenzene, in a stirred cell, using an acid phase composition of nitric acid (0.56 mol dm^{-3}) in 42.0 mole% sulphuric acid. A stirred cell is a device in which two immiscible phases are contacted in such a way that the interfacial area is known and fixed by the dimensions of the cell (See Section 4.7). By making an estimate of D, knowing a' and $[HNO_3]_a$ for their system, and measuring k_2 and $[ArH]_a^s$, Chapman and Strachan were able to compare experimentally determined values of R_a with those predicted from equation 3.38. Reasonable agreement was obtained which indicates that, under these conditions, the rate is fast reaction mass transfer controlled.

The Intermediate Region between the Slow Reaction Diffusional and Fast Reaction Regimes

In this intermediate regime both the rate of accumulation of the aromatic substrate at the interface and its rate of reaction in the aqueous phase contribute to the overall rate. The equation governing this process is the Danckwerts equation (3.31 and 3.32). This equation has been applied successfully to aromatic nitration, by Strachan and co-workers (25, 61), who used the equation in the form shown below:

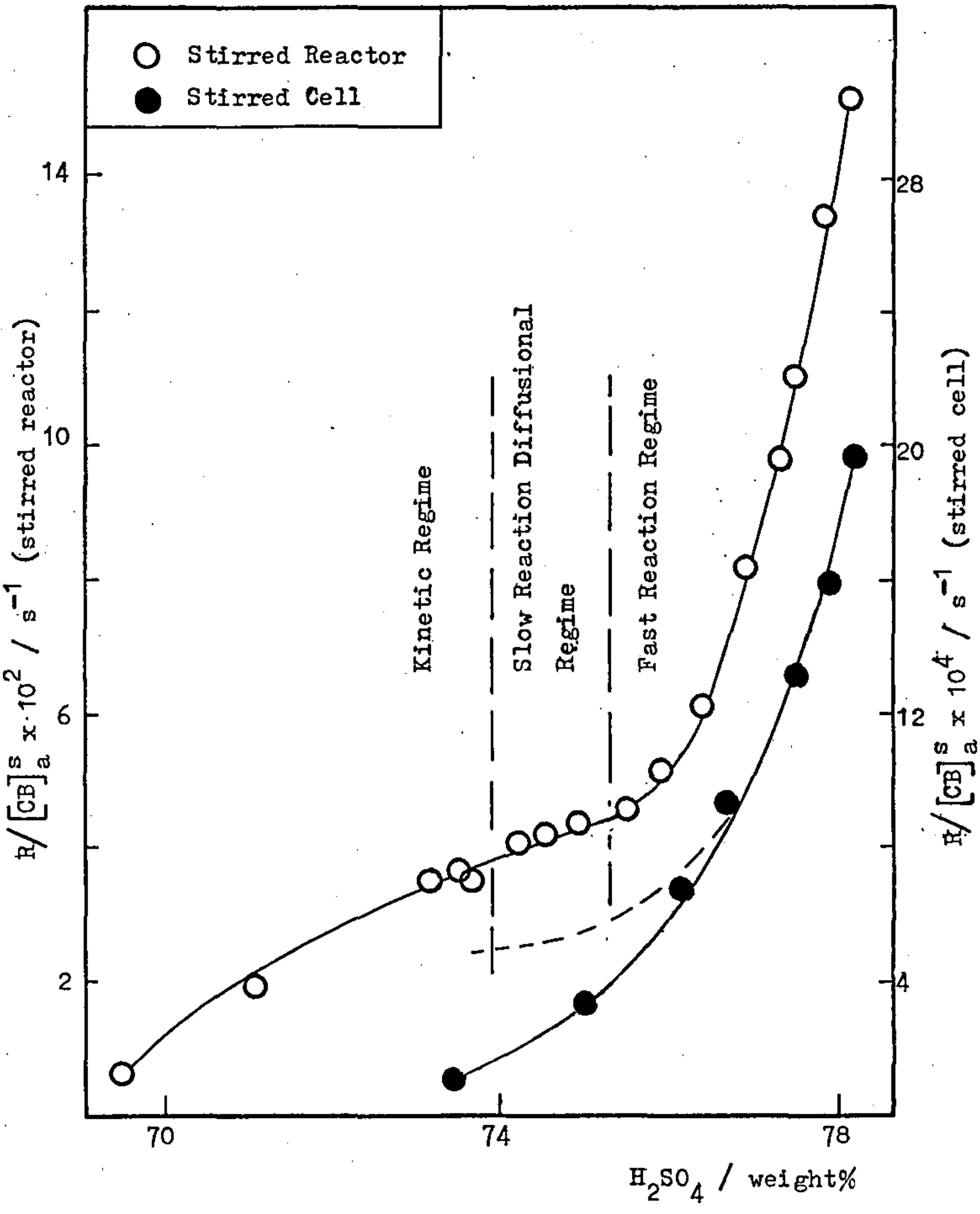
$$R_a/X_{ArH} = a'\sqrt{K_L^2 + Dk_2 \left[HNO_3\right]_a} \left[ArH\right]_a^s \quad .....3.39$$

Cox and Strachan (61) nitrated chlorobenzene both in a stirred reactor and a stirred cell. The overall initial rate of nitration in each contacting device was measured as a function of sulphuric acid composition. The profiles obtained are shown in Figure 3.3. At high sulphuric acid concentrations the plot for the stirred cell follows a similar trend to that for the stirred reactor.

Cox and Strachan were able to construct Danckwerts plots from their data and from these they obtained values of 2.10 x 10^{-3} and 2.29 x 10^{-3} cm s^{-1} for K_L, in the stirred reactor and the stirred cell respectively.

With the stirred reactor, as the reaction rate decreases, the transition to the slow reaction diffusional regime and then to the kinetic regime is observed. With the stirred cell, however, the expected levelling of the mass transfer rate (shown by the dotted line in Figure 3.3), with decreasing reaction rate, does not occur. Instead the mass transfer rate falls continuously. Chapman (25) found that

Figure 3.3 Rate Profiles for Nitration of Chlorobenzene in a Stirred Reactor and a Stirred Cell as a Function of % H_2SO_4 (after Chapman (25)).



K_L for chlorobenzene in the stirred cell, in the absence of chemical reaction, was only 1.73 x 10^{-4} cm s^{-1}. Cox and Strachan concluded that, in the stirred cell, chemical reaction promotes good surface renewal which the agitation alone is insufficient to maintain. As the reaction rate falls, the interface becomes increasingly stagnant and hence the value of K_L decreases.

3.2. THE DIFFUSIVITY OF AROMATIC COMPOUNDS IN MIXED ACID

According to Danckwerts Surface Renewal Theory (Section 3.1.3 and 3.1.4) the rate of nitration of an aromatic, when either the fast reaction diffusional regime or the intermediate regime are observed, is dependent on the diffusivity (D) of the aromatic in the aqueous phase. In the intermediate regime, a value of D can be calculated from stirred cell data using a Danckwerts plot, but it is desirable to be able to compare this value with one obtained by an independent method. A value of D in a given mixed acid composition is also required in the fast reaction diffusional regime to enable experimental and predicted rates of nitration to be compared. Some experimental methods of measuring diffusivities, directly, are available (62, 63) but these are difficult to employ (especially if nitration of the aromatic occurs during the measurement) and no values for the diffusivity of mononitrotoluenes in mixed acid have yet been published. The diffusivity must therefore be calculated. A number of methods of performing such a calculation have been reported and these are reviewed by Sherwood and Reid (64), Nienow (65), and Perkins and Geankoplis (66).

The method of calculation of diffusivities proposed by Wilke and Chang (62) has been used successfully by two workers (25, 59) in a similar system to that employed here. A modification of the Wilke-Chang equation, proposed by Perkins and Geankoplis (66) was used by Cox (59) to predict the diffusivities of toluene and chlorobenzene in mixed acid.

Wilke and Chang (62) developed an empirical equation, for the prediction of diffusivities in two component systems, based on the Stokes-Einstein equation (67) and the Eyring rate theory (68).

$$T/D\eta = 1.004 \times 10^{7} V_1^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots \quad 3.41$$

where D and V_1 are the diffusivity and molal volume of the solute respectively, η is the viscosity of the solvent and T is the temperature of the solution. Wilke and Chang found that the diffusivity, D_{12}, of a given solute 1 in a given solvent 2 could be expressed by the following equation

$$D_{12} = 7.4 \times 10^{-8} \frac{(\phi M_2)^{\frac{1}{2}} T}{\eta V_1^{0.6}} \quad \ldots\ldots\ldots \quad 3.42$$

where T, η and V_1 are defined as above; M_2 is the molecular weight of the solvent and ϕ is a correction factor which allows for the degree of association of the solvent.

Perkins and Geankoplis (66) used a diaphragm cell to measure the diffusivity of a dilute solute in a very non-ideal mixture of solvents (acetic acid in ethanol-water) and that of a second solute in a viscous solvent mixture (potassium chloride in ethylene glycol-water). Using only the diffusivities of the solute in the two pure solvents and the viscosity data of the mixtures, they were able to predict, using a modified form of the Wilke-Chang equation, the diffusion data over the whole solvent mixture concentration range. The equation they used was as follows

$$D_{1m} = \frac{7.4 \times 10^{-8} (\bar{\phi} \bar{M}_{23})^{\frac{1}{2}} T}{\eta_m \; V^{0.6}} \; \ldots\ldots\ldots \; 3.43$$

where D_{1m} is the diffusivity of the solute 1 at very low concentration in a mixture [m] of solvents 2 and 3 , T is the temperature of the solution in Kelvin, V_1 is the molal volume of the solute and ηm is the viscosity of the mixture. The mean associated molecular weight $\bar{\phi} \bar{M}_{23}$ of the mixture of pure solvents (2) and (3) may be defined, using a linear mixing rule, as follows

$$\bar{\phi} \bar{M}_{23} = X_2 \phi_2 M_2 + X_3 \phi_3 M_3 \; \ldots\ldots\ldots\ldots \; 3.44$$

where ϕ_2, ϕ_3; X_2, X_3; and M_2, M_3 are the association factors, mole fractions and molecular weights of pure solvents (2) and (3) respectively. The fact that Perkins and Geankoplis were able to obtain good correlations for both highly associated and viscous mixtures indicated to Cox (59) that this method of correlation could be used for aqueous acids, an indication that proved to be correct.

Use of the modified form of the Wilke-Chang equation for associated liquids requires a knowledge of the value of ϕ for each pure component of the solvent mixture to be employed. Wilke and Chang suggested a possible correlation between the association factor ϕ and the association number, J, proposed by Jacobson (69). The latter defined J as the average number of monomeric molecules clustered together in a liquid, and derived the following equation from a number of molecular models.

$$J = \left[\frac{L_p}{L_m}\right]^3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.45$$

L_p is the average free length between associated molecular aggregates and L_m is the hypothetical free length which would prevail in the liquid if there were no association. Jacobson and Heedman (70,71) have developed two empirical equations to enable L_p to be calculated. For pure liquids, L_p can be determined from the surface tension, σ :

$$\sigma = k_\sigma L_p^{-1.8} \quad \ldots\ldots\ldots\ldots \; 3.46$$

where k_σ is a constant at a given temperature. For both pure liquids and mixtures of liquids L_p can be determined from adiabatic compressibility measurements. The adiabatic compressibility, β, of any liquid may be determined from its density, ρ, and the velocity of sound c in that liquid from which:

$$\beta = \frac{1}{c^2\rho} = k_\beta L_p^{2.4} \quad \ldots\ldots\ldots 3.47$$

where k_β is a constant at a given temperature. L_m may be obtained graphically, for both pure liquids and liquid mixtures, from a knowledge of the density of the liquid at two different temperatures (59). Thus, having determined values of L_p and L_m, a value for J may be calculated from equation 3.45. Cox (59) was able to calculate J for a number of compounds for which the association factors ϕ were known and hence construct a plot of J versus ϕ for these compounds. He was then able to calculate values of J for various aqueous sulphuric acid compositions and hence obtain ϕ by interpolation. In this way Cox calculated ϕ for H_2SO_4, H_2O, HNO_3 and H_2SO_4 - H_2O mixtures. The values of ϕ calculated for the latter from experimental values were in good agreement with values of the mean association parameter $\overline{\phi}$ calculated using the linear mixing rule (equation 3.44) from values of ϕ for pure H_2SO_4 and H_2O. Cox then used the linear mixing rule to calculate values of $\overline{\phi M}$ for mixtures of H_2SO_4 - H_2O - HNO_3 for which experimental data are not available. This method of calculating $\overline{\phi M}$ will be used in the present work. Having obtained values of $\overline{\phi M}$ in this way the diffusivity of a given solute in a given solvent can be calculated using Equation 3.43.

3.3. SOLUBILITY OF AROMATIC COMPOUNDS IN AQUEOUS MEDIA

As shown in Section 3.1.4 the overall two phase rate of nitration of an aromatic compound, irrespective of whether it is kinetically or mass transfer controlled, is proportional to the solubility of the aromatic in the aqueous phase. Therefore,a knowledge of the factors which influence the solubility of aromatic compounds in aqueous media is required in any study of two phase aromatic nitration rates. A review of the theory of the solubility of non-electrolytes in aqueous media by Long and McDevitt (72) provides a good background to this subject. Some of the important points arising from this review and other relevant papers will be discussed here.

3.3.1. Solubility in Water

The Hole Theory

McGowan (73) attempted to rationalise the solubility of non-electrolytes in terms of the hole theory (68, 74). This supposes that the solubility of a non-polar non-electrolyte is dependent on the necessity of creating cavities in a solvent into which solute molecules can be transferred. Solute - solute interations (in the bulk solute) and solute - solvent interactions (in the bulk solvent) are considered to be of a similar magnitude and thus compensate for each other. The enthalpy of solution (ΔH_s) is then simply dependent on the difference between the work required to create cavities of volume V in the solvent and the work done in closing the cavities after removal of individual solute molecules. Hence

$$\Delta H_s = V \Delta P_i \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3.48$$

where ΔP_i is the difference between the internal pressures of the solute and the solvent and V is some measure of the volume of the solute (usually the molar volume or the parachor are used).

When molecules are transferred from the pure solute to a saturated solution in the aqueous phase they experience a change from a high concentration to a relatively low concentration. Therefore, there is an increase in entropy called the dilution or expansion entropy, ΔS_v, which is given by the expression (75), $R\ln(C_1/C_s)$ where R is the gas constant and C_1 and C_s are the solubilities of the solute in itself (pure solute) and in the solvent respectively. McGowan equated the entropy of solution to ΔS_v and hence:

$$\Delta S_s = \Delta S_v = R\ln (C_1/C_s) \text{ .... } 3.49$$

At equilibrium, the free energy of solution ΔG_s is given by the expression:

$$\Delta G_s = \Delta H_s - T\Delta S_s \text{ .... } 3.50$$

and since at equilibrium $\Delta G_s = 0$

$$\Delta H_s = T\Delta S_s \text{ .... } 3.51$$

from which McGowan's equation is obtained:

$$RT\ln(C_1/C_s) = V\Delta P_i \text{ .... } 3.52$$

Bohon and Clausen (76) criticised McGowan's assumption that the entropy of solution is simply equal to the expansion entropy. They determined the solubility of a number of non-electrolytes in water over a range of temperatures. The observed entropy of solution (calculated from equation 3.51) was always much smaller than ΔS_v (equation 3.49).

Frank and Evans (77) had previously suggested that water molecules in the vicinity of a dissolved solute molecule lose some of their disorder and hence in these regions an "ice-like" structure is thought to exist. This concept has been dealt with recently, in detail, by Dack (78). Bohon and Clausen attributed the difference between ΔS_s and ΔS_v to this effect and equated it to a new thermodynamic parameter ΔS_f. In aqueous acid solutions the "liquid structure" is likely to be somewhat different to that postulated for water. Therefore, a more general term, the entropy of interaction ΔS_I will be used here, where

$$\Delta S_I = \Delta S_s - \Delta S_v \qquad \text{3.53}$$

The Internal Energy of Liquids

As already explained, the hole theory is based on the necessity of creating cavities in a solvent to allow the introduction of solute molecules. The creation of these cavities requires that local volume changes must occur in the solvent. Two expressions relate the internal energy of liquids to these volume changes. These expressions are defined below.

The Cohesive Energy Density (c.e.d.) is the total molecular cohesion per unit volume of a liquid at a given temperature. If it is assumed that negligible intermolecular interaction occurs in the vapour phase, c.e.d. can be related to the total energy of vaporisation per mole of liquid, ΔU_{vap}, since this is the energy required to break all intermolecular bonds associated with one mole of liquid during its transfer to the vapour state.

Hence

$$\text{c.e.d.} = \frac{\Delta U_{vap}}{V_m} = \frac{\Delta H_{vap} - RT}{M/\rho} \qquad \text{3.54}$$

where M, V_m and ρ are the molecular weight, molar volume and density respectively of a liquid at a temperature T. ΔH_{vap} is the enthalpy of vaporisation, which may be determined experimentally.

The Internal Pressure (P_i) is the change in internal energy when a liquid undergoes a small isothermal volume expansion. The internal pressure is given by the expression:

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \approx \frac{T\alpha}{\beta} \quad \ldots\ldots\ldots 3.55$$

where α and β are the thermal expansion coefficient and compressibility of the liquid respectively.

Table 3.1 compares literature values of c.e.d. and P_i for a number of liquids of interest in the present work (78).

Table 3.1. Cohesive Energy Densities and Internal Pressures of Various Liquids (78)

Liquid	c.e.d/atm	P_i/atm
Water	22700	1690
Nitrobenzene	6660	-
Acetone	3890	3280
Benzene	3460	3650
Toluene	3280	3501
Carbon Tetrachloride	3040	3330
Hexane	2164	2360

Hildebrand (75) has shown that, for non-polar liquids

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = n\left(\frac{\Delta U}{V_m}\right) \quad \ldots\ldots\ldots\ldots 3.56$$

where n is a constant for a given liquid.

For non-polar liquids short range forces (repulsion and dispersion) predominate. In this case a small volume increase would totally disrupt the inter-molecular forces and hence P_i is equivalent to c.e.d. (n is unity) - see Table 3.1. For polar liquids, however, n is in the range 0.3 - 1.6 and P_i and c.e.d. differ. The presence of hydrogen bonding (e.g. in water) leads to very high c.e.d. values but does not greatly affect P_i values.

Dack (78) drew the following conclusions:

(a) Internal pressure is a measure of short range physical interactions in a liquid.

(b) The cohesive energy density represents the sum of all the interactions in a liquid.

(c) The quantity c.e.d. - P_i = E^c is a measure of the intermolecular energy due to hydrogen bonding and large dipole-dipole interactions.

McGowan (73) does not appear to have distinguished between P_i and c.e.d. He states that the internal pressure of water is about 15,000 atmospheres. This value is much closer to the cohesive energy density of water than it is to the internal pressure (see Table 3.1). Internal pressure differences provide a reasonable basis for the prediction of solubility in organic solvents but for water and other hydrogen bonded solvents c.e.d. must be taken into account.

3.3.2. Solubility in Aqueous Sulphuric Acid

Much that has already been written here about the solubility of non-electrolytes in water also applies to aqueous sulphuric acid. However, the great complexity of this medium has prevented the development of theoretical models to describe its behaviour as a solvent. The work on this topic has therefore been generally empirical in nature but such theoretical approaches as have so far been developed are reviewed by Yates and McClelland (79) and are discussed briefly here.

Low Sulphuric Acid Concentrations

The solubilities of many aromatic compounds in dilute aqueous sulphuric acid are less than those in water. These solutes are said to be "salted out" under such conditions. This behaviour is predicted by the Setschenow equation (80) which, for non-electrolytes of low solubility, is as follows:

$$\log_{10} (C_w/C_e) = k_s C_s \quad \ldots\ldots\ldots\ldots \quad 3.57$$

where C_w and C_e are the respective solubilities of the non-electrolyte in water and in a solution containing C_s mol dm^{-3} of electrolyte. The symbol k_s represents the salt-non-electrolyte parameter. When k_s is positive, C_e

is less than C_w and salting out occurs on adding a small quantity of sulphuric acid to an aqueous solution of the non-electrolyte. When k_s is negative the converse is true (salting in occurs). For benzene, the values of k_s are 0.548, 0.198 and 0.048 $dm^3 mol^{-1}$ for Na_2SO_4, NaCl and HCl respectively (72). The contributions of the ions to the k_s values are usually additive (72) and hence k_s would be expected to be given by the following:

$$\begin{aligned} k_s(H_2SO_4) + 2k_s(NaCl) &= 2k_s(HCl) + k_s(Na_2SO_4) \\ \therefore \quad k_s(H_2SO_4) &= 2k_s(HCl) + k_s(Na_2SO_4) - 2k_s(NaCl) \\ &= (2 \times 0.048) + (0.548) - (2 \times 0.198) \\ &= \underline{0.248} \end{aligned}$$

Since this value is positive benzene should be salted out in dilute H_2SO_4 and this is what is actually observed.

For the majority of aromatics k_s is positive in dilute aqueous sulphuric acid and so these compounds salt out. The degree of salting out increases with increasing molecular size but decreases with increasing dipole moment. The Hammett-Chapman effect (see later) also influences the degree of salting out.

Moderate and High Sulphuric Acid Concentrations

In solutions containing greater than 20 mole% H_2SO_4 the solubilities of many aromatics increase rapidly with increasing H_2SO_4 content. This effect, known as the Hammett-

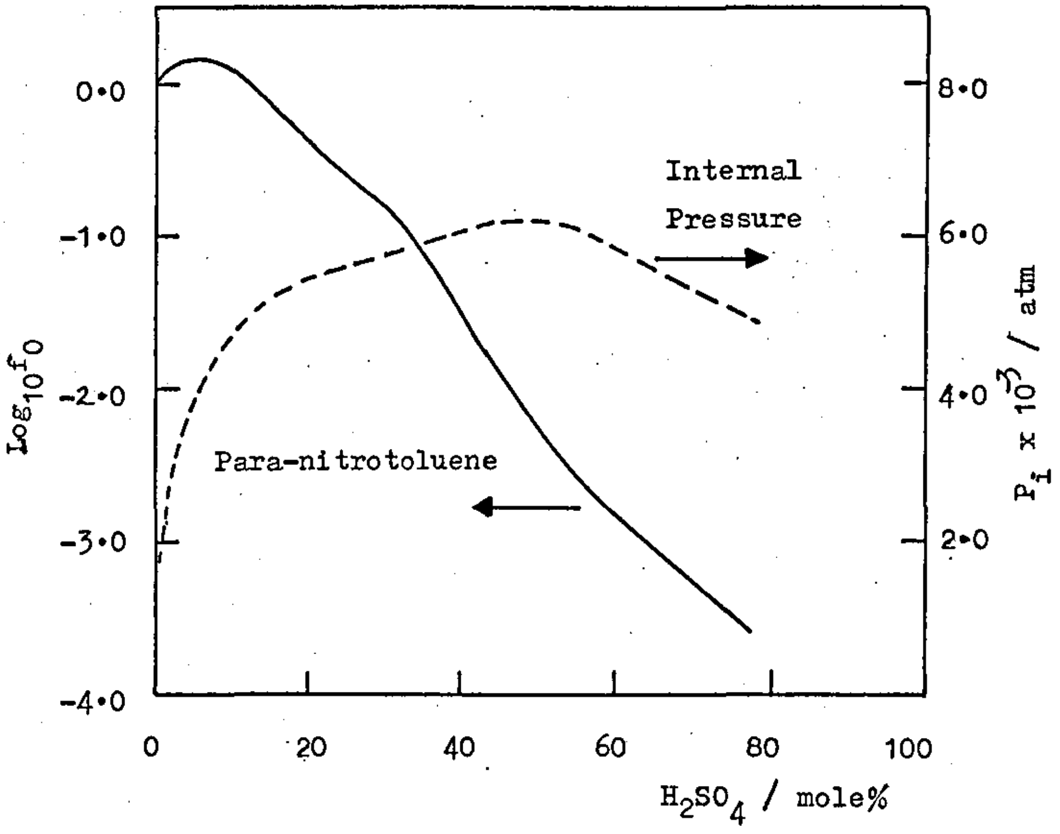
Chapman effect (see later) also influences the degree of salting out.

Moderate and High Sulphuric Acid Concentrations

In solutions containing greater than 20 mole% H_2SO_4 the solubilities of many aromatics increase rapidly with increasing H_2SO_4 content. This effect, known as the Hammett-Chapman effect after its first observers (81), applies to aromatics containing the functional groups $-NO_2$, -CN, -COR, $-CONH_2$, -COOMe, - COOH and -OH (79). In general, the more of these groups that a given compound contains the sharper the increase in solubility with H_2SO_4 content of the solvent. In fact for 1, 3, 5 - trinitrobenzene salting-in due to the Hammett-Chapman effect completely outweighs salting-out due to molecular size. Hence, no initial salting-out region is observed on adding sulphuric acid to dilute solutions of this compound (see Figure 6.2).

The sharp increase in the solubility of many aromatics, with increasing H_2SO_4 content, cannot be explained by changes in the internal pressure of the solvent. Figure 3.4 compares the variation of the internal pressure of aqueous sulphuric acid and $\log_{10}f_o$ for para-nitrotoluene (79) in this medium as a function of H_2SO_4- H_2O composition. The function f_o is the activity coefficient of a given solute and this is defined as:

Figure 3.4 Internal Pressure of Aqueous Sulphuric Acid and its Relationship to Activity Coefficient Variation for Para-nitrotoluene.

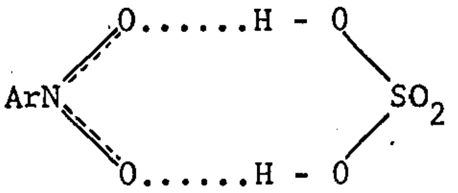


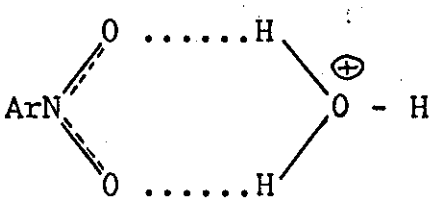
$$f_o = \frac{\text{solubility of a solute in water}}{\text{solubility of the same solute in aqueous } H_2SO_4} \quad \ldots\ 3.58$$

The internal pressures were calculated (82) from adiabatic compressibility and thermal expansion data (83). The internal pressure of aqueous sulphuric acid increases sharply with sulphuric acid concentration to a maximum in 50 mole% H_2SO_4 and then decreases as the acid concentration is further increased. From these data it might be expected that solutes would become less soluble (the activity coefficient would increase) with increasing acid concentration up to 50 mole% H_2SO_4 and would then increase in solubility (the activity coefficient would decrease). Some solutes, namely Iodine (84) and Oxygen (85), behave in this way but most nitroaromatics begin to salt-in considerably before 50 mole% H_2SO_4 is reached. No data are available for the cohesive energy density of aqueous sulphuric acid and so it is not possible to assess whether changes in the cohesive energy density with sulphuric acid concentration have a significant effect on the solubility of nitroaromatics in this medium.

It is possible that the observed solubility phenomena arise as a result of complex formation between the aromatic and one of the species present in aqueous sulphuric acid.

It is probable that either undissociated H_2SO_4 or H_3O^+ are involved in this complex formation. These species are present in negligible concentrations in dilute aqueous sulphuric acid solutions but their concentrations begin to become appreciable in 20-30 mole% H_2SO_4. In concentrated solutions H_2SO_4, H_3O^+ and HSO_4^- are the dominant species. The possibility that protonation is involved in the observed solubility increases was ruled out by Hammett and Chapman (81). Some workers (79, 87) have suggested that hydrogen bonding is involved and that species of the form (I) or (II) below are likely to be present.


(I)


(II)

3.3.3 Solubility in Mixed Acid

The published literature contains very little information on the solubility of aromatic compounds in mixed aqueous sulphuric and nitric acids despite the importance of this parameter in determining the rates of reaction in two phase industrial nitrators. Schiefferle, Albright and Hanson (88) have recently reported their work on the solubility of benzene, nitrobenzene and chlorobenzene in various mixed acids. They observed significant increases in the solubilities of these compounds when the nitric acid content or the sulphuric acid content of the mixed acid was increased.

EXPERIMENTAL

CHAPTER 4

EXPERIMENTAL TECHNIQUES

A general outline is given here of the basic experimental techniques used in this investigation. Precise details of particular experiments and any departures from these basic techniques are discussed in the appropriate chapters.

4.1. THE PREPARATION OF AQUEOUS SULPHURIC ACID SOLUTIONS

Aqueous solutions of sulphuric acid were prepared by adding concentrated sulphuric acid to ice-cold triply-distilled water. The compositions of aqueous sulphuric acid solutions used for homogeneous nitrations were determined by titration with standard sodium hydroxide solution. For all other work,the compositions were determined by measuring the densities of the solutions at 25°C and referring to standard conversion tables.

4.2. HOMOGENEOUS NITRATION OF MONONITROTOLUENES

4.2.1 Determination of the Rate of Nitration in the Acid Phase.

Runs with Nitric Acid in Excess.

A stock solution of aqueous sulphuric acid,having the desired composition,was prepared and analysed as described in section 4.1. A solution of a given mononitrotoluene isomer in aqueous sulphuric acid (about 10^{-4}mol dm^{-3}) was prepared (in the case of ortho- and meta-nitrotoluene) by adding the required volume of the isomer, using a microsyringe, to a known volume of aqueous sulphuric acid from the stock solution. To prepare para-nitrotoluene solutions the procedure was the same as above except that a known weight of the isomer was added to the stock aqueous acid (para-nitrotoluene is a solid at room temperature). Dissolution was achieved by vigorous shaking. A solution of nitric acid in aqueous sulphuric acid (about 10^{-2}mol dm^{-3}) was prepared by placing a known volume of nitric acid in a volumetric flask and making up to volume with aqueous sulphuric acid from the stock solution. The prepared solutions were then placed in a thermostatically controlled water bath at the desired test temperature until required.

Aliquots of 10 cm^3 from each solution were then mixed together. The absorbance of the resulting solution at a wavelength of 240 nm (the wavelength at which the difference in absorbance between the nitrotoluenes and their nitration products is at a maximum) was followed in an SP 30 UV spectrophotometer using sulphuric acid from the stock solution as a reference. The spectrophotometer was fitted with a thermostatically controlled cell block capable of maintaining a given temperature to within $\pm$ 0.1°C.

Runs with Reactant Concentrations Equal

This method was the same as that described above except for the following modifications. The initial concentration of each reactant was about 2.2 x 10^{-3}mol dm^{-3}. In order to calculate the second order rate constant it was necessary to determine the absorbance A_o that the reaction mixture would have at zero time. This was done by measuring the absorbance of each reactant solution before each run and calculating A_o as described in section 5.1.3.

4.2.2. Determination of the Rate of Nitration in the Organic Phase.

Mixed acid (170 cm^3) of known composition and ortho-nitrotoluene (23.6 cm^3) were agitated in the Stirred Cell (see Figure 4.2) at 25.0 ± 0.1°C, all experimental details being as described in section 4.7. In this case, however, agitation was only continued until saturation of the organic phase had been achieved (about 10 minutes). The phases were then separated, the aqueous phase being discarded. The flask containing the organic phase was placed in a thermostatically controlled water bath at 25.0 ± 0.1°C. Samples (10 microlitres) of the organic phase were removed at suitable time intervals, transferred to a 50 cm^3 volumetric flask and made up to volume with spectroscopic hexane. After shaking for one hour to ensure complete dissolution of the nitroaromatic, the absorption of each solution was measured at 234 nm, using the SP30UV spectrophotometer.

4.3. THE INFLUENCE OF TEMPERATURE AND H_2SO_4 - H_2O COMPOSITION ON PRODUCT RATIOS.

Nitration and Extraction Procedure.

For each run or group of runs, a fresh solution of nitric acid in aqueous sulphuric was prepared as described in section 4.2. An aliquot of the prepared solution was then placed in a stoppered flask and maintained at the required temperature in a thermostatically controlled water bath. After allowing sufficient time for thermal equilibrium to be established, the required volume of ortho-nitrotoluene was added and the solution stirred vigorously using a magnetic follower. At the end of the calculated reaction time, the reaction was quenched by pouring the solution into twice its own volume of ice-cold distilled water. The dilute solution was then treated three times with equal volumes of toluene to extract the product dinitrotoluenes. The extract was washed with distilled water, separated, dried over magnesium sulphate and concentrated using a rotary evaporator. The dinitrotoluenes were identified by comparison of their retention times on gas-liquid chromatographic (g.l.c.) analysis with those of recrystallised standards. Duplicate and sometimes triplicate runs were carried out for each set of reaction conditions. A separate experiment had previously been performed to confirm that the products are recovered quantitatively from simulated reaction conditions using the above extraction procedure.

Instrumentation

All analyses were performed using a Perkin Elmer F-33 Gas Chromatograph. This model is a single column instrument which was, in this case,fitted with a hydrogen flame ionisation detector and coupled to a Fisons "Vitatron" flat-bed chart recorder. The column used was a 3 metre long,stainless steel,tube (3.2 mm O.D., 2.4 mm I.D.). This column was packed with 4 weight % OV - 225 on Chromosorb G (HP) 100 x 120 mesh and coiled to fit into the column oven. When in operation,the column oven was held at 180°C and the injector port and detector oven were each held at 250°C.

The Determination of Product Ratios

Various methods of estimating relative peak areas are available. Of these methods, peak area triangulation; measurement of the weight of chart paper corresponding to each peak; and integration of the detector versus time profile for each peak (using a Kent Chromalog electronic integrator) were all investigated but were found to be too irreproducible to use for this work. The remaining methods, namely, use of a planimeter and measurement of peak heights were found to be more reproducible and were therefore investigated fully. The measurement of peak height ratios produced significantly more reproducible results than the use of a planimeter (see Appendix B). Hence, the measurement of peak height ratios was used for the determination of dinitrotoluene product ratios.

The extract from each run was chromatographed three times. A calibration mixture in which the dinitrotoluenes were present in a known ratio was chromatographed three times before and three times after each unknown sample . This was to ensure that the relative response factors for the dinitrotoluenes under test were within the range determined from the mean and standard deviation of the relative response factors from all the calibration runs.

4.4. THE MUTUAL SOLUBILITY OF AQUEOUS SULPHURIC ACID AND NITROAROMATICS.

4.4.1. Determination of the Solubility of Nitrotoluenes in Aqueous Sulphuric Acid.

A single-blade,glass stirrer was used to mix equal volumes (100 cm^3) of nitrotoluene and aqueous sulphuric acid (of known composition) at the required temperature. The temperature was maintained by partially immersing the stirring vessel (a 250 cm^3 round bottomed flask) in a water bath capable of maintaining a given temperature to within $\pm 0.1^{\circ}C$. After thirty minutes, the agitation was ceased and a straight tube, having a closed end of very thin glass, was inserted into the flask so that the closed end extended into the acid layer. After allowing sufficient time for the phases to separate, a glass rod was passed down the tube and the thin glass end was broken. A pipette was then used to remove a quantity of the acid layer via this tube and this acid was transferred to a weighed flask. By reweighing this flask the volume of acid phase taken could be calculated from its density. The dissolved nitrotoluene was extracted with "spectrograde" hexane. A number of such extractions were necessary to remove all the dissolved nitrotoluene. The hexane extracts were collected and made up to a known volume with further hexane. The absorbance of the resulting hexane solution was measured at a wavelength of 350 nm using an SP30 UV spectrophotometer. The concentration of nitrotoluene was determined by reference to a calibration graph obtained previously from the absorbance of a number of standard solutions of the appropriate nitrotoluene isomer in hexane. Each solubility determination was performed in duplicate.

4.4.2. Determination of the Solubility of Sulphuric Acid in Nitroaromatics.

The chosen nitroaromatic and aqueous sulphuric acid of known composition were mixed as described in section 4.4.1. After the phases had separated,a sample of the organic phase was removed, taking care not to disturb the aqueous phase, and transferred to a weighed flask. This flask was reweighed and the volume of the sample was calculated from its weight and the density of the pure nitroaromatic (which,to a good approximation,is the same as the density of the nitroaromatic containing a small concentration of sulphuric acid). The dissolved acid was titrated with standard sodium hydroxide using methyl orange as an indicator and hence the solubility of sulphuric acid in the chosen nitroaromatic could be calculated.

4.5. THE DISTRIBUTION OF NITRIC ACID BETWEEN AQUEOUS SULPHURIC ACID AND NITROAROMATICS.

The procedure was similar to that described in section 4.4.2. except that aqueous sulphuric acid was replaced by a mixture of aqueous sulphuric and nitric acids.

A range of solutions of mixed acid were prepared by adding various aqueous sulphuric acid solutions to nitric acid. Each mixed acid contained 1 cm^3 of nitric acid (70 weight%) per 100 cm^3 of solution (i.e. 0.158 mol dm^{-3}).

After mixing the phases by rapid stirring and allowing them to separate, the organic phase was analysed by titrating the dissolved acid with sodium hydroxide using methyl orange as an indicator. The concentration of nitric acid present in the organic phase was calculated, having allowed for the presence of dissolved sulphuric acid by reference to the results obtained from the experiment described in section 4.4.2.

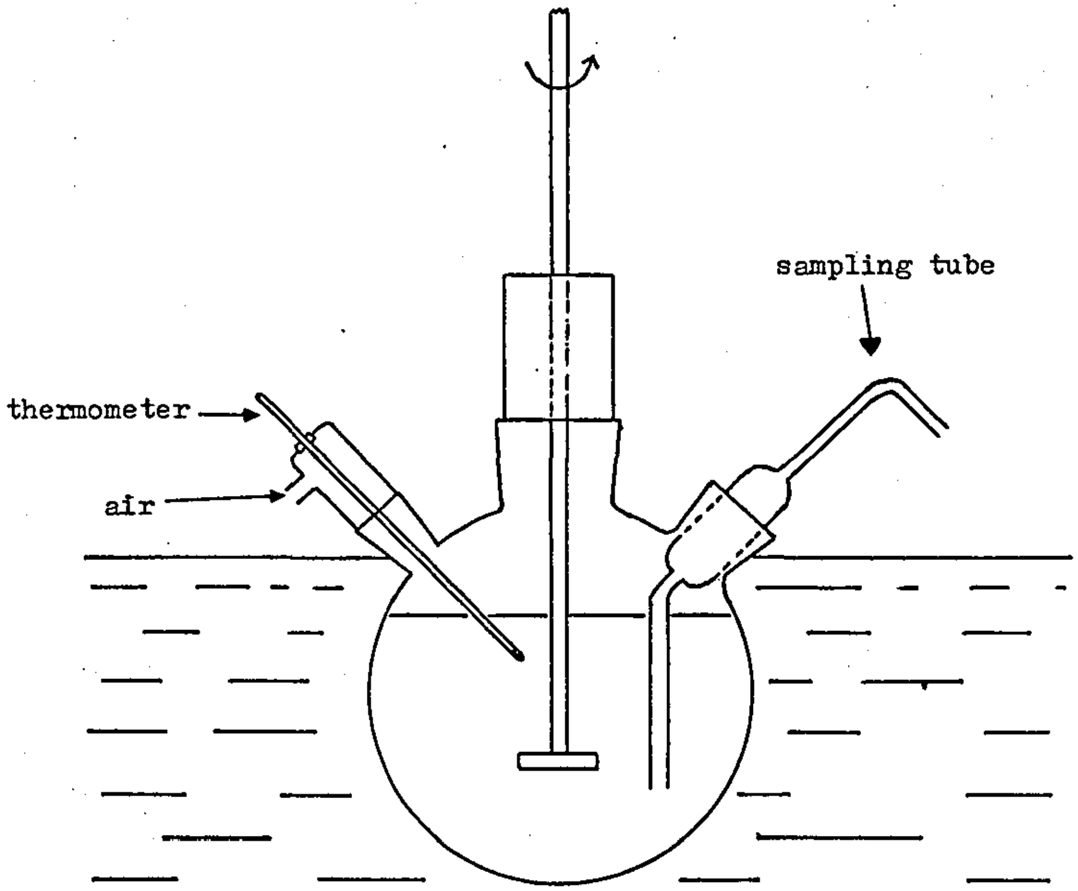
4.6. DETERMINATION OF THE RATE OF NITRATION IN A STIRRED BATCH REACTOR.

The Reactor System

The reactor used was a standard 500 cm^3 three-necked round-bottomed flask fitted with an air inlet, replaceable sampling probe and a thermometer (see Figure 4.1). The reactor was stirred with a single-blade stainless steel paddle (2 cm tip-to-tip) driven by a Velodyne Motor-Generator Unit Type 74 and its associated control unit. This combined unit is capable of regulating a given stirring speed to within ± 1% by virtue of the voltage feedback from a dynamo fitted concentric with the motor.

The position of the paddle blade and the stirring speed were held constant throughout all runs. The reactor was partially immersed in a thermostatically controlled water bath capable of maintaining a given temperature to within

Figure 4.1 The Stirred Reactor.



± 0.1°C.

Experimental Procedure.

Aqueous sulphuric acid (350 cm^3) of known composition and nitric acid (12.7 cm^3, 70 weight %) were placed in the reactor and mixed thoroughly. At the same time,a stoppered flask containing the ortho-nitrotoluene (23.6 cm^3) was placed in the same water bath as the reactor. The stirring speed was adjusted to 2500 ± 25 rpm using a stroboscope and a digital voltmeter (a calibration plot of speed versus voltage had been prepared previously for the stirrer motor).

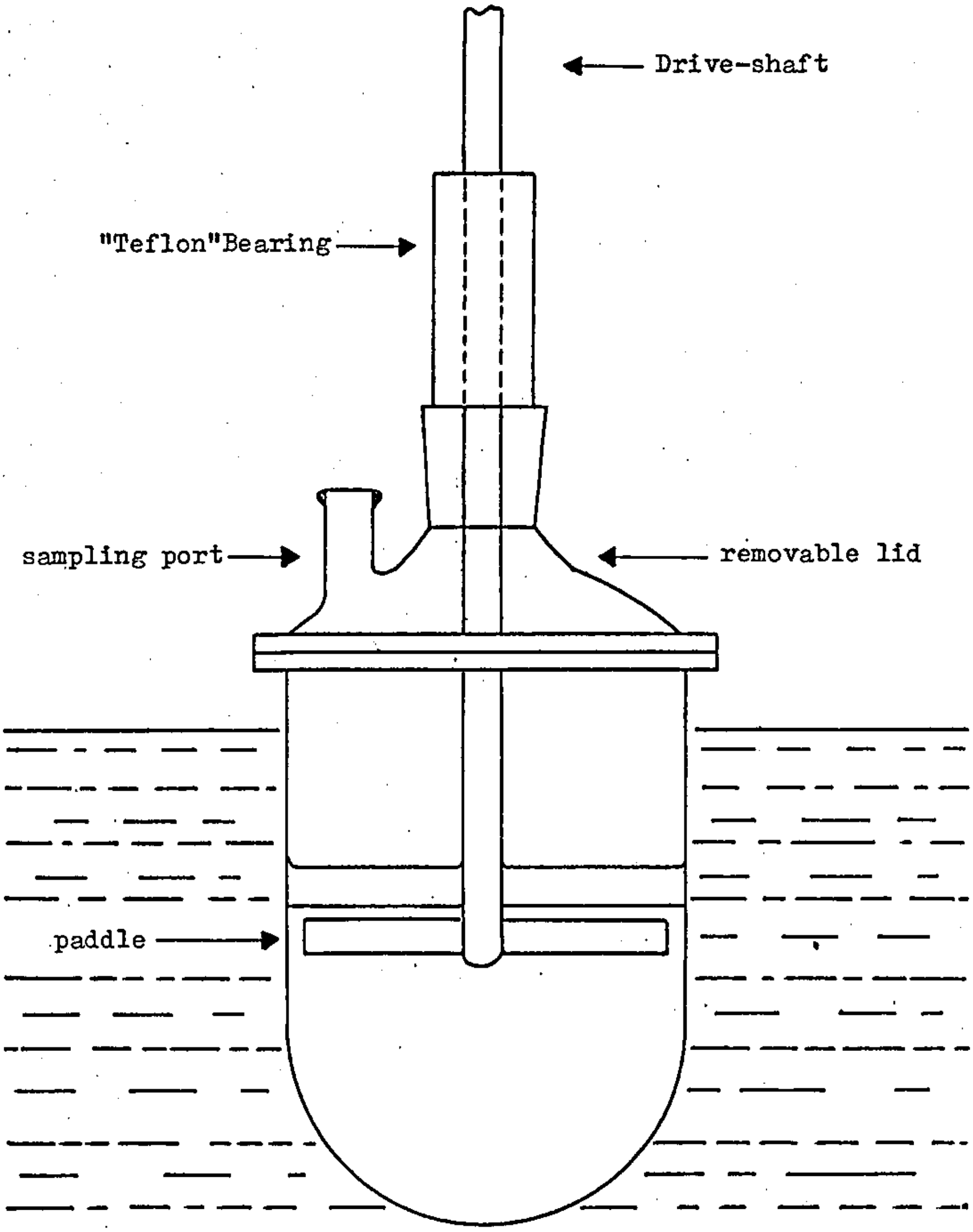
When both the mixed acid and the ortho-nitrotoluene had attained the required temperature,the latter was poured into the reactor and at the same time a stop-watch was started. After a suitable time interval,a sample (about 5 cm^3) of the reacting emulsion was removed from the reactor. To do this air pressure was applied gently to the air inlet and the sample was blown via the sampling probe into a flask containing cold distilled water (about 5 cm^3). This distilled water served to quench the reaction. This procedure was repeated at regular time intervals, a clean sampling probe being used in each case. The stoppered flasks containing the samples were each shaken gently for 30 minutes on a mechanical shaker. This ensured that any undissolved nitroaromatics present were contained in the organic phase rather than in the aqueous phase. The contents of each flask were separated and 10µl of the organic phase, in each case, was transferred to a volumetric flask (50 cm^3 capacity) and made up to volume with hexane (spectrograde). After shaking for one hour to ensure complete dissolution of the solute, the absorbance of each hexane solution was measured at a wavelength of 234 nm using an SP30 UV spectrophotometer. The absorbance of each hexane solution was then converted to fractional reaction using a calibration graph, as described in section 8.1.

4.7. DETERMINATION OF THE RATE OF NITRATION IN A STIRRED CELL.

The Cell.

The stirred cell described here was similar to that used by Cox (59) and Chapman(25). It was a cylindrical, round-bottomed vessel having a diameter of 6.58 cm and a capacity of about 200 cm^3. A removable two-necked lid allowed the stirrer to be inserted into the cell and provided access to the contents of the cell for ease of sample removal (see Figure 4.2). A stainless steel paddle (6 cm tip-to-tip), driven by the motor described in section 4.6 was used to stir the cell contents. The stirrer was, throughout all runs, placed at a fixed position within the cell (1 cm below the liquid-liquid interface). The cell was partially immersed in a thermostatically controlled water bath capable

Figure 4.2 <u>The Stirred Cell.</u>



of maintaining a given temperature to within ± 0.1°C.

Experimental Procedure

Aqueous sulphuric acid (164 cm^3) of known composition and nitric acid (6 cm^3, 70 weight %) were poured into the stirred cell and stirred rapidly to ensure homogeneity. At the same time, a stoppered flask containing ortho-nitrotoluene (23.6 cm^3) was placed in the water bath. The motor was adjusted to give a stirring speed of 55 ± 1 rpm. This speed was measured visually with the aid of a stop-watch.

When both the mixed acid and ortho-nitrotoluene were at the required temperature the latter was slowly poured into the cell and a stop-watch was started. At regular time intervals 10 microlitre samples of the organic phase were taken and dissolved in hexane (spectrograde, 50 cm^3). These solutions were then treated as described in Section 4.6.

4.8. SOURCES AND PURIFICATION OF MATERIALS

The sulphuric and nitric acids used in this work were of high purity (British Drug Houses AnalaR grade) as was the hexane used for spectroscopic measurements (Fisons spectrograde). The dinitrotoluenes used were prepared by recrystallising Koch-Light Laboratory grade reagents three times with acetone. The purified samples produced a single peak on g.l.c. analysis. The mononitrotoluenes used for solubility and distribution coefficient determinations were Fisons Laboratory grade reagents. For single and two phase rate studies the mononitrotoluenes were purified from Laboratory grade reagents as described below. All the purified mononitrotoluenes gave a single peak on g.l.c. analysis.

Para-nitrotoluene

Laboratory grade para-nitrotoluene was purified by recrystallising three times from absolute alcohol. The recrystallised sample was air dried and then further dried in a vacuum oven until it reached a constant weight. The melting point of this sample was in good agreement with the literature value.

Meta-nitrotoluene

Laboratory grade meta-nitrotoluene was dried over calcium hydride. After decantation the material was distilled under reduced pressure at 75°C and a middle fraction was collected for further use.

Ortho-nitrotoluene

Laboratory grade ortho-nitrotoluene was purified by passing it through a column of alumina using absolute alcohol as a solvent. The elutant was then fractionally distilled under reduced pressure. A middle fraction was taken for use in rate determinations.

RESULTS

CHAPTER 5

HOMOGENEOUS NITRATION OF MONONITROTOLUENES

5.1. RATES OF NITRATION

The second order rate constant, k_2, for the nitration of the three mononitrotoluenes has been determined as a function of temperature in 41.7 mole% H_2SO_4, either directly or by measuring the pseudo-first-order rate constant, k_1, where $k_1 = k_2 [HNO_3]$. The mononitrotoluenes used were purified as described in section 4.8. The methods used for the measurement of k_1 and k_2 are described in section 4.2.

The pseudo-first-order rate constant, k_1, was determined using Guggenheim's method (89) because, for the majority of runs, it was not possible to obtain a stable value of the absorbance of the reaction mixture at the completion of the reaction, A_∞, due to interference from side reactions.

Similarly, for the direct determination of k_2, a modified form of Guggeheim's method, developed by Roseveare (90), was used.

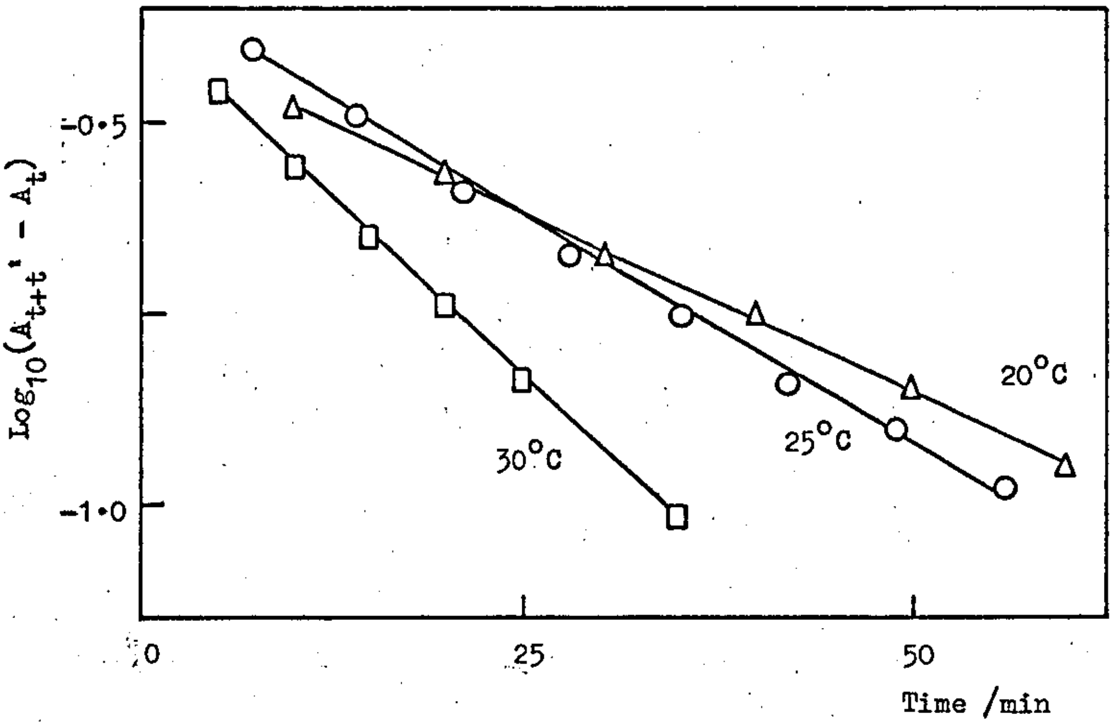
5.1.1. The Rate of Nitration of Meta-nitrotoluene

Meta-nitrotoluene (about 10^{-4} mol dm^{-3}) was nitrated, using the method described in section 4.2, in aqueous sulphuric acid containing a small quantity of nitric acid (3.94×10^{-2} mol dm^{-3}). The nitric acid: meta-nitrotoluene ratio of about 400:1 ensured that, at least at the beginning of each run, pseudo-first-order kinetics were obeyed.

Guggenheim plots for the pseudo-first-order nitration of meta-nitrotoluene in 41.7 mole% H_2SO_4,as a function of temperature,are shown in Figure 5.1. The runs performed at 20, 25 and 30°C show good pseudo-first-order behaviour (the Guggenheim plots are linear). However,the Guggenheim plots for temperatures above 30°C deviate from linearity for points corresponding to the later stages of each run. This indicates that some reaction,other than nitration of meta-nitrotoluene,begins to influence the absorbance of the reaction mixture under these conditions. The pseudo-first-order rate constant,k_1,at each temperature,was calculated from the slope of the linear portion of the appropriate Guggenheim plot. The second order rate constant,k_2,for each temperature,was then calculated from the corresponding value of k_1.

The values of k_1 and k_2 obtained are shown in Table 5.1.

Figure 5.1 Guggenheim Plots for Nitration of Metanitrotoluene.



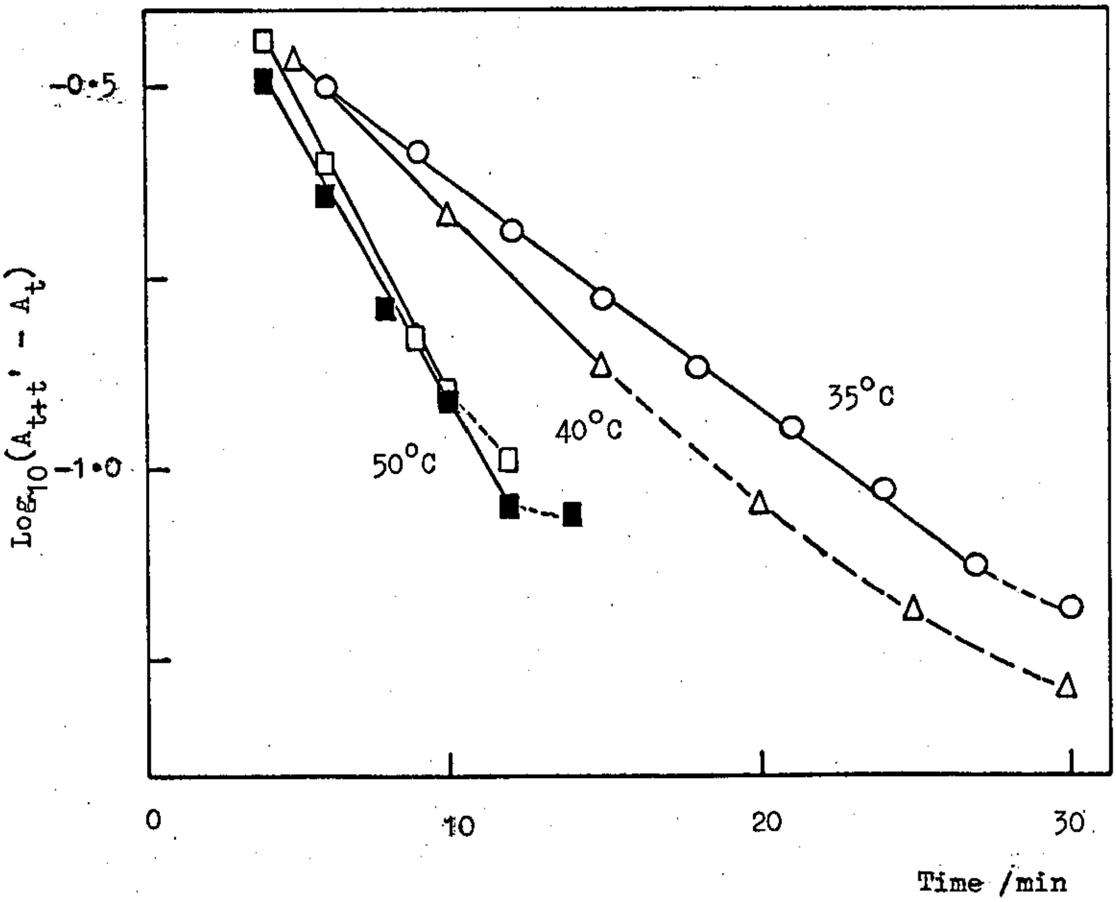


Table 5.1. Rate Constants for Nitration of Meta-nitrotoluene as a Function of Temperature in 41.7 mole% H_2SO_4.

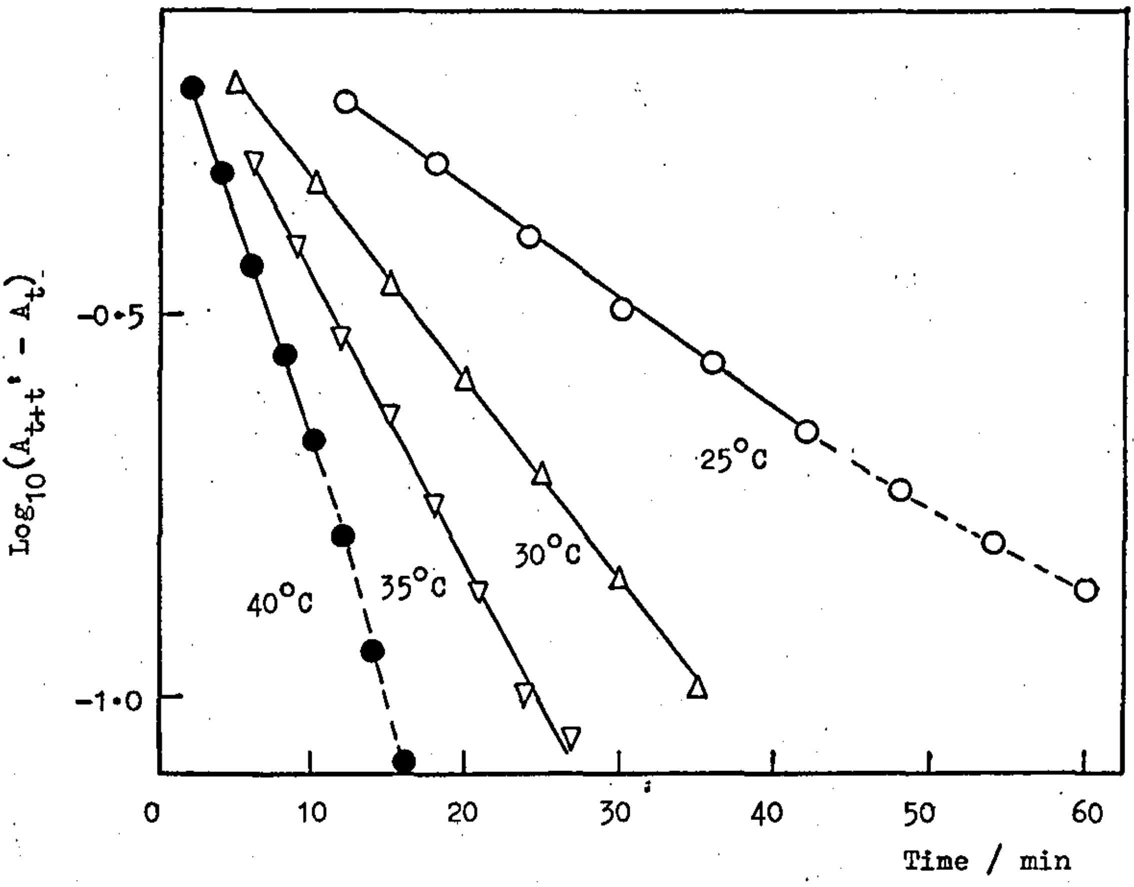
Temperature/^{o}C	$k_1 \times 10^3/s^{-1}$	$k_2 \times 10^2/dm^3mol^{-1}s^{-1}$
20	0.358	0.909
25	0.456	1.16
30	0.715	1.81
35	1.15	2.92
40	1.55	3.93
50	2.68,2.96	6.80, 7.51

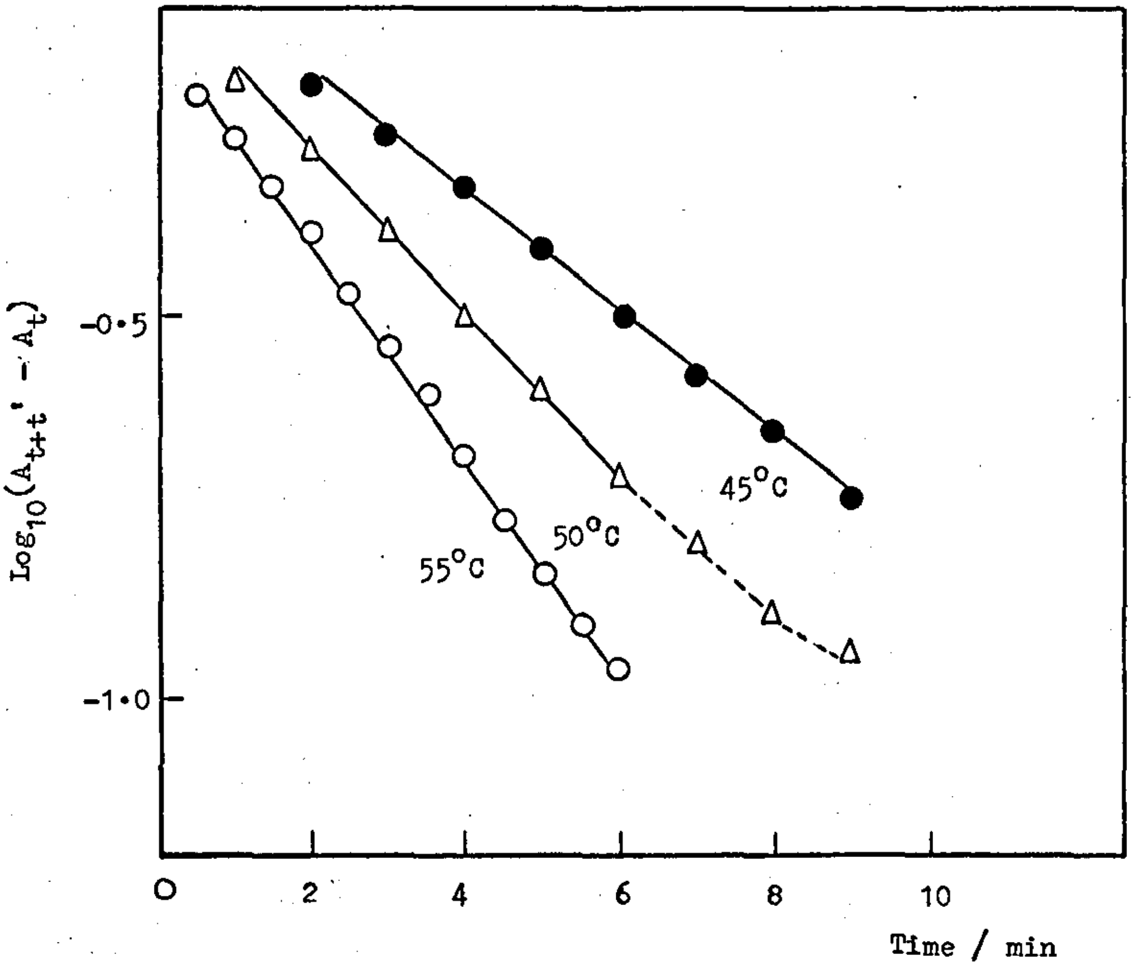
The value of k_2 determined at 25°C is in good agreement with the value of $1.23 \times 10^{-2}dm^3mol^{-1}s^{-1}$ obtained by interpolation from the work of Tillett (22).

5.1.2. The Rate of Nitration of Para-nitrotoluene.

The conditions employed for the pseudo-first-order nitration of para-nitrotoluene in 41.7 mole% H_2SO_4 were similar to those for meta-nitrotoluene. Determinations were carried out over the temperature range 20 to 55°C. The Guggenheim plots obtained are shown in Figure 5.2. In general, good pseudo-first-order behaviour is observed (the Guggenheim plots are again linear) although the Guggenheim plots again show some deviations from linearity near the end of some of the runs. The pattern of these

Figure 5.2 Guggenheim Plots for Nitration of Para-nitrotoluene.





deviations is not, however, as pronounced as that for meta-nitrotoluene. Values of the rate constants k_1 and k_2 obtained from these plots are listed in Table 5.2.

Table 5.2. Rate Constants for Nitration of Para-nitrotoluene as a Function of Temperature in 41.7 mole% H_2SO_4.

Temperature/^oC	$k_1 \times 10^3/s^{-1}$	$k_2 \times 10^2/dm^3mol^{-1}s^{-1}$
25	0.553	1.40
30	0.996	2.53
35	1.44	3.65
40	2.21	5.61
45	3.02	7.66
50	4.06	10.3
55	5.50	14.0

The value of k_2 determined at 25^oC is in reasonable agreement with the value of $1.86 \times 10^{-2}dm^3mol^{-1}s^{-1}$ obtained by interpolation from the results obtained by Vinnik, Grabovskaya and Arzamaskova (21).

5.1.3. The Rate of Nitration of Ortho-nitrotoluene.

Initially some runs were performed by using a large excess of nitric acid relative to ortho-nitrotoluene so that pseudo-first-order kinetics would be obeyed. However it was found that these conditions were unsatisfactory.

It was considered that the rate of nitration of ortho-nitrotoluene might be more easily determined if equal concentrations of nitric acid and ortho-nitrotoluene were used so that nitric acid would not be present after complete nitration of ortho-nitrotoluene had occurred. All runs were carried out in 41.7 mole% H_2SO_4.

Runs with Nitric Acid in Excess

These runs were performed in a similar way to those for meta- and para-nitrotoluene. Pseudo-first-order kinetics were only obeyed in the very early stages of each run, after which Guggenheim plots deviated significantly from linearity. A typical example of this type of behaviour is shown in Figure 5.3. The deviation from linearity of the Guggenheim plots was much more pronounced than that observed previously for meta- and para-nitrotoluene (Figures 5.1 and 5.2) and prevented the accurate determination of k_1. Further insight into this phenomenon may be gained by plotting the raw data used to construct the Guggenheim plot (Figure 5.3) as shown in Figure 5.4. In the later stages of the run the Absorbance versus Time plot becomes approximately linear, deviating from the exponential curve expected for pseudo-first-order kinetics. There are two processes which may occur during or after nitration of ortho-nitrotoluene and either or both of these processes could give rise to the observed phenomenon:

Figure 5.3 Typical Guggenheim Plot for Pseudo-first-order Nitration of Ortho-nitrotoluene in 41.7 mole% H_2SO_4.

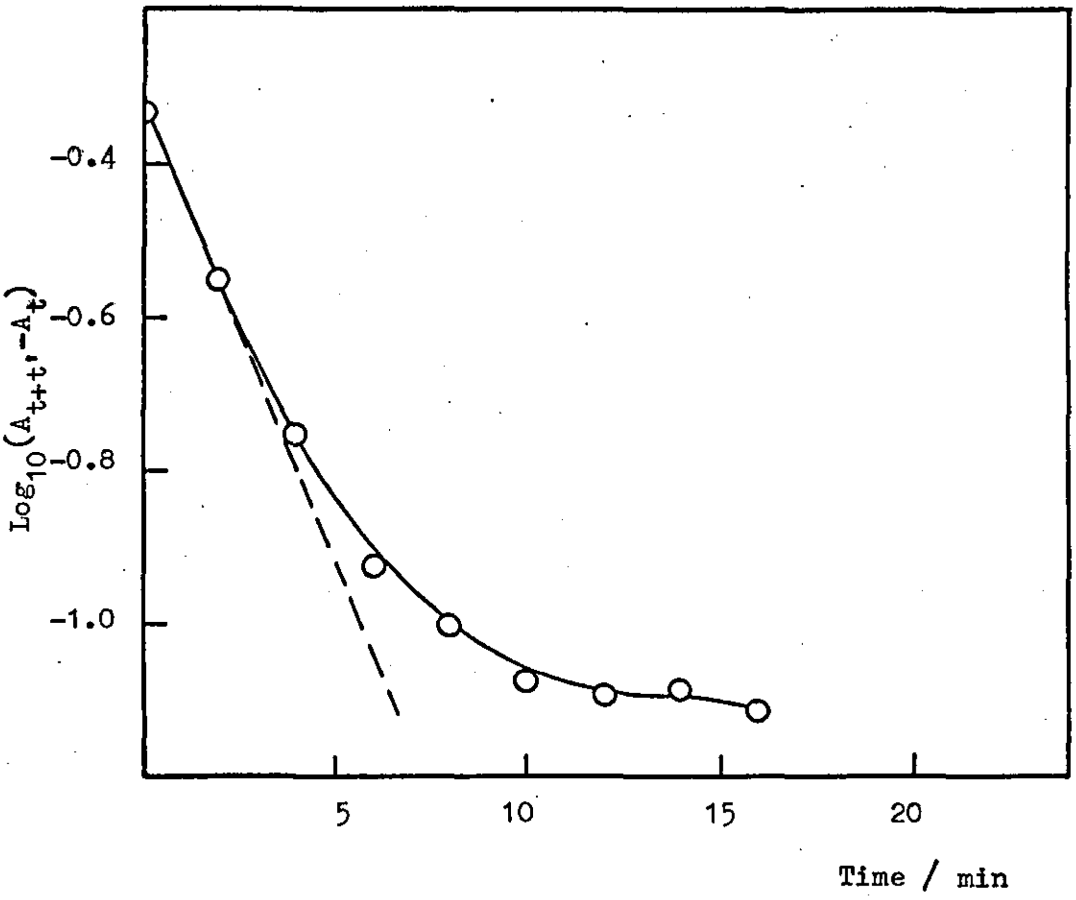
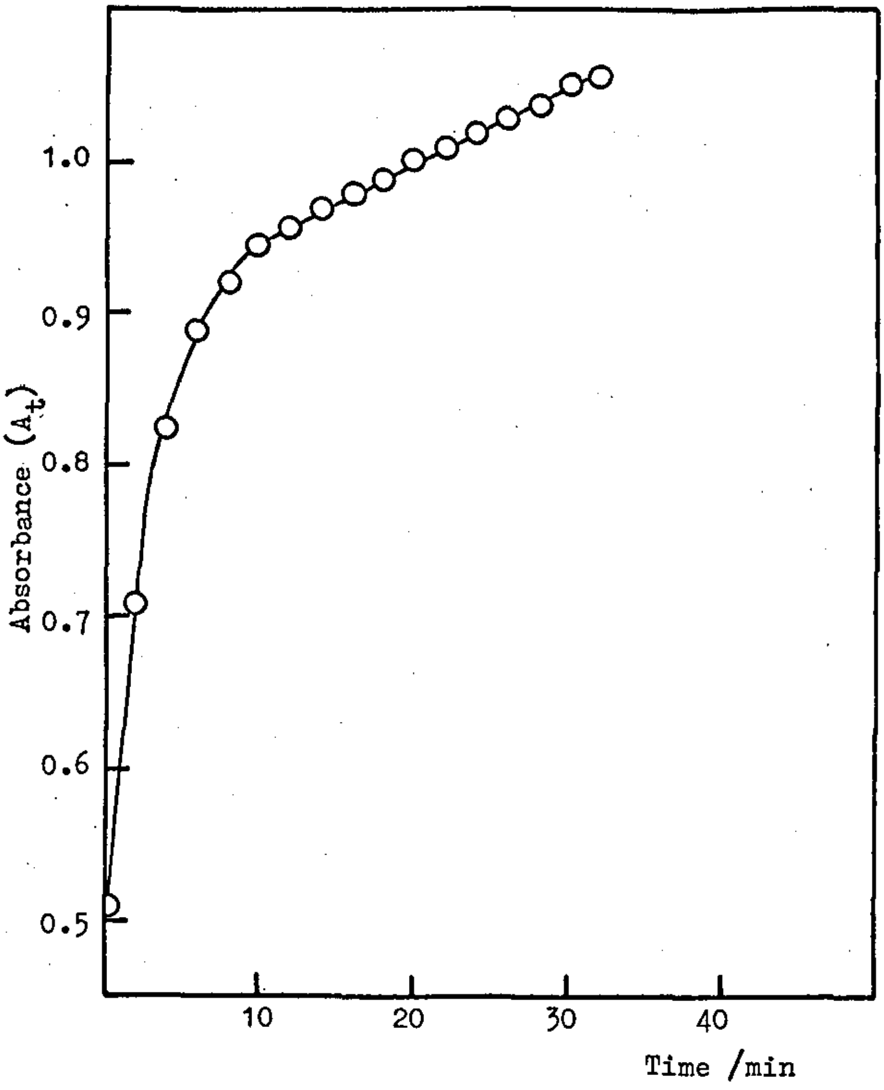


Figure 5.4 Typical Absorbance versus Time Plot for Pseudo-first-order nitration of Ortho-nitrotoluene in 41.7 mole% H_2SO_4.



(a) The nitration products of ortho-nitrotoluene (2, 4 - and 2, 6 - dinitrotoluene) may be oxidised in the presence of excess nitric acid.

(b) Ortho-nitrotoluene may be nitrated and oxidised simultaneously. The products formed by oxidation of ortho-nitrotoluene may then be further nitrated in the presence of excess nitric acid.

Detailed investigation of the side-reactions which take place during nitration of mononitrotoluenes was beyond the scope of the work described here. Therefore,it was decided to attempt to arrange the reaction conditions so that oxidation reactions would be minimised. To do this, equal concentrations of ortho-nitrotoluene and nitric acid were used so that nitric acid would not be in excess after nitration of ortho-nitrotoluene had been completed. It was thought that this method of nitration might reduce oxidation of the dinitrotoluenes formed but it was accepted that this would be unlikely to influence the oxidation of ortho-nitrotoluene, if this occurred in parallel with nitration of ortho-nitrotoluene.

Runs with the Reactant Concentrations Equal.

In these runs the initial concentration of both nitric acid and ortho-nitrotoluene was 2.2 x 10^{-3}mol dm^{-3}. Since the concentrations of the reactants were equal,second order kinetics were obeyed and for spectrophotometric measurements the following equation was applicable:

$$\frac{1}{A_\infty - A_t} - \frac{1}{A_\infty - A_o} = \frac{k_2 t}{\alpha} \quad \ldots\ldots\ldots \; 5.1$$

where A_∞, A_t and A_o are the absorbances at infinite time, time t and zero time respectively. The term, k_2, is the observed second order rate constant for the reaction and α is a proportionality constant such that:

$$1/\alpha = \frac{C_o}{A_\infty - A_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 5.2$$

C_o is the initial concentration of the reactants. A_o is the absorbance the reaction mixture would have (at a wavelength of 240 nm) in the absence of reaction. This value was determined by measuring the absorbance of each of the reactant solutions separately before each run, calculating the total absorbance of the mixture assuming no interaction takes place and taking into account the dilution of one solution by the other on mixing. The absorbances of the solutions of the reactants in aqueous acid, the sum of which constituted A_o, were found to remain constant from run to run, indicating that the method of preparation of these solutions enabled reproducible reactant concentrations to be obtained.

In this work it was not possible to measure A_∞, for the nitration reaction alone, due to interference from side-reactions, as explained earlier. For this reason it was necessary to adopt methods for calculating k_2 which did not require the direct measurement of A_∞. Two such methods were employed here.

(a) The Method of Successive Approximations.

In this method, a value of A_∞ of approximately the right order was chosen. The function $1/(A_\infty - A_t)$ was then calculated for each value of t from the observed values of A_t. If the value of A_∞ chosen was the true value for the nitration reaction and second order kinetics were obeyed, a plot of $1/(A_\infty - A_t)$ versus t would be linear and would have a slope equal to k_2/α. If, however, the value chosen for A_∞ was incorrect the plot would tend to deviate progressively from a straight line with increases in reaction time. A more accurate value of A_∞ could then be chosen. This procedure was repeated until the best straight line was obtained. A simple computer program, incorporating a repeated least-squares-fit calculation, was written to perform this calculation. Having determined the best value of A_∞, the second order rate constant for nitration, k_2, was calculated from equations 5.1 and 5.2.

(b) Roseveare's Method

Roseveare (90) adapted Guggenheim's method (89) for use in second order reactions in which the infinity value is unknown or inaccessible. Details of Roseveare's method of calculating k_2 are given in Appendix A.

By taking three groups of data values A_1, A_2 and A_3 separated by a constant time interval t,both A_∞ and k_2 can be calculated from the following equations:

$$A_\infty = \frac{A_1 A_2 + A_2 A_3 - 2A_1 A_3}{(A_2 - A_1) - (A_3 - A_2)} \quad \ldots\ldots\ldots \; 5.3$$

$$k_2/\alpha = \frac{\left\{(A_2 - A_1) - (A_3 - A_1)\right\}^2}{2t\,(A_3 - A_1)\,(A_3 - A_2)(A_2 - A_1)} \quad \ldots \; 5.4$$

Roseveare's method gives the most accurate values of A_∞ and k_2 when the time interval, t,is chosen so that 41% of the reaction occurs between A_1 and A_2.

i.e. $$\frac{A_2 - A_1}{A_\infty - A_1} = \frac{41}{100} \quad \ldots\ldots\ldots\ldots\ldots \; 5.5$$

The time intervals,t,in all runs (except that at 30°C) were such that the requirement stated in equation 5.5 was obeyed to a good approximation. In all runs except that at 30°C values of k_2 and A_∞ at each temperature were calculated by both methods described above. Table 5.3 shows the results obtained.

Excellent agreement was obtained between values of k_2 and A_∞ calculated by methods (a) and (b) above. There is considerable variation in the A_∞ values obtained at different temperatures,indicating that some side-reactions still occur even though equal concentrations of the reactants were used.

Table 5.3. Values of k_2 and A_∞ (at 240 nm) for Nitration of Ortho-nitrotoluene as a Function of Temperature in 41.7 mole% H_2SO_4.

Temperature/°C	A_∞			$k_2 \times 10^2/dm^3 mol^{-1} s^{-1}$		
	Method (a)	Method (b)	Mean	Method (a)	Method (b)	Mean
25	-	-	-	-	-	4.02
30	1.50	-	1.50	6.25	-	6.25
40	1.83	1.83	1.83	13.3	13.4	13.4
50	1.66	1.67	1.67	28.7	29.1	28.9
60	1.72	1.74	1.73	64.2	59.7	62.0
70	1.57	1.59	1.58	119	112	116
80	1.57	1.57	1.57	220	223	222

Note: The value given for k_2 at 25°C was obtained by extrapolation.

Hence, the value of k_2 determined is the rate constant for the disappearance of the initial reactants rather than that for the formation of 2, 4 - and 2, 6 - dinitrotoluene. However, recent work in this laboratory (91) has shown that, under dinitration conditions, the rate of formation of dinitrotoluenes (from nitration of ortho-nitrotoluene) is about fifty times the rate of formation of nitrous acid (which probably results from oxidation of ortho-nitrotoluene).

Hence, in the work which follows, it was assumed that the rate of oxidation of mononitrotoluenes is negligible compared with the rate of nitration of mononitrotoluenes. This is in line with most previous work on the nitration of mononitrotoluenes in which no references to oxidation reactions have been made.

5.1.4. Activation Energies for Nitration of Mononitrotoluenes in 41.7 mole% H_2SO_4.

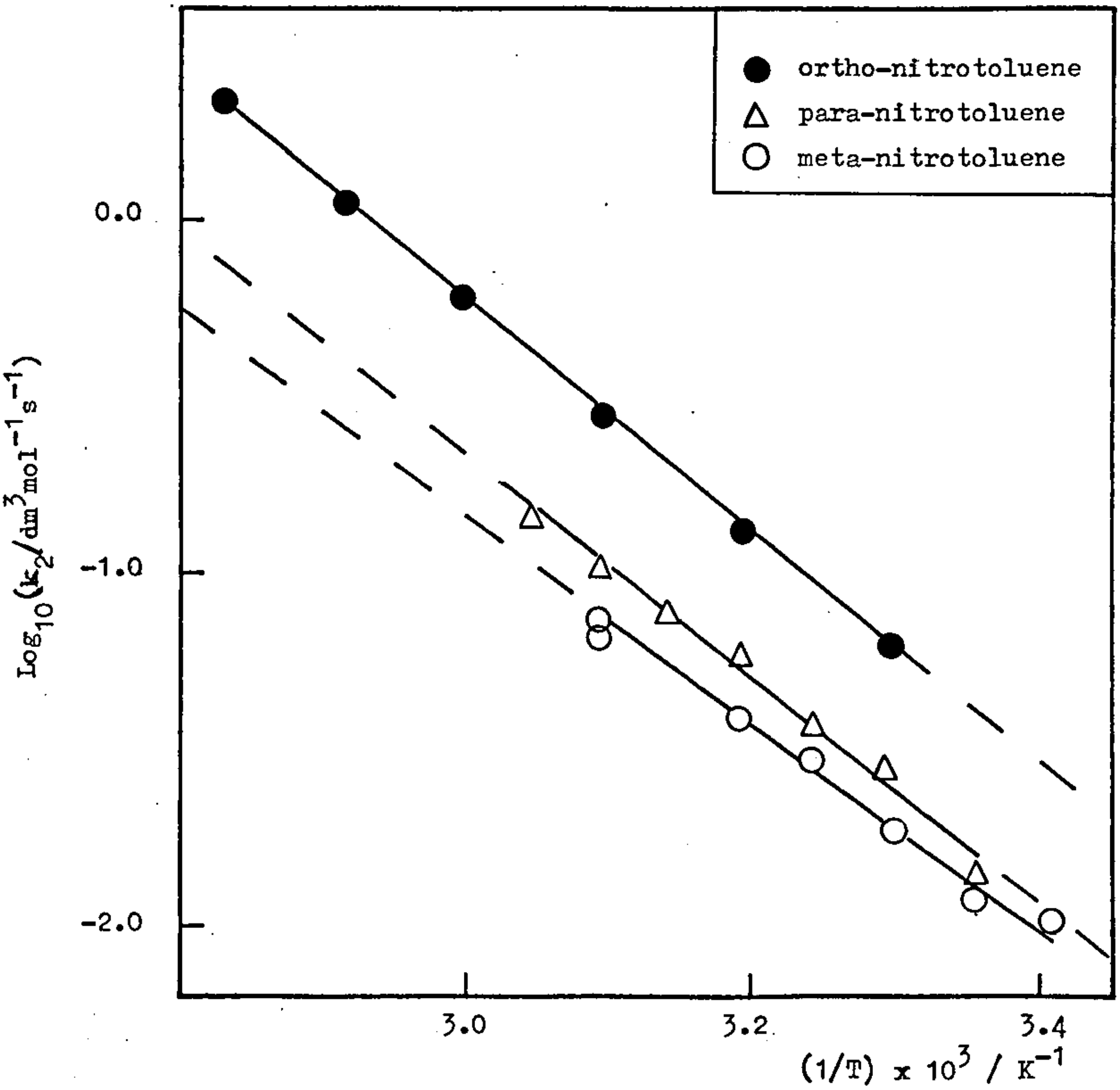
Arrhenius plots ($\log_{10}k_2$ versus reciprocal temperature) for nitration of all three mononitrotoluenes in 41.7 mole% H_2SO_4 are shown in Figure 5.5. The observed activation energies, E_2, calculated from the slopes of these plots are shown in Table 5.4.

Table 5.4. Activation Energies for Nitration of Mononitrotoluenes in 41.7 mole% H_2SO_4

Mononitrotoluene	E_2/kJ mol^{-1}	Temperature Range /°C
Meta-nitrotoluene	56.0	20 - 50
Para-nitrotoluene	60.8	25 - 55
Ortho-nitrotoluene	63.7	25 - 80

The scatter in the data used to construct the Arrhenius plot for ortho-nitrotoluene is somewhat less than that in the data used to construct the plots for meta- and para-nitrotoluene. The data for ortho-nitrotoluene also extend over a wider temperature range. For these reasons it is considered that the value of E_2 for ortho-nitrotoluene is probably more reliable than those

Figure 5.5 Arrhenius Plot for Nitration of Mononitrotoluenes in 41.7 mole % H_2SO_4.



for meta- and para-nitrotoluene. The calculated values of E_2 for these isomers are all quite similar and differences between them are probably within experimental error.

Vinnik, Grabovskaya and Arzamaskova (21) obtained a value of 90.4 kJ mol^{-1} for E_2 for the nitration of para-nitrotoluene in 30.8 mole% H_2SO_4. Chapman and Strachan (26) found that for several aromatics E_2 decreased by 2.80 kJ mol^{-1} for each weight % increase in H_2SO_4 concentration. If this relationship applies to para-nitrotoluene it can be shown, from the value obtained by Vinnik, Grabovskaya and Arzamaskova, that E_2 for para-nitrotoluene in 41.7 mole% H_2SO_4 would be 65.8 kJ mol^{-1}. This value is in reasonable agreement with that obtained here.

5.1.5. Relative Rates of Nitration of Mononitrotoluenes

Extrapolation of the Arrhenius plots for the three mononitrotoluenes (dashed lines in Figure 5.5) enables a comparison to be made of the relative rates of nitration of these isomers at 25°C with literature values. This comparison is shown in Table 5.5. The estimated relative rates of nitration of the isomers at 50°C are shown in the same table.

Table 5.5. Relative Rates of Nitration of Mononitrotoluenes

Source of Data	H_2SO_4 /mole%	Temp. /°C	Ratio of k_2 values		
			o/p	o/m	p/m
Competitive Nitration (27)	39.4	16	-	-	1.76
Direct Nitration (21, 22)	39.4	25	-	-	1.44*
" "	41.7	25	-	-	1.51*
This work	41.7	25	2.51	3.12	1.24
Direct Nitration (12)	46.4	25	1.9	2.3	1.2
Direct Nitration (21, 22)	46.4	25	-	-	1.65*
" "	85.6	25	-	-	2.60*
Competitive Nitration (22)	85.6	25	1.96	2.23	1.14
This work	41.7	50	2.77	4.00	1.45

Values marked * were obtained by comparison of the results of Tillett (22) and Vinnik and co-workers(21).

There is considerable scatter in the data shown in Table 5.5. For this reason it is not possible to draw any firm conclusions regarding the effect of H_2SO_4 concentration on the relative rates of nitration of mononitrotoluenes. The only data available for temperatures other than 25°C are those derived from the present work at 50°C and that by Shutov and co-workers (27) at 16°C. It has already been pointed out that the differences observed here between the values of E_2 for the mononitrotoluenes are probably within experimental error. Therefore the difference between the relative nitration rates at 25°C and at 50°C may not be significant.

5.1.6. Prediction of k_2 for Nitration of Ortho-nitrotoluene at a Given Temperature and H_2SO_4 - H_2O Composition.

In order to compare predicted and experimental two phase rates of nitration of ortho-nitrotoluene (Chapter 8) a knowledge of k_2 is required for a range of reaction conditions. Measurement of k_2,for nitration of ortho-nitrotoluene over the whole range of conditions covered by the two phase nitration studies performed here, was not considered practicable both because of the limited time available and because of the difficulties encountered in measuring homogeneous rates of nitration due to the effect of side-reactions (see section 5.1.3.). However, a reasonable estimate of k_2 at a given temperature and

H_2SO_4 - H_2O composition may be made by using a combination of the information obtained in the present work and that in the published literature. The method of using this information is described below.

Values of k_2,for the nitration of meta- and para-nitrotoluene at 25°C, as a function of H_2SO_4 - H_2O composition, were obtained from the literature (21, 22) and relative rates of nitration of the mononitrotoluenes in 41.7 mole% H_2SO_4 were determined in the present work (Table 5.5). By assuming that the change in the relative rates of nitration of the mononitrotoluenes,with H_2SO_4 - H_2O composition,is small compared to the corresponding changes in k_2, it was possible to estimate k_2 for the nitration of ortho-nitrotoluene at 25°C as a function of H_2SO_4 - H_2O composition (see Figure 5.6). The activation energy, E_2, of ortho-nitrotoluene in 41.7 mole% H_2SO_4 has also been determined here (section 5.1.4). Using the relationship (26), between E_2 and weight % changes in H_2SO_4, found for several aromatics, values of k_2 for ortho-nitrotoluene at 50°C and 80°C as a function of H_2SO_4 - H_2O composition were estimated. Values of k_2 and E_2 calculated in this way are shown in Table 5.6 together with values experimentally determined in this work in 41.7 mole% H_2SO_4. Plots of $\log_{10}k_2$ (at 25°C, 50°C and 80°C) versus weight % H_2SO_4 constructed from the data in Table 5.6 are shown in Figure 5.6.

Table 5.6. Values of k_2 and E_2 for Nitration of Ortho-nitrotoluene as a Function of Reaction Conditions.

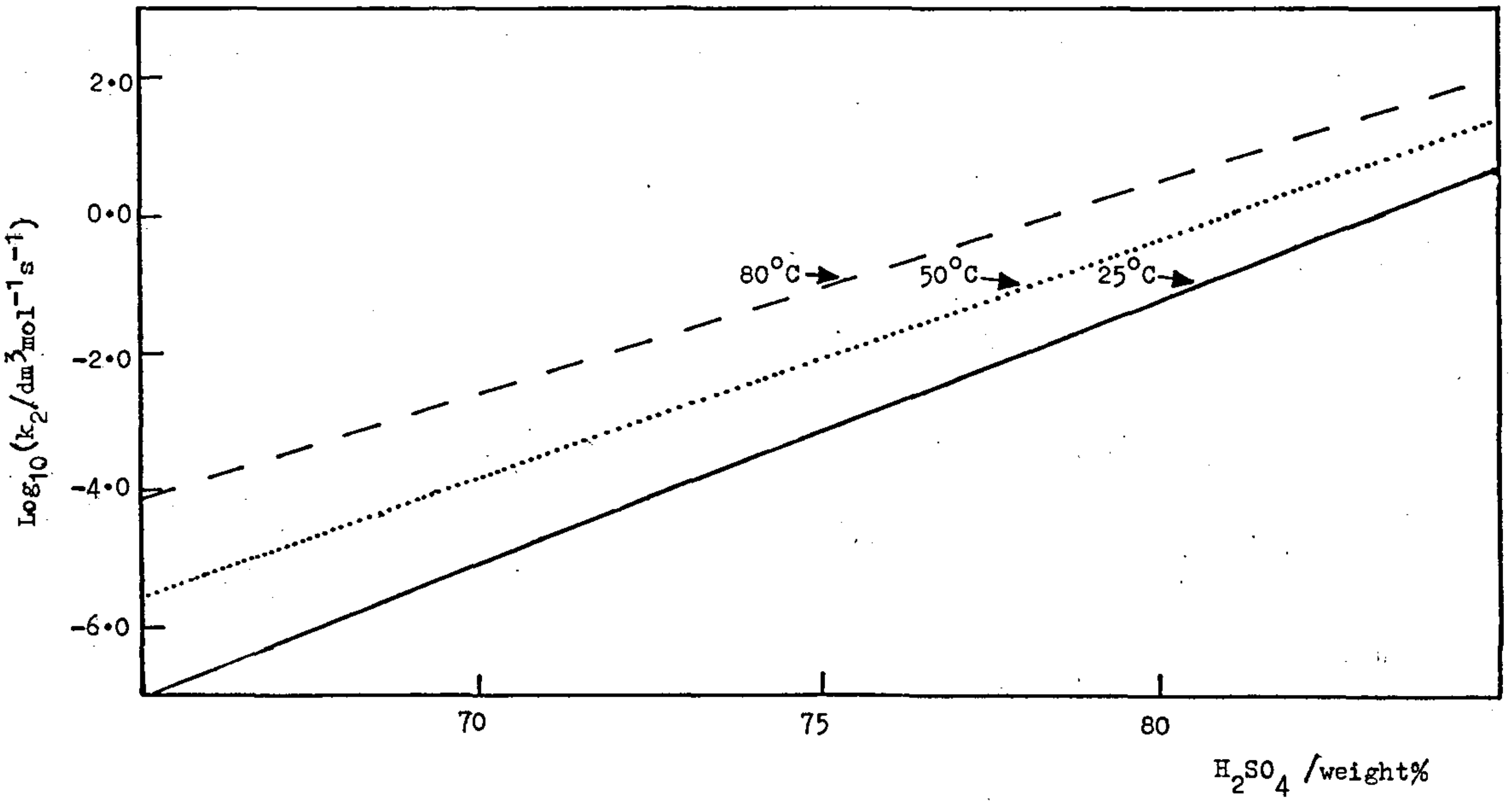
H_2SO_4 /mole%	H_2SO_4 /Weight%	$k_2/dm^3mol^{-1}s^{-1}$ 25°C	$k_2/dm^3mol^{-1}s^{-1}$ 50°C	$k_2/dm^3mol^{-1}s^{-1}$ 80°C	E_2 /kJ mol^{-1}
25.4	65.0	1.08×10^{-7}	2.83×10^{-6}	7.76×10^{-5}	105
30.0	70.0	8.99×10^{-6}	1.51×10^{-4}	2.64×10^{-3}	90.3
35.5	75.0	7.52×10^{-4}	8.22×10^{-3}	9.27×10^{-2}	76.5
41.7	79.6	4.02×10^{-2}	0.289*	2.22*	63.7*
42.3	80.0	6.33×10^{-2}	0.444	3.19	62.3
51.0	85.0	5.34	24.3	113	48.5

Values marked with an asterisk were determined experimentally in this work. All other values were obtained by calculation.

5.2. PRODUCTS OF NITRATION

The products formed when each of the isomers of mononitrotoluene are nitrated are well known (see section 2.2.6). However, very little is known about the way the ratio of products formed from each isomer varies with temperature and H_2SO_4 - H_2O composition. Para-nitrotoluene

Figure 5.6 Variation of k_2 for Nitration of Ortho-nitrotoluene as a Function of Temperature and % H_2SO_4.



is nitrated almost exclusively to 2, 4 - dinitrotoluene whereas meta- and ortho-nitrotoluene form more than one product on nitration. The isomers formed from the nitration of meta-nitrotoluene are not of great commercial value and hence no work was performed here on the effect of reaction conditions on the ratio of products formed from this isomer. In contrast,the products of nitration of ortho-nitrotoluene are of considerable commercial value (see Introduction) and therefore the ratio of these products formed,as a function of temperature and H_2SO_4 - H_2O composition,were studied here. Full details of the experimental methods used for the determination of dinitrotoluene product ratios are given in section 4.3.

Analysis of the products formed from nitration of ortho-nitrotoluene was carried out using gas-liquid chromatography. The technique used was capable of separating all six dinitrotoluenes. For a constant carrier gas flow-rate and oven temperature the retention times of the isomers remained constant, thus enabling them to be identified in an unknown mixture. The relative areas and the relative heights of the peaks obtained from a solution containing a known ratio of the isomers were also fairly constant (see Appendix B). It was found that the ratio of peak heights,obtained by chromatographing such a mixture, was significantly more reproducible than the ratio of peak areas and hence the former parameter was used for all experiments on unknown dinitrotoluene mixtures.

The apparatus was calibrated by chromatographing a number of standard solutions of mixtures of 2, 4 - and 2, 6 - dinitrotoluene. From a knowledge of the isomer weight ratio $W_{2,4}/W_{2,6}$ and the peak height ratio $H_{2,6}/H_{2,4}$ a relative response factor R' was calculated in each case such that

$$R' = \frac{W_{2,4}}{W_{2,6}} \cdot \frac{H_{2,6}}{H_{2,4}} \qquad \ldots\ldots\ldots\ldots \; 5.6$$

The mean value of R' was found from these calibration runs. The ratio $W_{2,4}/W_{2,6}$ could then be found for solutions containing unknown mixtures of the isomers. Further calibrations were also carried out before and after each analysis of an unknown mixture.

The ratios of the isomers formed on nitrating orth-nitrotoluene at two temperatures (25°C and 80°C) over a range of H_2SO_4 - H_2O compositions are listed in Table 5.7.

These ratios are plotted against H_2SO_4 - H_2O composition for each temperature in Figure 5.7.

Table 5.7. Products of Nitration of Ortho-Nitrotoluene.

H_2SO_4 /mole%	$\frac{\text{Weight of 2, 4 - dinitrotoluene}}{\text{Weight of 2, 6 - dinitrotoluene}}$
25°C	
29.7	2.00
"	2.06
30.6	2.03
"	2.03
"	2.13+
32.6	1.97
"	2.03
36.9	2.03
"	2.04
41.4	2.09
"	2.15
41.9	2.13
"	2.16
"	2.16
80°C	
30.5	1.85
"	1.85
30.6	1.85
"	1.86
"	1.92+

Table 5.7. Products of Nitration of Ortho-Nitrotoluene Continued

H_2SO_4 /mole%	Weight of 2, 4 - dinitrotoluene / Weight of 2, 6 - dinitrotoluene
80°C (Continued)	
34.0	1.83
"	1.85
36.9	1.89
"	1.92
38.5	1.94*
"	1.95*
41.9	1.92
"	1.94
"	1.92
"	1.94
"	1.95

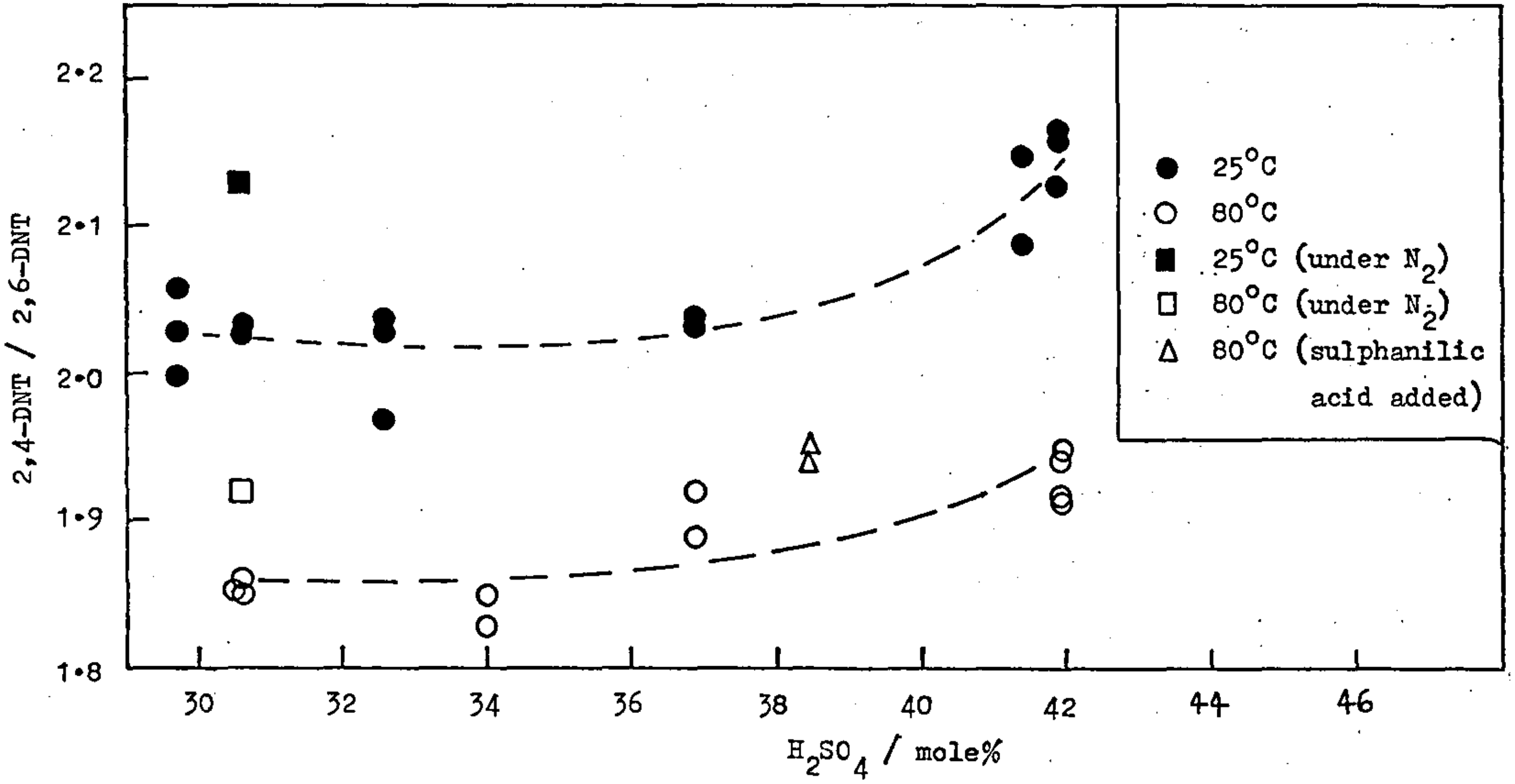
Notes: (i) Runs marked + were carried out under an atmosphere of nitrogen.

(ii) Runs marked * were carried out in the presence of sulphanilic acid (10^{-2}mol dm^{-3}).

There is considerable scatter in the results obtained but the following general observations can be made:

(a) At a given H_2SO_4 concentration the ratio of 2, 4 - dinitrotoluene to 2, 6 - dinitrotoluene

Figure 5.7 Products of Nitration of Ortho-nitrotoluene as a Function of Reaction Conditions.



found in the product mixture obtained from nitration of ortho-nitrotoluene decreases with increases in temperature.

(b) At a given temperature, the above ratio decreases with decreases in sulphuric acid concentration.

These observations are in agreement with the findings of Shutov and co-workers (27) who claim that the percentage of 2, 6 - dinitrotoluene formed from the nitration of ortho-nitrotoluene is only slightly affected by temperature but is increased by using lower sulphuric acid concentrations.

In one pair of runs, sulphanilic acid was added to the reaction mixture as a nitrous acid trap but the results obtained indicate that this has no significant effect on the ratio of products formed.

In two runs, the reactions were performed under an atmosphere of nitrogen gas. This appeared to increase the ratio of 2, 4 - to 2, 6 - dinitrotoluene formed but further work would be necessary to establish whether or not this observation is significant.

The activation energies for nitration of ortho-nitrotoluene, at ring positions 4 and 6, have been calculated for two sulphuric acid compositions from a knowledge of the variation of the ratio of the products of nitration and the variation of k_2, with temperature and sulphuric acid composition (see Figures 5.6 and 5.7). These activation energies are shown in Table 5.8. The difference between the activation energies for nitration at these ring positions is quite small. This is in agreement with the findings of Shutov and co-workers (27) who said that this difference was less than 4.2 kJ mol^{-1} in 77.7 mole% sulphuric acid.

Table 5.8. Activation Energy for Nitration at Ring Positions 4 and 6 as a Function of H_2SO_4 - H_2O Composition.

H_2SO_4 /mole%	$E_{2,6}$ /kJ mol^{-1}	$E_{2,4}$ /kJ mol^{-1}	$E_{2,6}$ - $E_{2,4}$ /kJ mol^{-1}
30.6	89.7	88.2	1.50 ± 1.53
41.9	64.4	62.7	1.70 ± 1.70

CHAPTER 6

THE MUTUAL SOLUBILITY OF MONONITROTOLUENES AND AQUEOUS SULPHURIC ACID

6.1 SOLUBILITY OF MONONITROTOLUENES IN AQUEOUS SULPHURIC ACID

6.1.1 Solubility as a Function of $H_2SO_4 - H_2O$ Composition at 25°C.

A general description of the dependence of the solubility of non-electrolytes on aqueous sulphuric acid composition was given in section 3.3. The solubility of ortho-nitrotoluene in aqueous sulphuric acid has been determined here over a limited range of H_2SO_4-H_2O compositions at $25.0 \pm 0.1^{\circ}C$. The results obtained are shown in Figure 6.1 and compared with literature values for para-nitrotoluene and 2,4 - dinitrotoluene (79, 92) in Table 6.1. The solubility of meta-nitrotoluene in 43.1 mole% H_2SO_4 at 25°C was also determined and the value obtained is included in Table 6.1 for comparison with the other nitro-aromatics shown.

Table 6.1 Solubility of Mononitrotoluenes as a Function of H_2SO_4 - H_2O Composition at 25.0 ± 0.1°C.

H_2SO_4/mole%	Solubility x 10^2/mol dm^{-3}			
	ortho-nitrotoluene a	meta-nitrotoluene a	para-nitrotoluene	2,4- DNT b, c
21.6	1.17	-	0.62^b	-
25.5	1.55	-	0.87^b	-
29.3	1.95	-	1.3^b	-
29.8	2.22	-	1.4^b	2.4
35.9	4.23	-	3.6^b	3.6
36.4	4.00	-	3.7^b	3.8
42.0	7.55	-	8.9^b	6.9
43.1	9.82	8.64	11^c	7.9
44.2	12.8	-	13^c	8.9
47.6	24.0	-	22^c	14
49.4	39.8	-	29^c	17
50.6	58.4	-	37^c	20

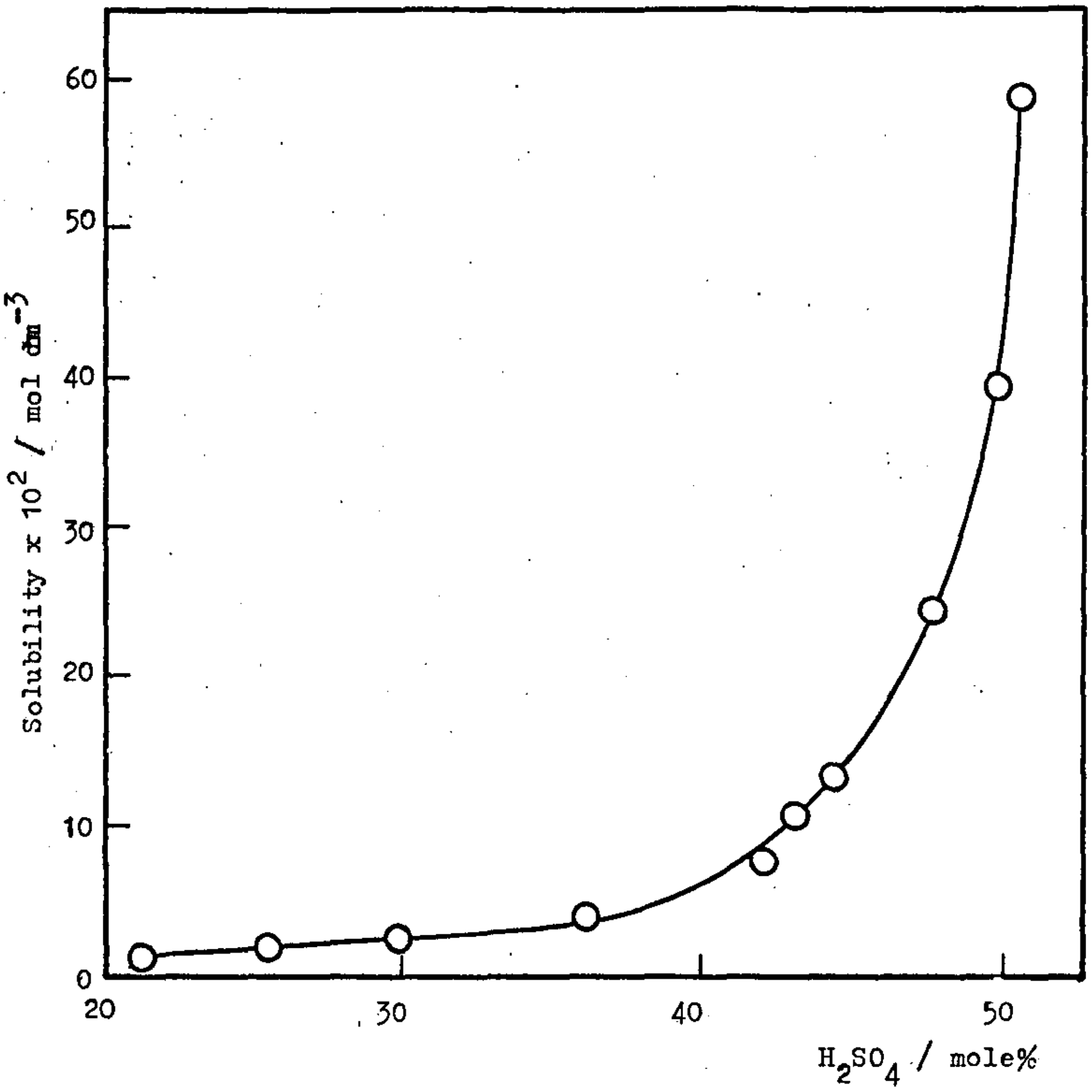
Notes

a - This work

b - Values interpolated from work by Yates and McClelland (79)

c - Values interpolated from work by Grabovskaya and Vinnik (92).

Figure 6.1 Solubility of Ortho-nitrotoluene as a Function of H_2SO_4-H_2O Composition at 25°C.

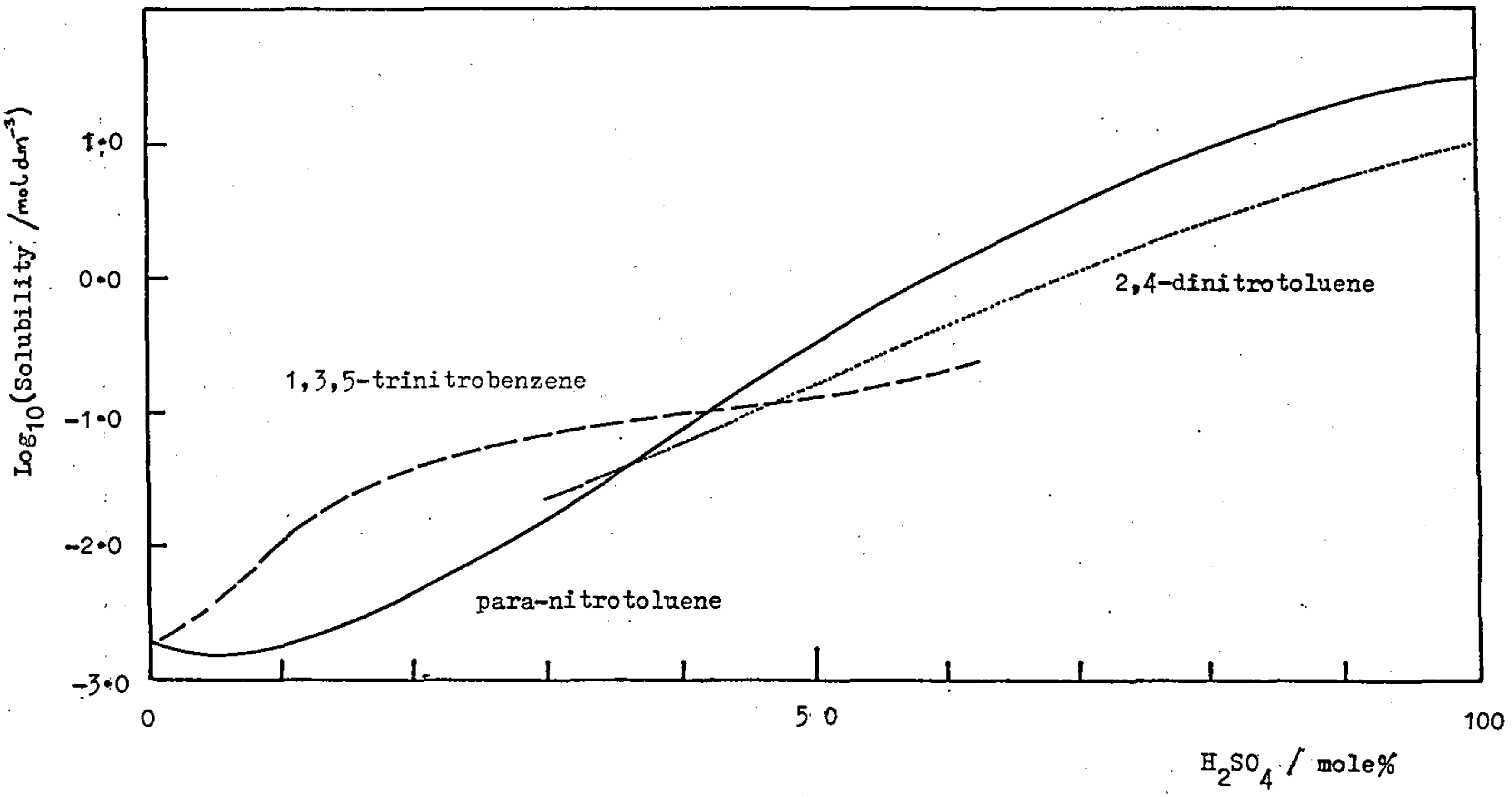


Ortho- and para- nitrotoluene have very similar solubilities in aqueous sulphuric acid over the range of H_2SO_4 - H_2O compositions considered here, their values never differing by more than a factor of two. In 43.1 mole% H_2SO_4 the solubilities of the three mono-nitrotoluenes are almost the same. It is likely that the solubility behaviour of ortho- and meta-nitrotoluene will be similar to that of para-nitrotoluene over the complete range of H_2SO_4 - H_2O compositions. Figure 6.2 compares data taken from the literature for several nitroaromatics. It shows that para-nitrotoluene is slightly salted-out in dilute aqueous sulphuric acid (less than 10 mole% H_2SO_4). It is likely that all the mono-nitrotoluenes and perhaps the dinitrotoluenes behave in this way.

As the H_2SO_4 concentration is increased beyond 10 mole% H_2SO_4 the mononitrotoluenes show a steady increase in solubility. Above 40 mole% H_2SO_4, the solubilities of the mononitrotoluenes increase very sharply (e.g. the solubility of ortho-nitrotoluene increases eight-fold as the H_2SO_4 concentration is increased from 40 to 50 mole% H_2SO_4) until 50 mole% H_2SO_4 is reached.

Above 50 mole% H_2SO_4, however, the increase in solubility with increasing H_2SO_4 content begins to decline. For dilute aqueous acid solutions ($<$40 mole% H_2SO_4) the solubilities

Figure 6.2 Log$_{10}$(Solubility) of Various Nitroaromatics as a Function of H_2SO_4-H_2O Composition.



of the nitroaromatics shown in Figure 6.2 rank in the order:

1, 3, 5 - trinitrobenzene > 2, 4 - dinitrotoluene > para-nitrotoluene.

This is in line with the general trend that salting-in of non-electrolytes by aqueous sulphuric acid increases with the number of salting-in groups (in this case nitro-groups) present in the solute molecule. This trend does not, however, extend to higher H_2SO_4 concentrations (> 40 mole% H_2SO_4) where the ranking order shown above is reversed. It is possible that at higher H_2SO_4 concentrations (higher internal pressures) the salting out effect due to molecular size predominates over the salting-in effect due to the presence of nitro-groups and hence the solubilities rank in the reverse order.

6.1.2. Solubility as a Function of Temperature at a Given H_2SO_4 - H_2O Composition.

The temperature dependence of the solubility of a substance in a particular solvent is usually given by the expression:

$$\frac{d\,(\ln C)}{dT} = \frac{\Delta H_s}{RT^2} \qquad \ldots\ldots\ 6.1$$

where C is the solubility in a given solvent, T is the absolute temperature, R is the Gas Constant and ΔH_s is the heat of solution.

Equation 6.1 may be regarded as a form of the Van't Hoff equation which governs the temperature dependence of the equilibrium constant K:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 6.2$$

where ΔH is the enthalpy change for the reaction concerned.

Integrating Equation 6.1 we have:

$$\ln \left[\frac{C_1}{C_2}\right] = \frac{\Delta H_s}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \ldots\ldots\ldots\ldots \quad 6.3$$

or

$$\log_{10} \left[\frac{C_1}{C_2}\right] = \frac{\Delta H_s}{2.303R} \left[\frac{T_1 - T_2}{T_1 T_2}\right] \ldots\ldots\ldots \quad 6.4$$

If the solubilities C_1 and C_2 of a substance in a given solvent can be determined at two temperatures T_1 and T_2 respectively an approximate heat of solution may be calculated from Equation 6.4. A more accurate value of ΔH_s may be obtained by measuring solubilities at a number of different temperatures, integrating Equation 6.1 and converting to $\log_{10}$ as follows:

$$\log_{10} C = \frac{-\Delta H_s}{2.303R} \cdot \frac{1}{T} + \text{constant} \quad \ldots\ldots \quad 6.5$$

If a plot of $\log_{10} C$ against $1/T$ is linear (i.e. equation 6.5 is obeyed)

$$\Delta H_s = -2.303R \times (\text{slope of plot}) \quad .....6.6$$

However, if the plot is curved, the heat of solution varies with temperature and values of ΔH_s are calculated from the slope of tangents to the curve at various temperatures.

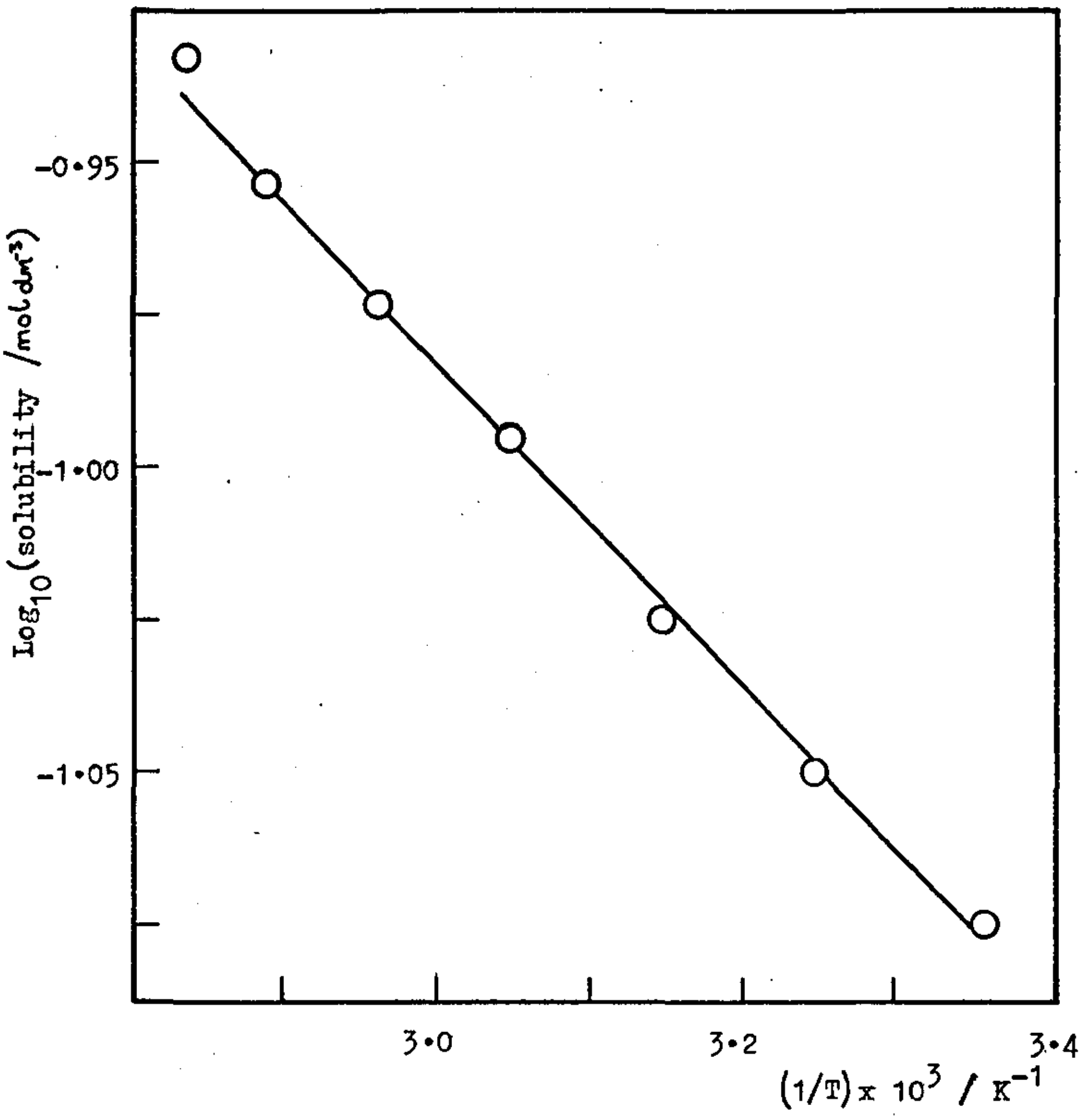
The solubility of meta-nitrotoluene in 43.1 mole% sulphuric acid has been determined over the temperature range 25 - 80°C. The results obtained are listed in Table 6.2.

Table 6.2. Solubility of Meta-nitrotoluene in 43.1 mole% H_2SO_4 as a Function of Temperature.

Temperature /°C	Solubility x 10^2/mol dm^{-3}
25	8.64
35	9.08
45	9.52
55	10.1
65	10.5
75	10.9
80	11.3

A plot of $\log_{10}$ (solubility) versus 1/T constructed from these data (Figure 6.3) is linear. The heat of solution of meta-nitrotoluene in this solvent was calculated from the slope of this plot and a value of 4.07 kJ mol^{-1} was obtained.

Figure 6.3 Arrhenius Plot for Solubility of Meta-nitrotoluene in 43.1 mole% H_2SO_4.



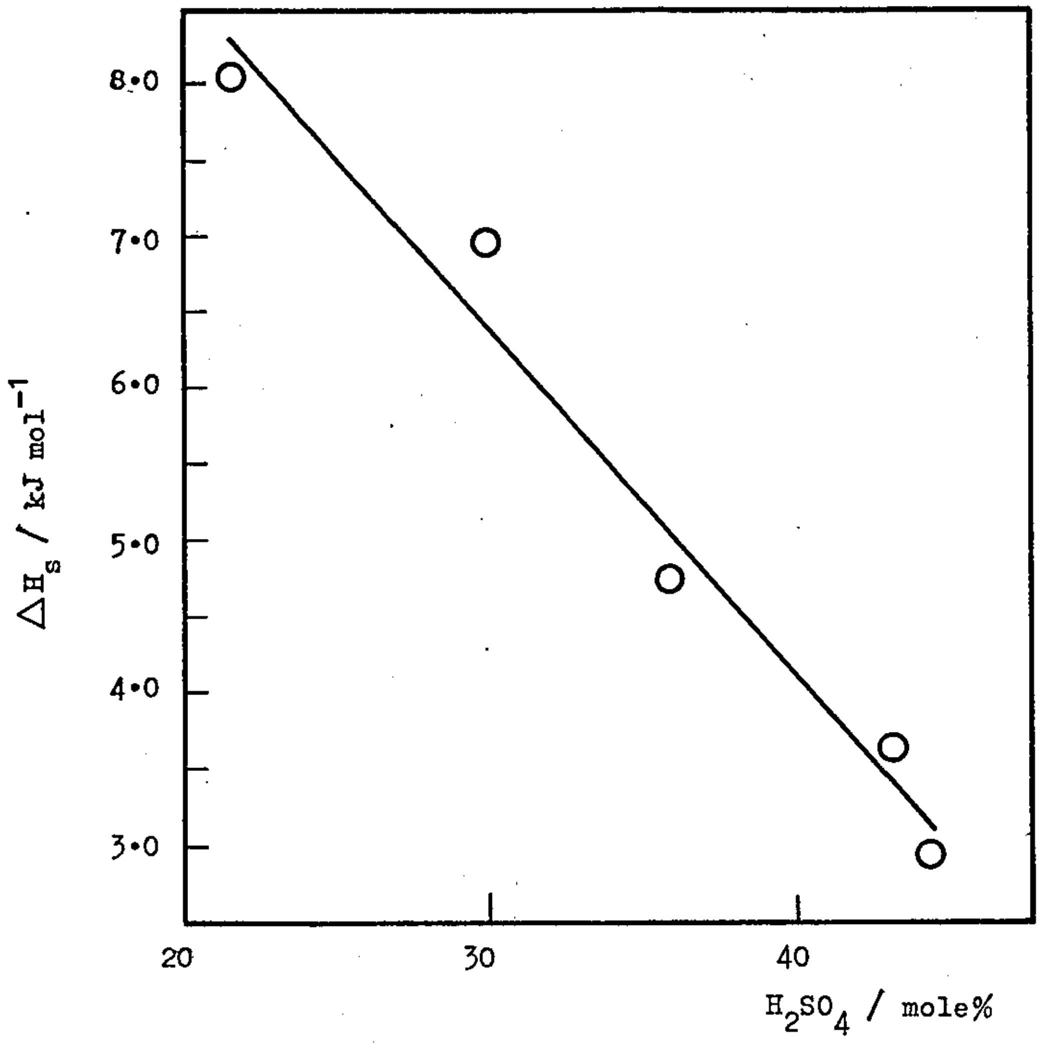
6.1.3. Solubility as a Function of H_2SO_4 - H_2O Composition and Temperature

An extensive series of experiments was carried out to determine the combined effects of variations in temperature and H_2SO_4 - H_2O composition on the solubility of ortho-nitrotoluene. The heat of solution was determined as a function of composition over the range 21.6 - 44.2 mole% H_2SO_4 for temperatures in the range 25 - 80°C. The solubilities determined at various temperatures and the heats of solution calculated for each composition are shown in Table 6.3. A plot of heat of solution against sulphuric acid composition constructed from these data is shown in Figure 6.4.

Table 6.3. Solubility of Ortho-Nitrotoluene as a Function of H_2SO_4 - H_2O Composition and Temperature

H_2SO_4/mole%	Solubility x 10^2/mol dm^{-3}			Heat of Solution /kJ mol^{-1}
	25°C	50°C	80°C	
21.6	1.17	1.50	1.94	8.05
29.8	2.22	2.73	3.48	6.96
35.9	4.23	-	5.76	4.76
43.1	9.82	10.8	12.2	3.52
44.2	12.8	-	15.4	2.97

Figure 6.4 Heat of Solution of Ortho-nitrotoluene as a Function of H_2SO_4-H_2O Composition.



The solubility of ortho-nitrotoluene in aqueous sulphuric acid is found to increase both with increases in the temperature and the H_2SO_4 content of the acid. Over the range 21.6 - 44.2 mole% H_2SO_4 an approximately linear relationship is observed between the heat of solution and sulphuric acid composition, ΔH_s decreasing by about 0.23 kJ mol^{-1} for each mole% increase in H_2SO_4 content. Decreases in the heat of solution with increase in H_2SO_4 concentration have also been observed for nitrobenzene (93) and hexafluoro-meta-xylene (HFMX) (94). In the latter case,the heat of solution decreases from 15.9 kJ mol^{-1} in 30 mole% H_2SO_4 to become negative (about - 36 kJ mol^{-1}) in 83.5 mole% H_2SO_4. Extrapolation of the plot shown in Figure 6.4 indicates that the heat of solution of ortho-nitrotoluene will be zero in 57.9 mole% H_2SO_4 and negative for H_2SO_4 concentrations greater than this.

6.2. ENTROPY CHANGES DURING SOLUTION OF MONONITROTOLUENES IN AQUEOUS SULPHURIC ACID

In section 3.3.2 it was pointed out that the rapid increase in the solubility of nitroaromatics in aqueous sulphuric acid,as the H_2SO_4 content is increased,may involve hydrogen bonding and that cyclic complexes between the nitroaromatic and either undissociated H_2SO_4 or H_3O^+ may be formed. It was considered that a study of the entropy changes which take place during solution of mononitrotoluenes in aqueous sulphuric acid might give some insight into changes in solute - solvent interactions in the aqueous phase as a function of solvent composition. The method of calculating these entropy changes, based on the work of McGowan (73) and Bohon and Clausen (76), has been fully described in section 3.3.1.

6.2.1. Entropy of Solution of Mononitrotoluenes in Aqueous Sulphuric Acid at 25°C.

The entropy of solution, ΔS_s, of ortho-nitrotoluene in aqueous sulphuric acid at 25°C, as a function of H_2SO_4 - H_2O compostion, has been calculated from equation 3.51 using the heats of solution shown in Table 6.3. The values of ΔS_s obtained are shown in Table 6.4.

ΔS_s has also been calculated for meta-nitrotoluene in 43.1 mole% H_2SO_4 using the heat of solution of 4.07 kJ mol^{-1} calculated from the slope of the plot shown in Figure 6.3.

6.2.2. Entropy of Dilution of Mononitrotoluenes in Aqueous Sulphuric Acid at 25°C.

The entropy change, ΔS_v, due to dilution when one mole of solute dissolves in a given solvent can be calculated from the expression $R\ln(C_1/C_s)$ as described in section 3.3.1. Values of ΔS_v for ortho-nitrotoluene as a function of H_2SO_4 - H_2O composition and for meta-nitrotoluene in 43.1 mole% H_2SO_4 have been calculated and these are shown in Table 6.4. Values of C_1 for these solutes were calculated from density data and values of C_s were obtained from the solubility data shown in Tables 6.2 and 6.3.

6.2.3. Entropy of Interaction of Mononitrotoluenes in Aqueous Sulphuric Acid at 25°C.

The entropy of interaction, ΔS_I, of a given solute in a given solvent is given by equation 3.53. Values of ΔS_I for ortho-nitrotoluene as a function of H_2SO_4 - H_2O composition and meta-nitrotoluene in 43.1 mole% H_2SO_4 have been calculated and these are shown in Table 6.4 together with the values of ΔS_s and ΔS_v from which they were calculated.

The values of ΔS_I calculated for ortho- and meta-nitrotoluene are all negative. This indicates that these solutes interact with the solvent, or cause association of the solvent to occur, during solution. The entropy of interaction appears to remain relatively constant or perhaps shows a tendency to become less negative (i.e. the degree of interaction or association decreases) as the H_2SO_4 content of the acid increases.

Table 6.4. Some Thermodynamic Solution Parameters for Several Aromatics as a Function of Acid Composition at 25°C.

Acid Composition /mole%			ΔH_s /$\mathrm{Jmol^{-1}}$	ΔS_s /$\mathrm{Jmol^{-1}K^{-1}}$	ΔS_v /$\mathrm{Jmol^{-1}K^{-1}}$	ΔS_I /$\mathrm{Jmol^{-1}K^{-1}}$
H_2SO_4	H_2O	HNO_3				
			ortho-nitrotoluene			
21.6	78.4	0.0	8050	27.0	54.8	-27.8
29.8	70.2	0.0	6960	23.4	49.4	-26.0
35.9	64.1	0.0	4760	16.0	44.1	-28.1
43.1	56.9	0.0	3520	11.8	37.1	-25.3
44.2	55.8	0.0	2970	9.97	34.9	-24.7
			meta-nitrotoluene			
43.1	56.9	0.0	4070	13.7	38.1	-24.4
			hexafluoro-meta-xylene*			
30.0	70.0	0.0	16320	54.8	77.4	-22.6
83.5	16.5	0.0	-36100	-121	49.6	-171
0.0	60.0	40.0	16740	56.2	49.9	6.3

*These data were obtained from the work of Field (94)

6.2.4. Comparison of ΔS_I for Mononitrotoluenes and Hexafluoro-meta-xylene.

The calculated values of ΔS_I for ortho-nitrotoluene and meta-nitrotoluene in 43.1 mole% H_2SO_4 are in good agreement indicating that these isomers interact similarly with aqueous sulphuric acid.

Hexafluoro-meta-xylene (HFMX) is a valuable compound for use in studies of the behaviour of aromatic compounds in concentrated sulphuric and mixed acids because of its low reactivity in these media. From published solubility data for HFMX (94) it is possible to calculate ΔS_I for this compound as a function of solvent composition. These values, together with the ΔH_s, ΔS_s and ΔS_v values from which they were calculated, are shown in Table 6.4.

The value of ΔS_I for solutions of HFMX in 30 mole% H_2SO_4 is quite similar to the values calculated for ortho- and meta-nitrotoluene. The large negative value of ΔS_I for solutions of HFMX in 83.5 mole% H_2SO_4 indicates that strong solute-solvent interactions occur in this medium. For HFMX the solute-solvent interactions appear to increase with increasing H_2SO_4 concentration in contrast to the behaviour observed with the mononitrotoluenes.

The value of ΔS_I for solution of HFMX in $HNO_3 - H_2O$ is slightly positive. This indicates that solute-solute interactions in the organic phase are greater than solute-solvent interactions in the aqueous phase.

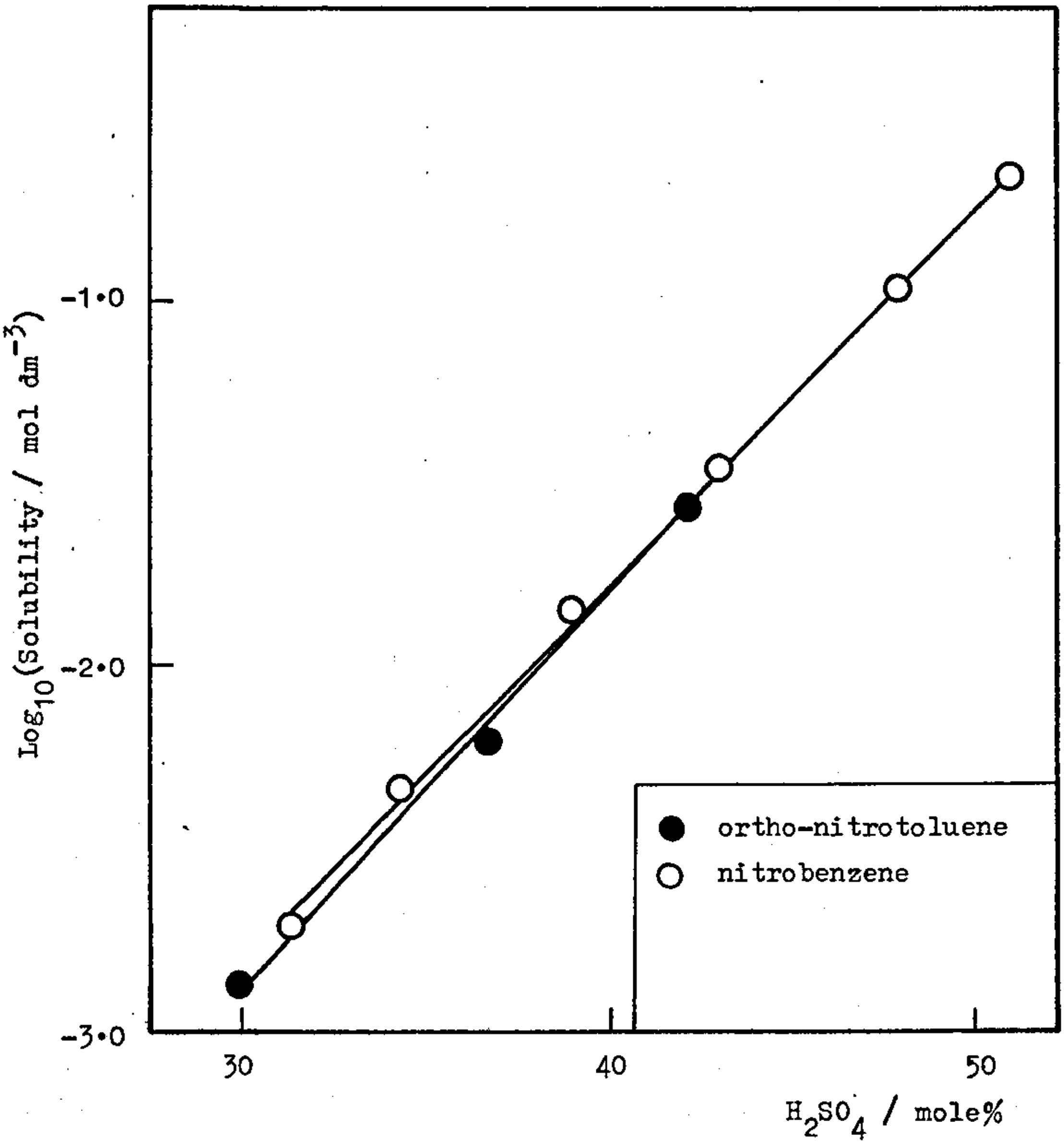
6.3. SOLUBILITY OF SULPHURIC ACID IN NITROAROMATICS AS A FUNCTION OF H_2SO_4 - H_2O COMPOSITION.

The solubility of H_2SO_4 in ortho-nitrotoluene and nitrobenzene as a function of H_2SO_4 - H_2O composition was determined by the method described in section 4.4.2. The results obtained are shown in Table 6.5. and Figure 6.5.

Table 6.5. Solubility of H_2SO_4 in Nitrobenzene and Ortho-nitrotoluene as a Function of H_2SO_4 - H_2O composition at 25°C.

H_2SO_4/mole%	Solubility/mol dm^{-3}
NITROBENZENE	
31.5	2.11×10^{-3}
34.4	4.57×10^{-3}
39.0	1.41×10^{-2}
42.9	3.49×10^{-2}
47.8	1.11×10^{-1}
50.8	2.15×10^{-1}
ORTHO-NITROTOLUENE	
30.2	1.31×10^{-3}
36.4	6.11×10^{-3}
42.2	2.78×10^{-2}

Figure 6.5 Logarithm of Solubility of Sulphuric Acid in Nitroaromatics as a Function of H_2SO_4-H_2O Composition at 25°C.



A possible criticism of the method used here to determine the solubility of H_2SO_4 in nitroaromatics is that it does not distinguish between H_2SO_4 dissolved in the nitroaromatic and very small droplets of the H_2SO_4 entrained in the nitroaromatic. Milligan (32) has pointed out that, in commercial separation plants, water has been found to become entrained in dinitrotoluene in droplets about one micron in diameter. These droplets are sufficiently small to remain in solution as a result of Brownian motion and their high surface energy. To resolve doubts about the test method used here several simple confirmatory tests were carried out, as follows:

Ortho-nitrotoluene and aqueous sulphuric acid (42.2 mole% H_2SO_4) were mixed using the method employed previously to determine the solubility of H_2SO_4 in ortho-nitrotoluene. After complete separation of the phases (determined by visual observation) had been achieved, samples taken from the organic phase were examined using a high powered optical microscope (with a resolution of 1 μm). No droplets of sulphuric acid were observed in these samples. If these samples did contain droplets of sulphuric acid which were too small to be detected by microscopic examination they would be removed by using a centrifuge. Therefore, several samples taken from the organic phase were placed in an ultracentrifuge for ten minutes at 20,000 r.p.m. before being analysed for H_2SO_4. Unfortunately, the ultracentrifuge could not operate above 20°C and some sulphuric acid separated from the organic sample due to cooling. However the concentration of H_2SO_4 found to be present in these samples was only slightly less than that in samples treated in the usual way. These experiments indicate that sulphuric acid found in ortho-nitrotoluene and nitrobenzene,after mixing with aqueous sulphuric acid, is actually dissolved rather than merely being entrained.

6.4. STABILITY OF ORTHO-NITROTOLUENE IN AQUEOUS SULPHURIC ACID.

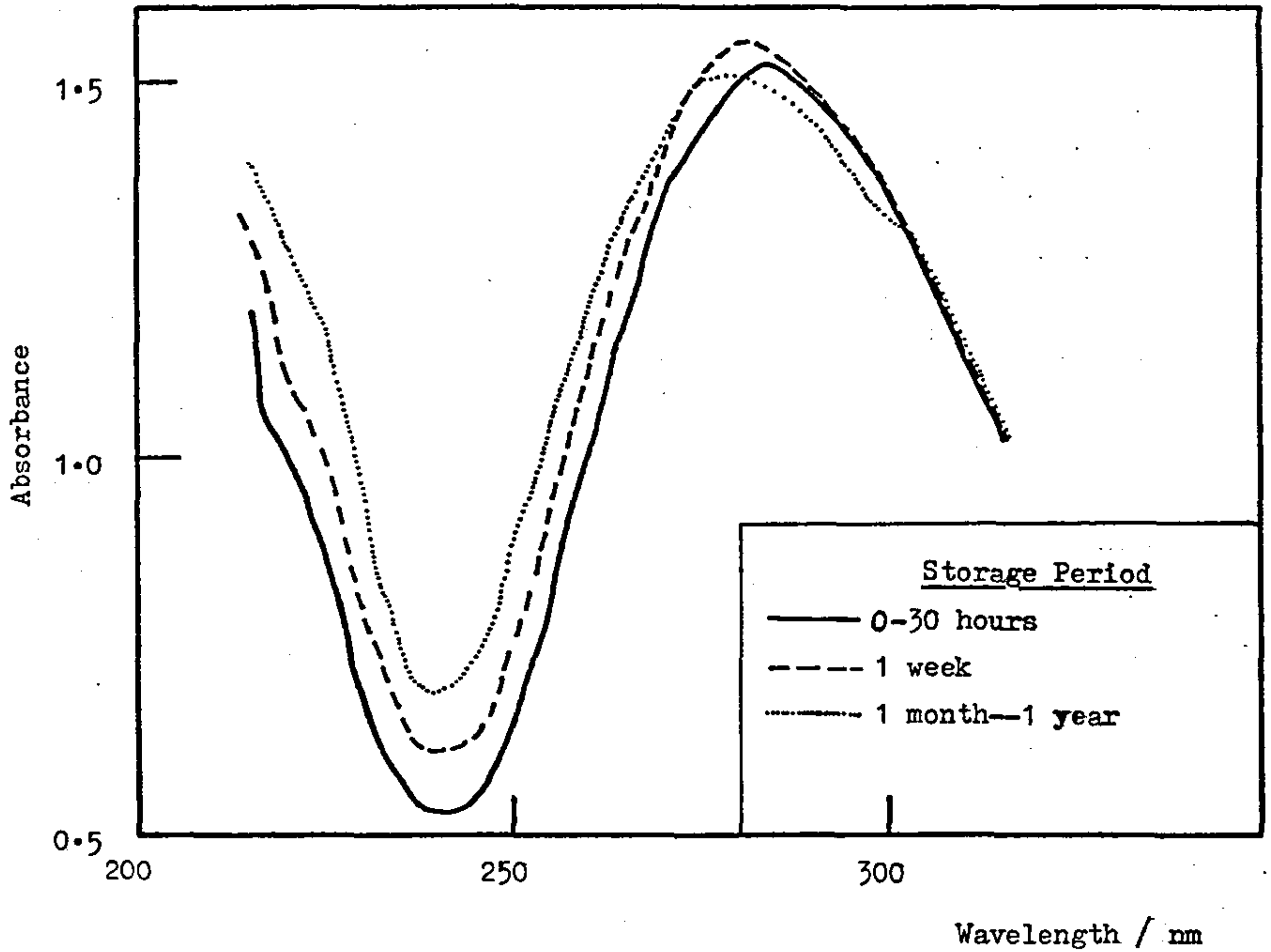
In the work described here,it has been assumed that the mononitroaromatics chosen for study do not react appreciably with aqueous sulphuric acid during the time required to perform solubility derminations.

However,it might be argued that sulphonation of mononitrotoluenes could contribute to the observed sharp rise in the apparent solubility of the latter as the H_2SO_4 content of the solvent is increased. Therefore,some experiments were carried out to investigate the reaction of ortho-nitrotoluene with aqueous sulphuric acid. It was assumed that para- and meta-nitrotoluene would behave similarly.

Sulphonation of mononitrotoluenes by aqueous sulphuric acid would cause the apparent solubility of the former to vary with time, the rate of variation probably being greatest in solutions with the highest sulphuric acid content. During determination of the solubility of ortho-nitrotoluene in 50.6 mole% H_2SO_4 (the composition with the highest sulphuric acid content used here) several samples were taken over a period of about twenty-four hours. No significant variations in solubility were observed during this period.

To provide additional confirmation of the stability of mononitrotoluenes in aqueous sulphuric acid a further experiment was carried out in which a solution of ortho-nitrotoluene (2.6×10^{-3} mol dm^{-3}) in aqueous sulphuric acid (43.1 mole% H_2SO_4) was stored at room temperature (in a closed darkened container) for about one year. The U.V. absorption spectrum of this solution was recorded at convenient intervals during this period (see Figure 6.6). The spectra obtained after 3, 24 and 30 hours storage were identical. A slight change in the spectrum of the stored solution was observed after about one week, followed by a further change after about one month. The spectrum of the solution after a storage period of about one year was very similar to that observed after one month. Hence a slight change in the spectrum of ortho-mononitrotoluene

Figure 6.6 UV Spectra of Ortho-nitrotoluene in Aqueous H_2SO_4 as a Function of Storage Period.



does take place, the change being completed within about one month at room temperature in 43.1 mole% H_2SO_4. Whether this change is due to sulphonation or some other chemical reaction remains unresolved. The changes that do take place,however, appear to be too slow either to influence the solubility determinations reported here or to explain the large increases in solubility observed as the H_2SO_4 content of the solvent is increased.

CHAPTER 7

THE DISTRIBUTION OF NITRIC ACID BETWEEN AQUEOUS SULPHURIC ACID AND NITROAROMATICS.

With the exception of the Slow Reaction Diffusional regime, the heterogeneous nitration rate in all regimes described in Section 3.14 is dependent on the concentration of nitric acid in the aqueous phase, $[HNO_3]_a$. Hence, in order to calculate the heterogeneous rate of nitration of aromatic compounds in contact with mixed acid (HNO_3 - H_2SO_4 - H_2O) it is necessary to know $[HNO_3]_a$ for the mixed acid composition under consideration.

When mixed acid is contacted with an aromatic compound the nitric acid present is distributed between the two phases in a ratio K_t, which is likely to vary with both temperature and the composition of the aqueous phase. In the present work, an attempt has been made to study the effect of variations in sulphuric acid composition on the distribution of nitric acid between aqueous sulphuric acid and two aromatic compounds (ortho-nitrotoluene and nitrobenzene), at constant temperature. The data obtained were used (Chapter 8) to predict the heterogeneous rate of nitration of ortho-nitrotoluene.

7.1. TRUE AND EXPERIMENTAL DISTRIBUTION CONSTANTS

The true distribution constant, K_t, for HNO_3 is defined by equation 7.1.

$$K_t = \frac{[HNO_3]_o}{[HNO_3]_a} = \frac{M_o}{V_o} \cdot \frac{V_a}{M_a} \quad \ldots\ldots\ldots \; 7.1$$

where $[HNO_3]_a$ is the concentration of HNO_3 in the organic phase and M_o, M_a are the moles of undissociated HNO_3 in organic and aqueous phases of volume V_o and V_a respectively.

In this work K_t was not determined directly since this would require a knowledge of the concentrations of undissociated HNO_3 in both phases. Under certain conditions nitric acid dissociates in aqueous sulphuric acid and the method of analysis used here is not capable of taking this into account. Instead, an experimental distribution constant K_e, which can be related to K_t, was determined by measuring the concentration of nitric acid in the organic phase $[HNO_3]_o$ (see Section 4.5). In this phase, nitric acid is thought to exist as undissociated HNO_3 or a hydrate of the form $(HNO_3)_x(H_2O)_y$ where x and y are small integers (95). The quantity of undissociated HNO_3 present in the aqueous phase (M_a) is assumed to be given by the difference between the total number of moles present in the system, M_T, and the number of moles found to be present in the organic phase, M_o. Hence K_e is given by equation 7.2.

$$K_e = \frac{M_o}{M_T - M_o} \cdot \frac{V_a}{V_o} \quad \text{........... } 7.2$$

From a knowledge of the degree of dissociation of HNO_3 in aqueous sulphuric acid as a function of H_2SO_4 - H_2O composition it is possible to relate K_e to K_t. Figure 7.1 shows the mole fractions X_a, X_j and X_k of undissociated nitric acid, nitrate ions and nitronium ions respectively in mixed acid as a function of H_2SO_4 - H_2O composition. The data used to construct Figure 7.1 were obtained from published U.V. absorption and Raman spectral data (10, 96).

Now:

$$X_a = \frac{M_a}{M_a + M_j + M_k} \quad \text{.................... } 7.3$$

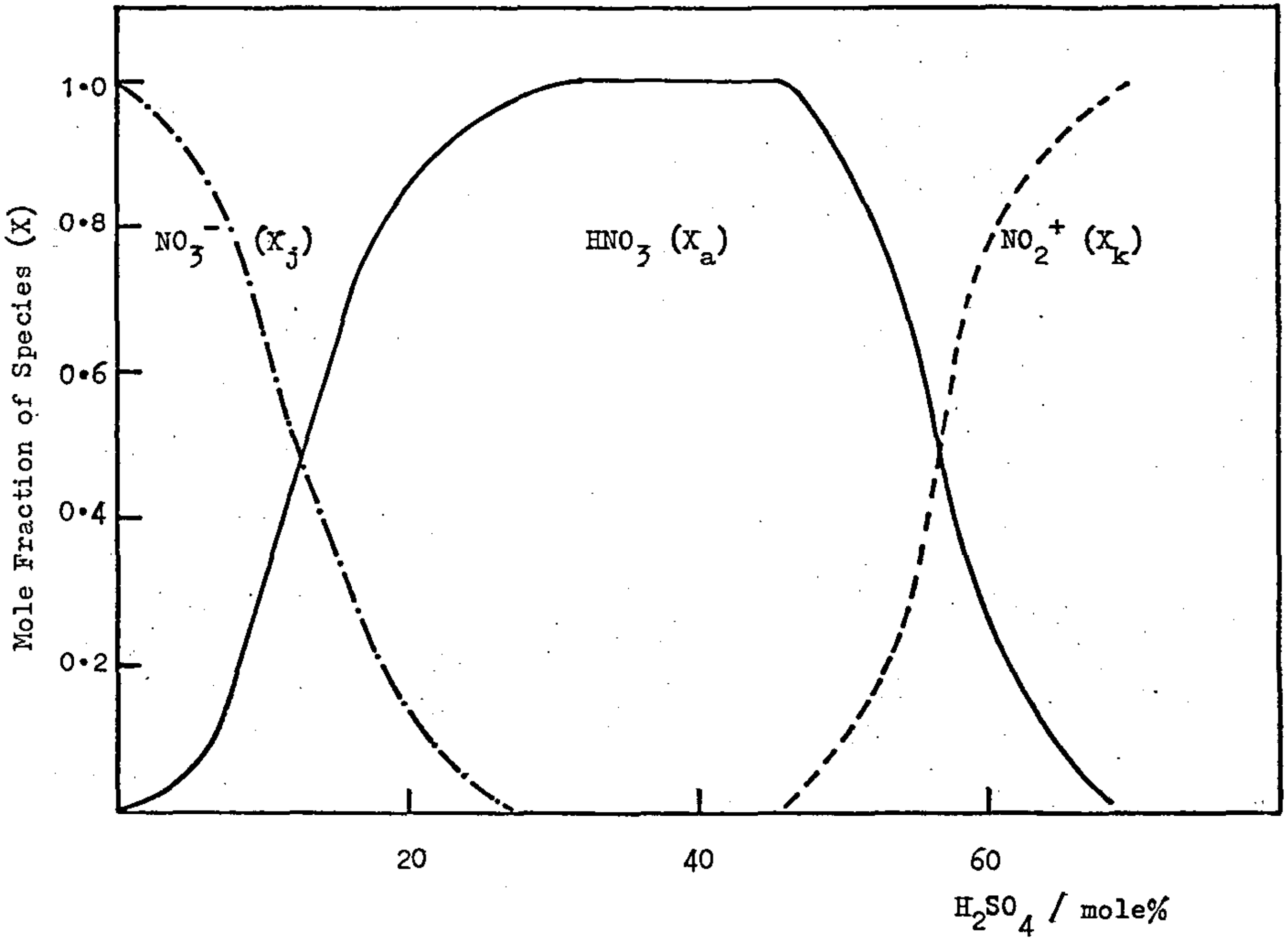
where M_j and M_k are the moles for the nitrate ion and the nitronium ion respectively in the aqueous phase and

$$M_a + M_j + M_k = M_T - M_o \quad \text{.......... } 7.4$$

and therefore

$$\frac{K_t}{K_e} = \frac{M_a + M_j + M_k}{M_a} = \frac{1}{X_a} \quad \text{...... } 7.5$$

Figure 7.1 Relative Mole Fractions of HNO_3, NO_3^-, NO_2^+ in Mixed Acid as a Function of H_2SO_4–H_2O Composition at 25°C.



Hence

$$K_t = \frac{K_e}{X_a} \quad \text{.........................7.6}$$

7.2 DETERMINATION OF K_e FOR MIXED ACIDS IN WHICH ORTHO-NITROTOLUENE IS NITRATED.

An indirect method of measuring the distribution of nitric acid between aqueous sulphuric acid and ortho-nitrotoluene has been employed here with only partial success. In two-phase systems in which the aqueous phase contains a high H_2SO_4 concentration ($>$ about 35 mole% H_2SO_4) the rate of nitration of ortho-nitrotoluene is sufficiently high to cause considerable depletion of nitric acid during the measurement of the distribution of the latter between the phases. Recourse was therefore made to an indirect method of determining distribution coefficients for such systems. In this method,the distributions of nitric acid between aqueous sulphuric acid solutions having low H_2SO_4 concentrations ($<$ 36 mole% H_2SO_4) and both ortho-nitrotoluene and nitrobenzene were determined. The distribution of nitric acid between nitrobenzene (which is less easily nitrated than ortho-nitrotoluene) and aqueous sulphuric acid solutions with relatively high H_2SO_4 concentrations (in which ortho-nitrotoluene would be rapidly nitrated) were then determined. An estimate of the distributions of nitric acid between ortho-nitrotoluene and the latter solutions was then made by extrapolating the data obtained for low H_2SO_4 concentrations to higher H_2SO_4 concentrations, using the data for nitrobenzene as a guide. However, the fact that nitrobenzene is only slightly less reactive than ortho-nitrotoluene limits the range of this extrapolation. It would be desirable to extend this extrapolation by using an aromatic compound which is significantly less reactive than nitrobenzene, whilst still having a molecular structure similar to that of ortho-nitrotoluene, but such a compound is not readily available. Dinitrotoluenes may be sufficiently unreactive and similar in structure to ortho-nitrotoluene but the high melting points of the pure isomers ($\geqslant$ 52°C) prevent measurements being made at 25°C using the methods employed here. Instead, determinations would have to be made at temperatures above 52°C so that both phases are liquid. The data obtained would then have to be extrapolated to 25°C. A compromise could possibly be achieved by using the dinitrotoluene eutectic which melts at 32°C (32).

7.3 RESULTS

In each run, a known volume of mixed acid (in which the nitric acid concentration was in all cases 0.158 mol

dm^{-3}) was contacted with the nitroaromatic under consideration. After separation of the phases the organic phase was analysed as described in section 4.5. Each run employed a mixed acid solution in which the H_2SO_4 content was within, or close to, the range in which X_a is equal to unity (about 30 - 43 mole% H_2SO_4, see Figure 7.1) i.e. nitric acid is present in the aqueous phase only as undissociated HNO_3. From equation 7.6 it can be seen that, under these conditions, the experimental and true distribution constants are equal.

Table 7.1 and Figure 7.2 show values of K_t as a function of mole% H_2SO_4 for both ortho-nitrotoluene and nitrobenzene. Also included in Figure 7.2 for comparison are data reported by Field (95) for nitrobenzene. These data, however, were obtained using a nitric acid concentration of 1.58 moles per dm^3 of aqueous phase. The agreement between Field's data for nitrobenzene and the data reported here for the same compound indicates that, for low nitric acid concentrations, K_t is only slightly dependent on nitric acid concentration.

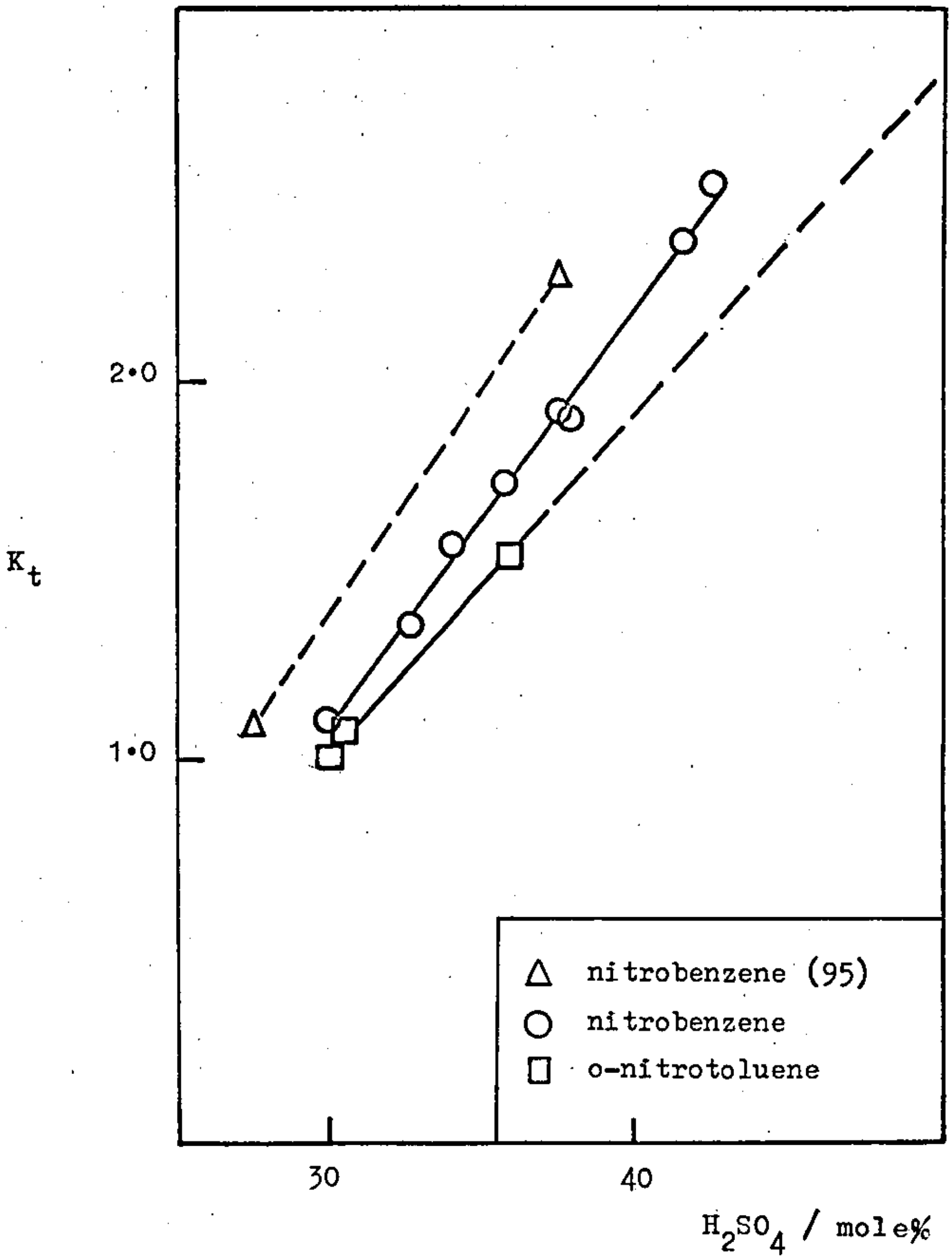
Field (95) determined K_t for a number of different aromatics in contact with mixed acid and found that, in general, plots of K_t versus mole% H_2SO_4 exhibited maxima at about 50 mole% H_2SO_4.

Table 7.1. Dependence of K_t on H_2SO_4 - H_2O Composition at 25°C.

H_2SO_4 /mole%	K_t
NITROBENZENE	
29.9	1.11
32.7	1.36
34.1	1.57
35.8	1.74
37.6	1.93
37.9	1.92
41.7	2.39
42.6	2.54
ORTHO-NITROTOLUENE	
29.9	1.01
30.5	1.07
35.8	1.54

Since the internal pressure of H_2SO_4 - H_2O solutions is also at a maximum in 50 mole% H_2SO_4 (82, 83)-see Figure 3.4, it appears that undissociated HNO_3 becomes less soluble in H_2SO_4 - H_2O solutions as the internal pressures of the latter increase. If this applies to the ortho-nitrotoluene/aqueous sulphuric acid system, the plot of K_t versus mole% H_2SO_4 for

Figure 7.2 Dependence of K_t on H_2SO_4-H_2O Composition at 25°C.



this system would be expected to level off (in line with the levelling off of the internal pressure of the aqueous acid) as 50 mole% H_2SO_4 is approached. Since, with the limited data available, it is difficult to quantify the degree of levelling off, a simple linear extrapolation was used for the purpose of the calculation of two phase nitration rates (Chapter 8). This will probably lead to a slight overestimate of K_t and hence a slight underestimate of $[HNO_3]_a$.

CHAPTER 8

TWO PHASE NITRATION OF ORTHO-NITROTOLUENE

In the preceding chapters, homogeneous rate constants, k_2, and solubilities, $[ONT]_a^s$, have been determined for ortho-nitrotoluene over a range of reaction conditions. In addition, the constant, K_t, has been determined for the distribution of nitric acid between aqueous sulphuric acid and both ortho-nitrotoluene and nitrobenzene over a range of H_2SO_4 - H_2O compositions. The combination of these determinations with data reported in the literature enables the two phase rate of nitration of ortho-nitrotoluene in both the stirred reactor and the stirred cell to be predicted and assigned to one or more of the reaction regimes described in section 3.1.4. In this chapter experimentally determined two phase nitration rates are compared with these predictions.

8.1. CONSTRUCTION OF CALIBRATION GRAPH

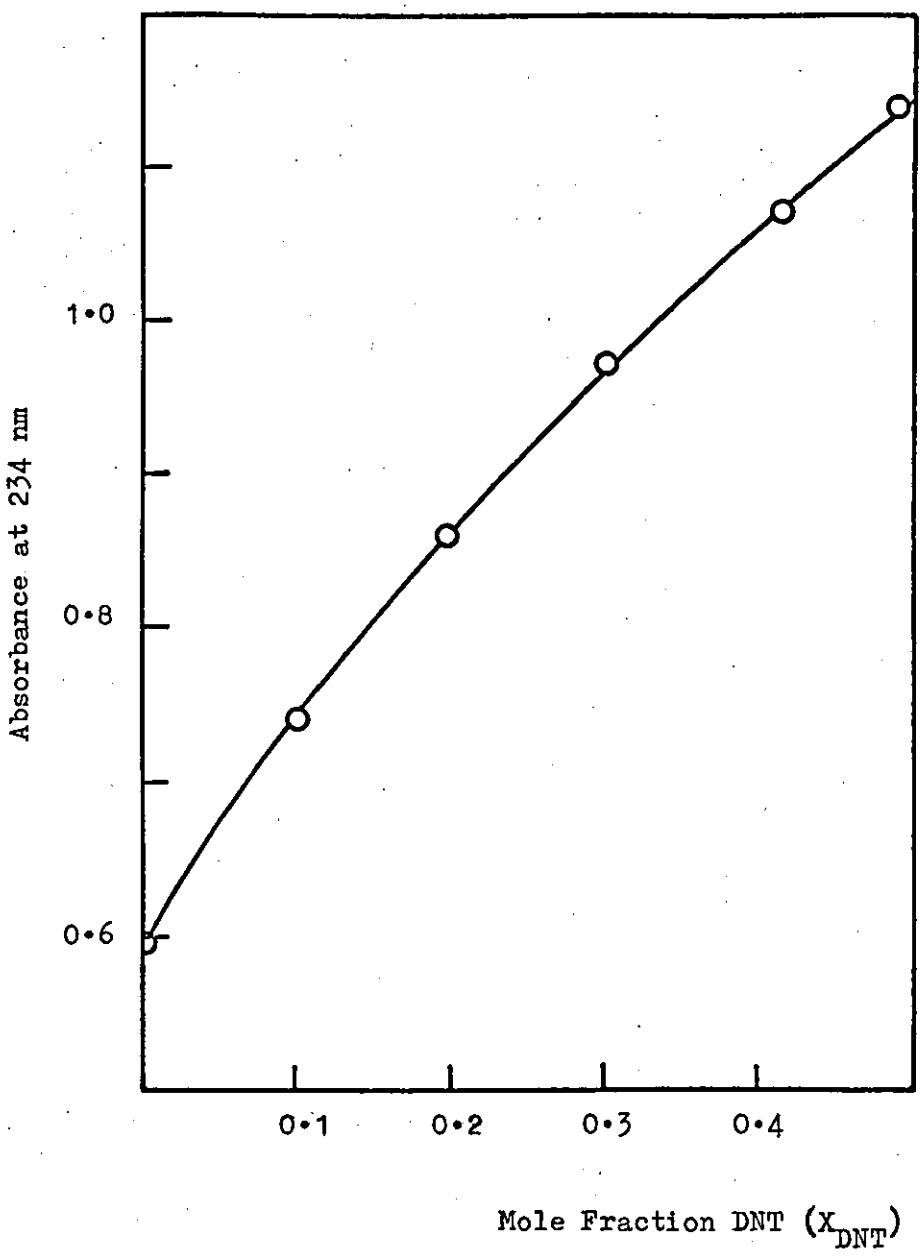
In order that absorbance measurements, made during the nitration runs, could be converted directly into % reaction and moles of ortho-nitrotoluene nitrated, a mixture was made of dinitrotoluenes in the ratio (68.1% 2, 4 - DNT, 31.9% 2, 6 - DNT. - See Figure 5.7) in which they are formed in 43 mole% H_2SO_4 - the middle of the H_2SO_4 - H_2O composition range used. A series of solutions of this mixture and ortho-nitrotoluene in varying proportions was prepared. Each solution was then diluted with hexane (spectrograde) and its absorbance measured in exactly the same way as during a run in either the stirred reactor or the stirred cell (see sections 4.6 and 4.7 respectively). The calibration graph obtained is shown in Figure 8.1. Subsequent calibrations, using mixtures of dinitrotoluenes representative of the ratio of products formed over the range of H_2SO_4 - H_2O compositions covered by the two phase nitrations, showed that the calibration graph was not significantly altered by such small changes in the ratio of the dinitrotoluene isomers.

8.2. TWO PHASE NITRATION IN A STIRRED REACTOR

The stirred reactor used here was of the same design as that employed previously by Cox (59) and Chapman (25) to study the nitration of toluene and chlorobenzene.

All runs were carried out at a constant stirring speed of 2500 ± 25 r.p.m. In each run equimolar quantities of ortho-nitrotoluene and nitric acid were used. If $\left[HNO_3\right]_a^i$ and $\left[HNO_3\right]_a^t$ are the acid phase nitric acid concentrations at the start of the run and at time t respectively the mole fraction of ortho-nitrotoluene in the organic phase, X_{ONT} at time t is given by equation 8.1.

Figure 8·1 Calibration Graph for Two Phase Nitration of Ortho-nitrotoluene.



$$X_{ONT} = \frac{[HNO_3]_a^t}{[HNO_3]_a^i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 8.1$$

The concentration of ortho-nitrotoluene in the acid phase, $[ONT]_a$, has an initial value of $[ONT]_a^s$, the saturation concentration in the acid phase, when the organic phase is pure ortho-nitrotoluene.

At time t, the concentration of ortho-nitrotoluene in the acid phase is

$$[ONT]_a^t = [ONT]_a^s \, X_{ONT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 8.2$$

$$= [ONT]_a^s \, \frac{[HNO_3]_a^t}{[HNO_3]_a^i} \quad \ldots\ldots\ldots\ 8.3$$

assuming that ortho-nitrotoluene and its nitration products form ideal or near-ideal mixtures.

If the two phase rate of nitration R_a is kinetically controlled

$$R_a = \frac{-d\,[HNO_3]_a^t}{dt} = k_2 \, [HNO_3]_a^t \, [ONT]_a^t \quad \ldots\ldots\ 8.4$$

$$= k_2 \, [HNO_3]_a^t \, [ONT]_a^s \, \frac{[HNO_3]_a^t}{[HNO_3]_a^i} \quad \ldots\ldots 8.5$$

$$= \left(\frac{k_2 \, [ONT]_a^s}{[HNO_3]_a^i} \right) \left([HNO_3]_a^t \right)^2 \quad \ldots\ldots\ldots\ 8.6$$

Hence simple second order kinetics should be observed.

Integration of equation 8.6 leads to equation 8.7.

$$\frac{1}{[HNO_3]_a^t} - \frac{1}{[HNO_3]_a^i} = \left[\frac{k_2\ [ONT]_a^s}{[HNO_3]_a^i}\right] t \quad .....8.7$$

therefore

$$\frac{[HNO_3]_a^i}{[HNO_3]_a^t} - 1 = \left[\frac{k_2\ [ONT]_a^s \cdot \cancel{[HNO_3]_a^i}}{\cancel{[HNO_3]_a^i}}\right] t \quad .....8.8$$

If X_{DNT} is the mole fraction of dinitrotoluene in the aqueous phase and

$$X_{ONT} = 1 - X_{DNT} \quad .... \quad 8.9$$

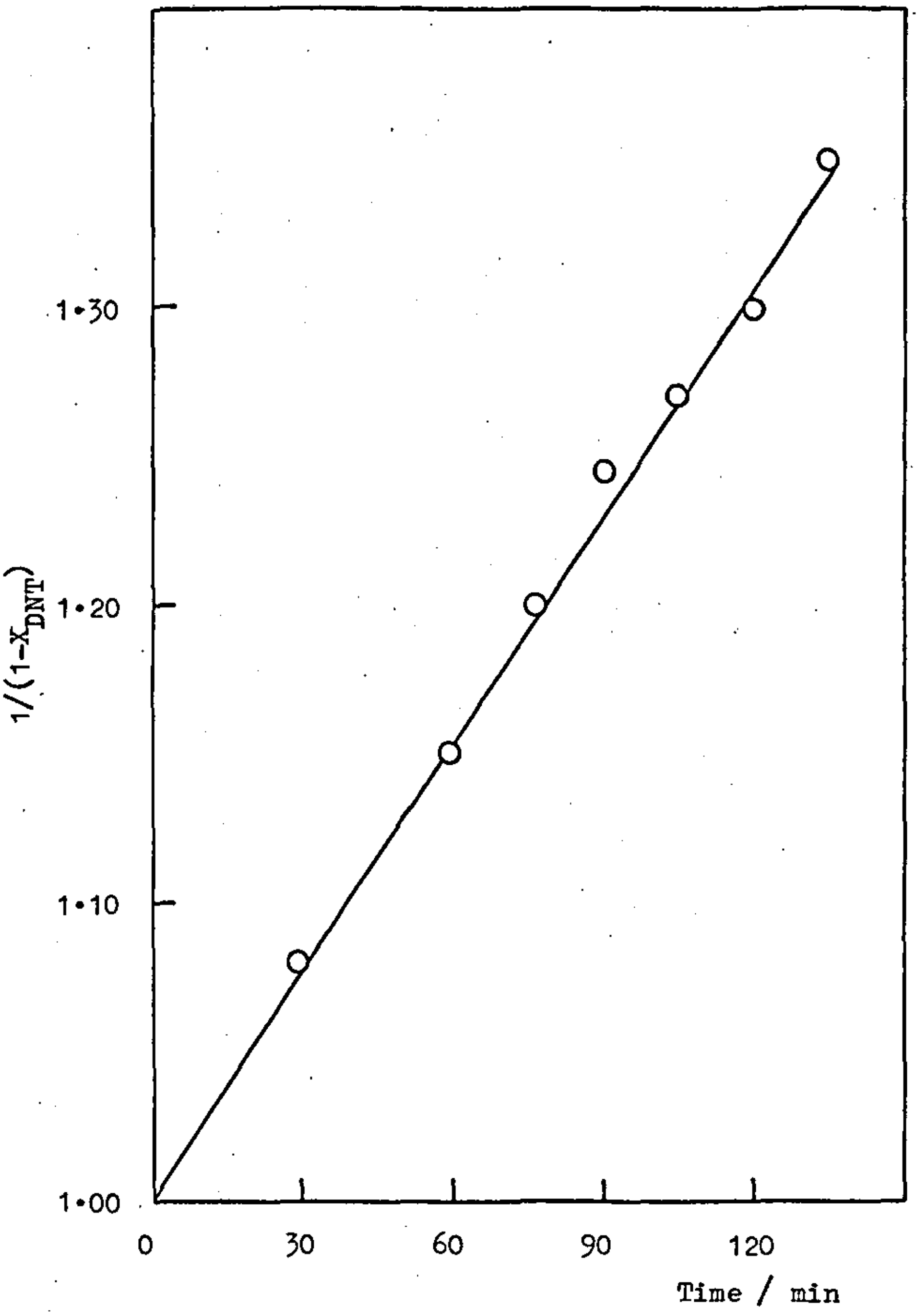
then from equations 8.1 and 8.8

$$\frac{1}{1 - X_{DNT}} - 1 = k_2\ [ONT]_a^s\ t \quad .... \quad 8.10$$

Hence a plot of $1/(1 - X_{DNT})$ versus t will have a slope $k_2\ [ONT]_a^s$.

The two phase rate of nitration of ortho-nitrotoluene in a stirred reactor was measured for a range of conditions using the method described in section 4.6. Plots of $1/(1 - X_{DNT})$ versus time were found to be linear over about the first 30% of reaction. A typical plot is shown in Figure 8.2.

Figure 8.2 Typical 1/(1-X) Plot for the Stirred Reactor.



8.2.1. Effect of Changes in H_2SO_4 - H_2O Composition.

Two phase nitration of ortho-nitrotoluene was carried out in the stirred reactor at 25.0 ± 0.1°C for H_2SO_4 - H_2O compositions in the range 34.6 - 38.0 mole% H_2SO_4. In each run, the initial nitric acid concentration was 0.56 moles per dm^3 of the aqueous phase. Values of k_2 for each H_2SO_4 - H_2O composition used in the two phase nitration runs were predicted from the data presented earlier (section 5.1.6.). Although these data were determined in solutions containing very low nitric acid concentrations (2.2×10^{-3} mol dm^{-3}) they are not likely to differ significantly from the values that would be obtained in 0.56 mol dm^{-3}. Table 8.1 compares k_2 values determined using nitric acid concentrations of 2.2×10^{-3} and 0.56 mol dm^{-3} in 35.9 mole% H_2SO_4.

It can be seen from Table 8.1 that the experimental and predicted values of k_2 agree within a factor of about two. The E_2 values are in excellent agreement. It was not possible to perform experiments at the highest H_2SO_4 concentrations employed in this work, using a nitric acid concentration of 0.56 mol dm^{-3} because, in such media, the rate of nitration would be too fast to follow using the experimental technique employed here. However, although limited, these experiments indicate that the presence of up to 0.56 moles of nitric acid per dm^3 of aqueous acid does not alter k_2 or E_2 values greatly from those obtained using very low concentrations of nitric acid.

Table 8.1 Comparison of k_2 for Two Nitric Acid Concentrations in 35.9 mole% H_2SO_4.

$k_2/dm^3mol^{-1}s^{-1}$		$E_2/kJmol^{-1}$	Reaction Conditions
25°C	70°C		
1.05×10^{-3}	5.78×10^{-2}	75.7	Determined from experimental values of k_1 (pseudo-first-order rate constant) $[HNO_3] = 0.56$ mol dm^{-3}
0.52×10^{-3}	2.62×10^{-2}	74.1	Predicted from Figure 5.6. Assumes $[HNO_3] = 2.2 \times 10^{-3}$ mol dm^{-3}.

Solubilities of ortho-nitrotoluene in each of the H_2SO_4 - H_2O compositions used in the two phase nitration runs were interpolated from the data presented earlier (section 6.1). Since it was not possible to make accurate solubility determinations in mixed acids it has been assumed that the solubility of ortho-nitrotoluene is not significantly affected by concentrations of nitric acid up to 0.56 mol dm^{-3}.

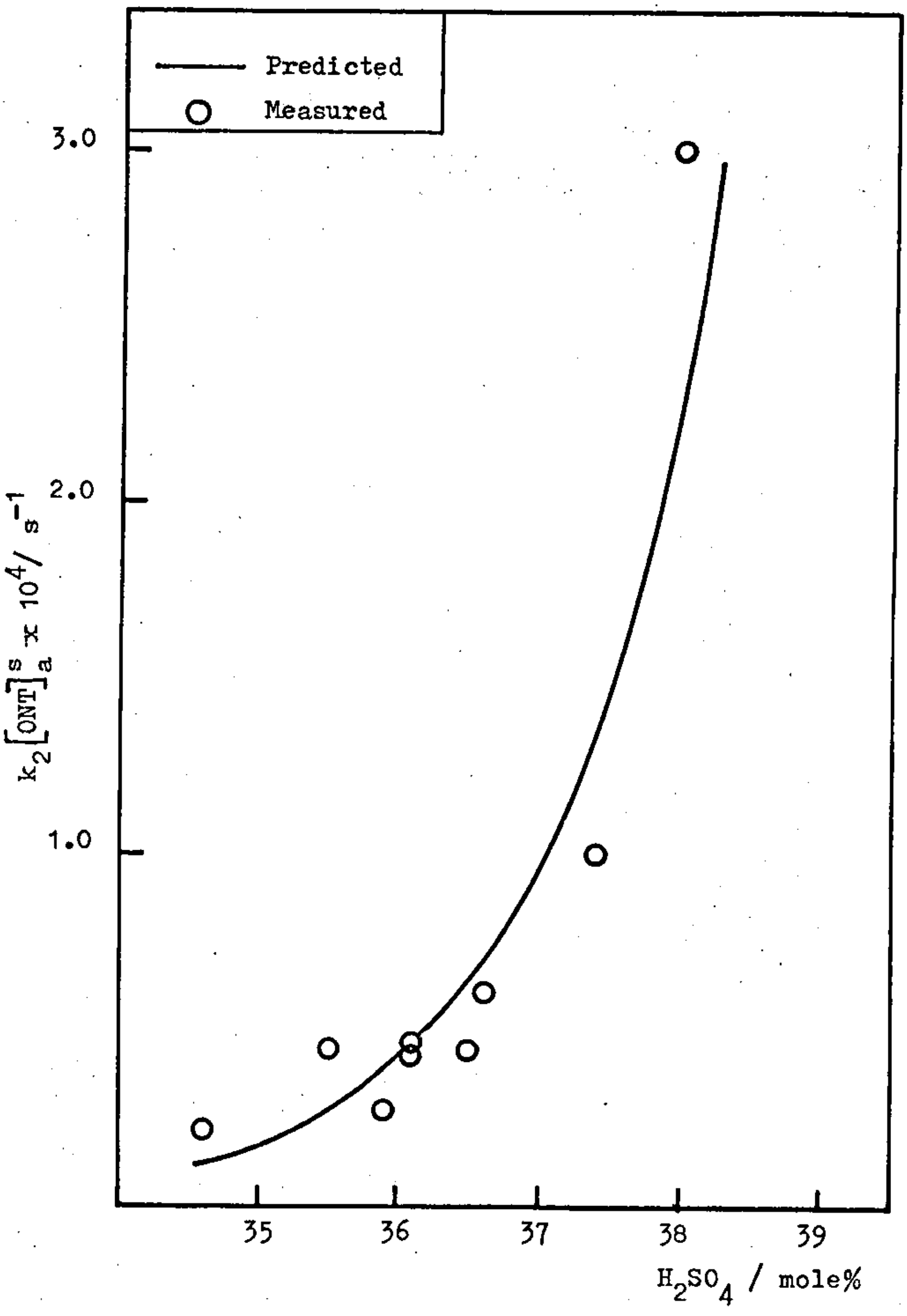
Interpolated values of k_2, $[ONT]_a^s$ and their product $k_2[ONT]_a^s$ are shown in Table 8.2 together with values of $k_2[ONT]_a^s$ determined experimentally by two phase nitration.

Table 8.2. Nitration of Ortho-nitrotoluene in a Stirred Batch Reactor as a function of $H_2SO_4 - H_2O$ Composition at 25°C.

H_2SO_4 /mole%	$[ONT]_a^s \times 10^2$ /mol dm^{-3}	$k_2 \times 10^3$ /dm^3 mol^{-1}s^{-1}	$k_2[ONT]_a^s \times 10^4$/s^{-1} Predicted	Measured
34.6	3.31	0.373	0.12	0.22
35.5	3.63	0.780	0.28	0.45
35.9	3.80	1.05	0.40	0.28
36.1	3.89	1.18	0.46	0.42,0.46
36.5	4.06	1.56	0.63	0.44
36.6	4.07	1.67	0.68	0.61
37.4	4.47	3.10	1.4	1.0
37.7	4.68	3.73	1.8	1.5
38.0	4.79	4.59	2.2	3.0
38.5	5.01	5.92	3.0	-

Figure 8.3 compares predicted and experimental values of $k_2[ONT]_a^s$ as a function of $H_2SO_4 - H_2O$ composition. Good agreement between measured and predicted values is obtained. This is clear evidence that, for low nitric acid

Figure 8.3 Initial Rate of Nitration in a Stirred Batch Reactor as a Function of H_2SO_4-H_2O Composition at 25°C.



concentrations, the two phase rate of nitration is kinetically controlled over this range of H_2SO_4 - H_2O compositions.

8.2.2. Effect of Changes in Temperature

Two phase nitration of ortho-nitrotoluene was carried out in the stirred reactor using the same H_2SO_4 - H_2O composition (35.9 mole% H_2SO_4) and the same nitric acid concentration (0.56 moles per dm^3 of aqueous phase) for each run. The temperature range covered by these experiments was 25 - 50°C. The results obtained are shown in Table 8.3.

Table 8.3. Nitration of Ortho-nitrotoluene in a Stirred Batch Reactor as a Function of Temperature in 35.9 mole% H_2SO_4.

Temperature /°C	$k_2 \left[ONT\right]_a^s \times 10^4$ /s^{-1}
25	0.282
30	0.53
35	0.93
40	1.4
45	2.2
50	3.5

An Arrhenius plot of the data (Figure 8.4) is linear, indicating that the activation energy for two phase nitration, E, is constant over this temperature range. The value of E derived from the slope of this plot is 79.1 kJ mol^{-1}.

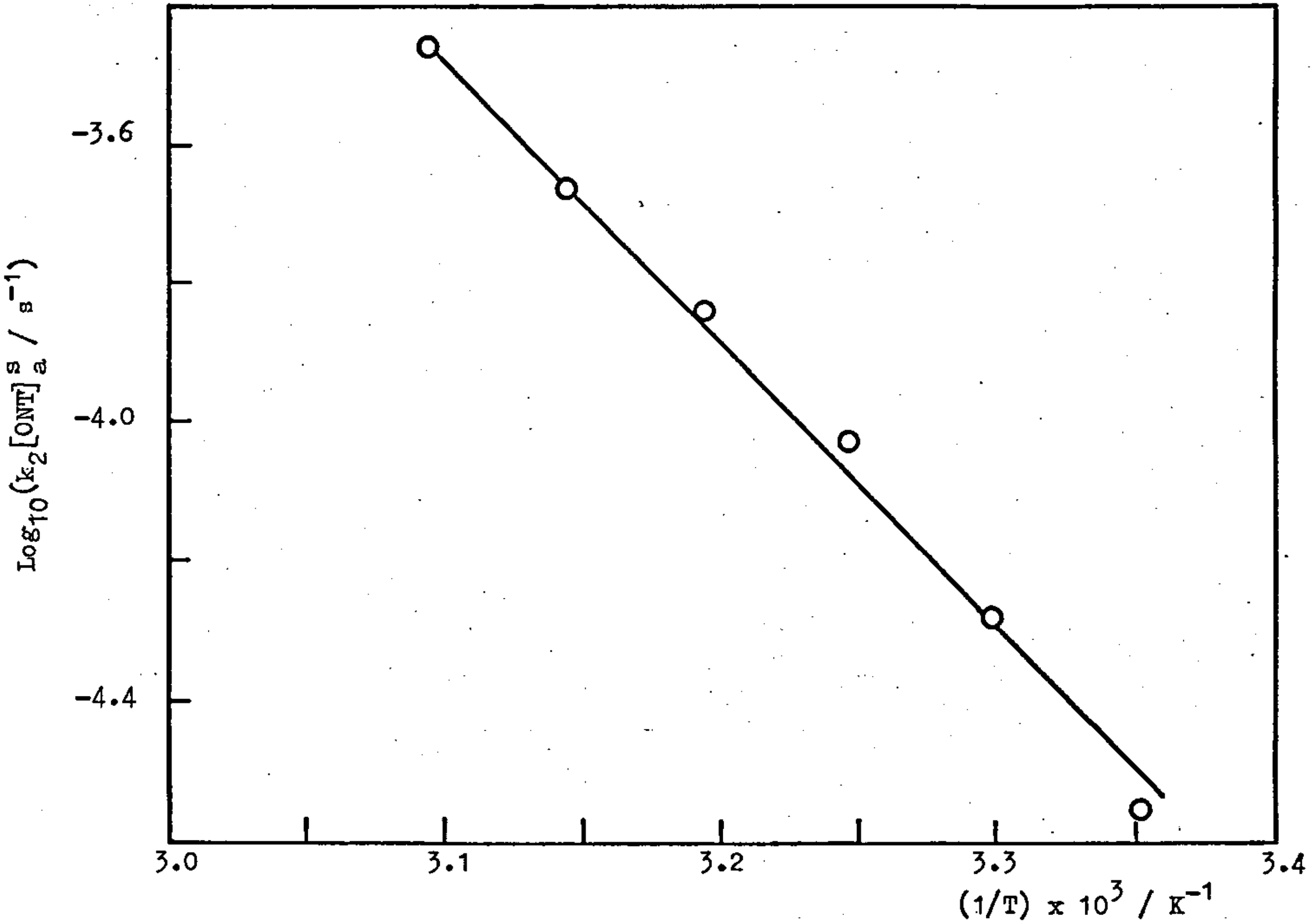
It can be shown that, if the two phase reaction is kinetically controlled, the nitration rate R_a increases with temperature with an activation energy given by equation 8.11.

$$E = E_2 + \Delta H_s \text{ .... } 8.11$$

where E_2 is the activation energy for homogeneous nitration in a given H_2SO_4 - H_2O composition and ΔH_s is the heat of solution in the same composition.

The heat of solution of ortho-nitrotoluene in 35.9 mole% H_2SO_4 is 4.76 kJ mol^{-1} (See Table 6.3). The activation energy E_2 of ortho-nitrotoluene in 35.9 mole% H_2SO_4 has not been measured directly. However, E_2 for ortho-nitrotoluene in 41.7 mole% (79.6 weight %) H_2SO_4 is 63.7 kJ mol^{-1} (see Table 5.4). Previous work (25) has shown that, for several aromatics, E_2 increases linearly by about 2.80 kJ mol^{-1} for each weight % decrease in H_2SO_4. If the same relationship holds for ortho-nitrotoluene, E_2 in 35.9 mole% (75.3 weight %) H_2SO_4 will be about 75.7 kJ mol^{-1}.

Figure 8.4 Arrhenius Plot for Nitration in a Stirred Batch Reactor in 35.9 mole% H_2SO_4.



By substituting these values of E_2 and ΔH_s into equation 8.11, a value for E of 80.5 kJ mol^{-1} is obtained. This is in excellent agreement with the experimental value of 79.1 kJ mol^{-1} and provides further evidence that the rate of nitration of ortho-nitrotoluene in a stirred batch reactor is kinetically controlled under these conditions.

8.3. TWO PHASE NITRATION IN A STIRRED CELL

The initial two phase rate of nitration of ortho-nitrotoluene in a stirred cell was measured over a range of reaction conditions using the method described in section 4.7. The use of the calibration graph shown in Figure 8.1 enabled absorbance readings to be converted directly into moles of ortho-nitrotoluene nitrated. The initial rate of nitration in each run was calculated from the slope of a least-squares plot of moles nitrated against time. The plots were found to be linear for about the first 25% of the reaction.

The interfacial area per unit volume of aqueous phase, a', was constant and determined from the cell dimensions and the aqueous phase volume ($a' = 0.200\ cm^2/cm^3$). A constant stirring speed of 55 ± 1 r.p.m. was used in all runs. In each run the initial nitric acid concentration was 0.56 moles per dm^3 of aqueous acid.

8.3.1. Effect of Changes in $H_2SO_4 - H_2O$ Composition.

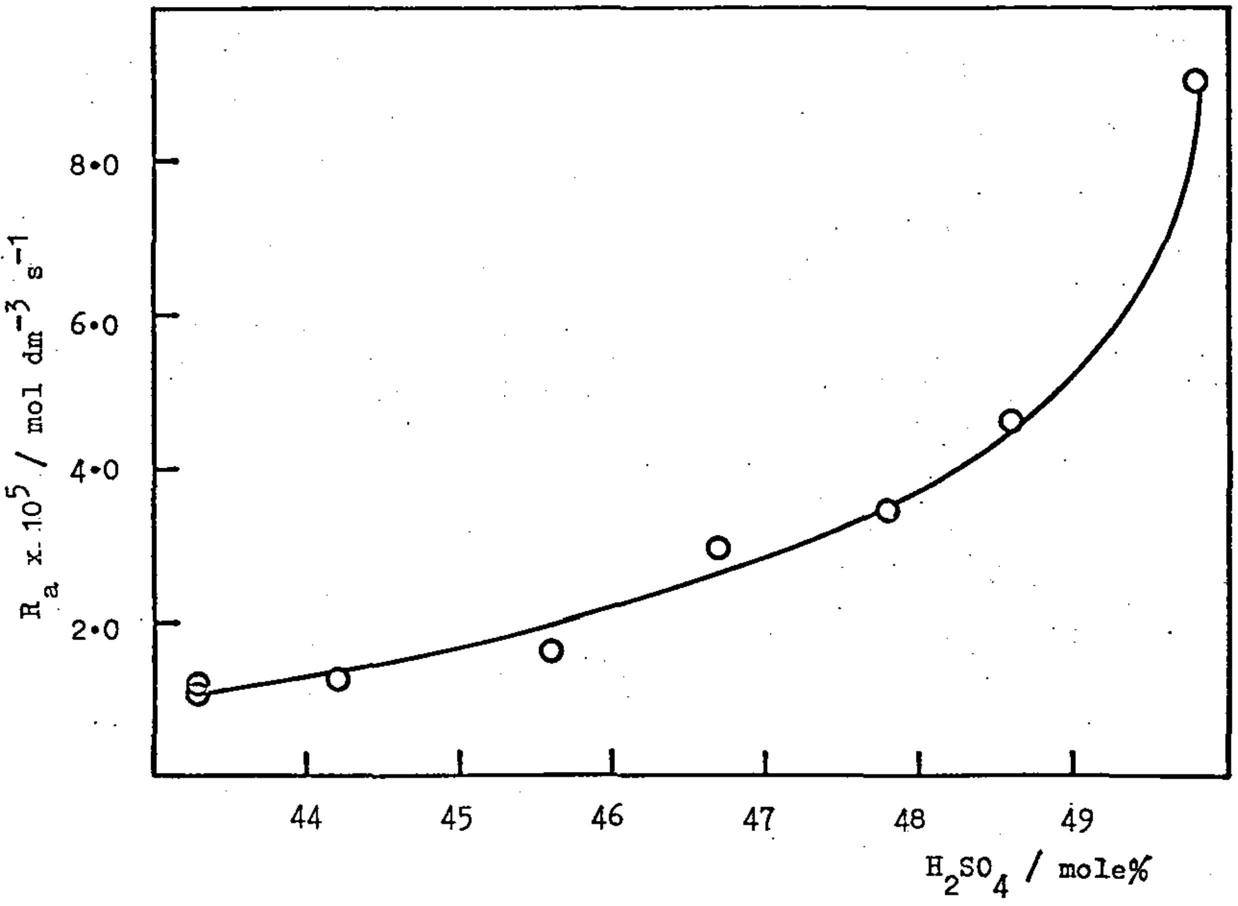
The two phase rate of nitration, R_a, of ortho-nitroluene in a stirred cell has been determined at a constant temperature ($25.0 \pm 0.1^{\circ}C$) as a function of $H_2SO_4 - H_2O$ composition. The results obtained are shown in Figure 8.5.

If the experimental, initial rate of nitration is significantly less than $k_2[HNO_3]_a [ONT]_a^s$ the rate will be mass transfer controlled. Using the data presented in Chapters 5, 6 and 7 of this work, it is possible to calculate k_2, $[ONT]_a^s$ and $[HNO_3]_a$ over the range of $H_2 SO_4 - H_2O$ compositions (43.3 - 49.8 mole% H_2SO_4) employed for the stirred cell runs. Over this composition range, $k_2 [HNO_3]_a [ONT]_a^s$ increases from 5.03×10^{-3} to 6.20×10^{-1} mol dm^{-3}s^{-1} whereas the measured initial rate is never greater than 1×10^{-4}mol dm^{-3}s^{-1}. Hence, it is clear that, under these conditions, the two phase rate of nitration of ortho-nitrotoluene is mass transfer controlled.

Identification of Reaction Regimes

The major reaction regimes which exist in systems where mass transfer and chemical reaction occur simultaneously were described in section 3.1.4.

Figure 8.5 Initial Rate of Nitration of Ortho-nitrotoluene in a Stirred Cell as a Function of H_2SO_4-H_2O Composition at 25°C.



(i) Slow Reaction Diffusional Regime.

The plot shown in Figure 8.5 exhibits an apparent plateau over the composition range 43.3 - 45.6 mole% H_2SO_4. This indicates that, in this range, the reaction rate is almost independent of H_2SO_4 - H_2O composition and that the slow reaction diffusional regime is observed. Use of equation 3.37, which governs this regime, enables values of both $a'K_L$ and the "area-free" mass transfer coefficient, K_L, to be calculated since the terms R_a, a' and $[ONT]_a^s$ are known or can be predicted and X_{ArH} is approximately unity as R_a is defined as the initial two phase nitration rate. Table 8.4 lists values of $a'K_L$ and K_L calculated from the data for the "plateau" region. The values of $a'K_L$ are considerably lower than those published previously (48, 58, 61) which are in the range 3×10^{-2} - $0.4 \ s^{-1}$.

Table 8.4. Mass Transfer Coefficients in the Stirred Cell at 25°C

H_2SO_4 /mole%	$R_a \times 10^5$ /mol $dm^{-3} s^{-1}$	$[ONT]_a^s$ /mol dm^{-3}	$K_L \times 10^4$ /cm s^{-1}	$a'K_L \times 10^4$ /s^{-1}
43.3	1.20	0.10	6.0	1.2
44.2	1.26	0.13	5.3	1.1
45.6	1.67	0.16	5.2	1.0

(ii) Fast Reaction Diffusional Regime

In Table 8.5 the initial rates of nitration of orthonitrotoluene at 25°C in the stirred cell are compared with rates calculated by assuming that the Fast Reaction Diffusional regime, governed by Equation 3.38, is observed. For each $H_2SO_4 - H_2O$ composition, values of k_2, $\left[ONT\right]_a^s$ and $\left[HNO_3\right]_a$ were calculated by extrapolation or interpolation of the data shown in Chapters 5,6 and 7, and D was calculated using equation 3.43 (see Appendix E for calculation of diffusivities).

Table 8.5. Comparison of Measured and Predicted Two Phase Nitration Rates in the Stirred Cell at 25°C as a Function of $H_2SO_4 - H_2O$ Composition.

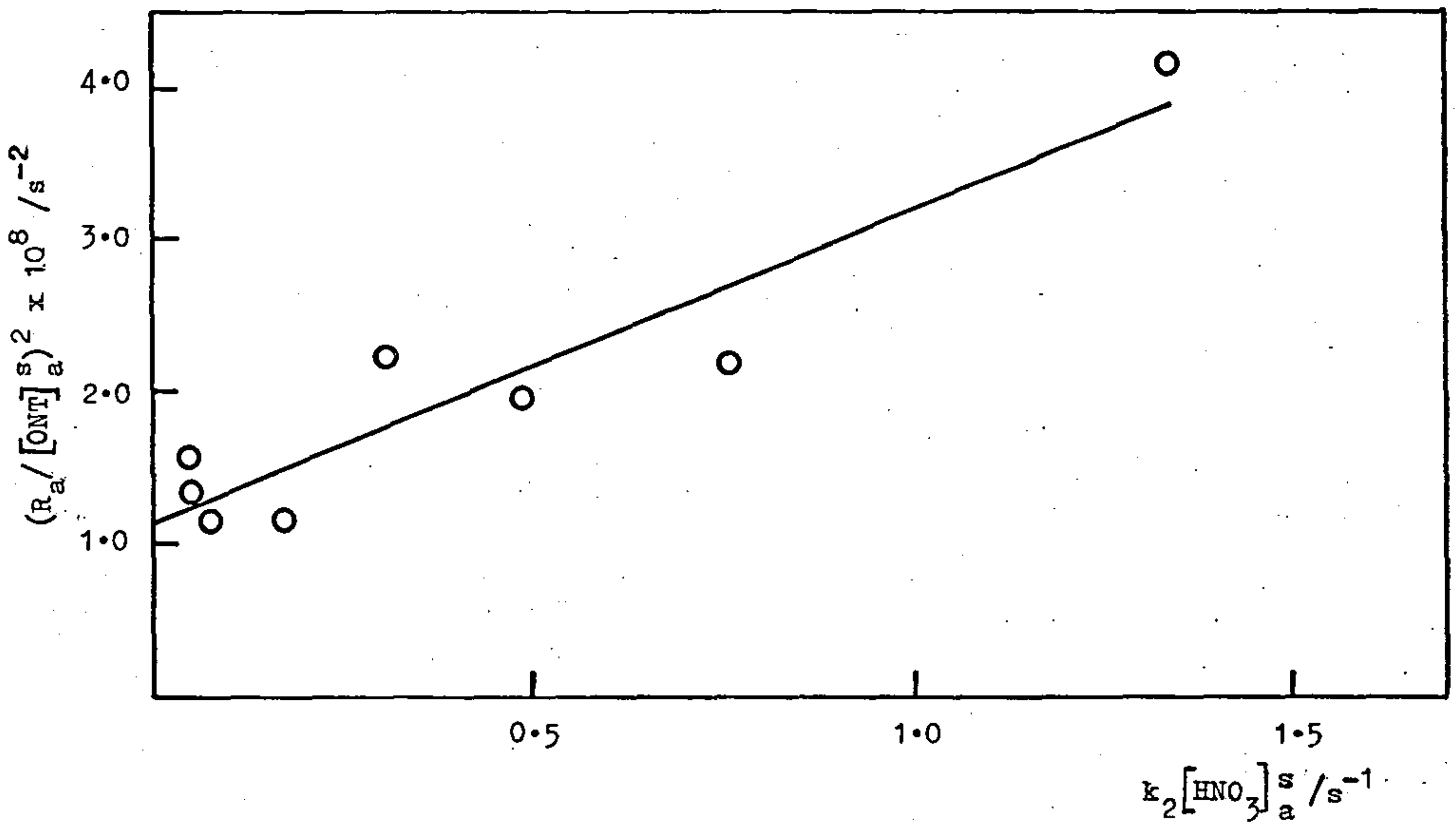
H_2SO_4 /mole%	(Measured Rate) $R_a \times 10^5$ /mol $dm^{-3}s^{-1}$	(Predicted Rate) $a'\left[ONT\right]_a^s\sqrt{Dk_2\left[HNO_3\right]_a} \times 10^5$ /mol $dm^{-3}s^{-1}$
43.3	1.16, 1.20	0.41
44.2	1.26	0.61
45.6	1.67	1.2
46.7	2.98	2.0
47.8	3.50	3.1
48.6	4.67	5.0
49.8	9.12	9.4

For H_2SO_4 - H_2O compositions in the range 43.3 - 46.7 mole% H_2SO_4,the reaction rate,calculated from equation 3.38,is considerably less than the measured rate. However, good agreement is obtained when experimental and calculated rates are compared for H_2SO_4 - H_2O compositions in the range 47.8 to 49.8 mole% H_2SO_4 indicating that the Fast Reaction Diffusional regime is observed in this region.

(iii) Intermediate Regime between the Slow and Fast Reaction Diffusional Regimes.

As shown above, the transition from the Slow to the Fast Reaction Diffusional regime appears to occur within the range of H_2SO_4 - H_2O compositions used for stirred cell runs in this work. In this transition region an intermediate reaction regime should exist which is governed by the Danckwerts equation (3.39). A Danckwerts plot,constructed using the stirred cell data and predicted values of $[ONT]_a^s$, k_2 and $[HNO_3]_a$,is shown in Figure 8.6. The slope and intercept of the least-squares line through the points yield values of $2.05 \times 10^{-8} s^{-1}$ and $1.06 \times 10^{-4} s^{-1}$ for $(a')^2$ D and $a'K_L$ respectively. The dimensions of the cell and the volume of the acid phase give rise to a value of 0.200 cm^2/cm^3 for a'. Hence , D must have an average value of $5.1 \times 10^{-7} cm^2 s^{-1}$ which is

Figure 8.6 <u>Danckwerts Plot for Nitration of Ortho-nitrotoluene in a Stirred Cell.</u>



in reasonable agreement with values of D calculated from the modified Wilke-Chang equation (3.43). These range from 7.7 to 7.6 x $10^{-7} cm^2 s^{-1}$ over the range of H_2SO_4 - H_2O compositions (43.3 - 49.8 mole% H_2SO_4) covered by the points included in the Danckwerts plot. The value of D calculated from the modified Wilke-Chang equation is slightly greater than that determined from the Danckwerts plot. Garner and Marchant (97) observed a similar effect in their determinations of the diffusivities of a number of organic liquids in water. Their experimental values of D were always slightly less than values calculated from the Wilke-Chang equation. The known value of a' also leads to a value of 5.27 x 10^{-4} cm s^{-1} for K_L. This value is in excellent agreement with those values shown in Table 8.4 which were calculated by the method described in section 8.3.1 (i). It is, however, considerably lower than the values of 6.3 x 10^{-3} and 2.8 x 10^{-3}cm s^{-1} determined for Toluene and Chlorobenzene respectively by Cox (59), using a similar stirred cell.

Predicted values of k_2, $[ONT]_a^s$, $[HNO_3]_a$ and D used in (i), (ii) and (iii) above are listed in Appendix C.

8.3.2. Effect of Changes in Temperature

In section 8.3.1. it was shown that the Slow Reaction Diffusional regime is observed for two phase nitration of ortho-nitrotoluene in 44.2 mole% H_2SO_4 at 25°C. The condition for this regime to be observed is that $K_L^2 \gg Dk_2 \left[HNO_3\right]_a$ (See section 3.1.4). Both K_L^2 and Dk_2 are likely to increase with temperature according to equations 8.12 and 8.13.

$$K_L^2 = DS = S(A_1 e^{-E_D/RT}) \quad \ldots\ldots\ 8.12$$

$$Dk_2 = A_2 e^{-(E_D + E_2)/RT} \quad \ldots\ldots\ldots\ldots\ 8.13$$

where A_1 and A_2 are constants, E_D and E_2 are the activation energies for diffusion and homogeneous nitration respectively and S is the rate of surface renewal. The rate of surface renewal may also vary slightly with temperature but for simplicity it is considered to be temperature insensitive in the discussion which follows.

In the modified Wilke-Chang equation (3.43) the diffusivity, D, of a solute in a given medium is given by equation 8.14.

$$D = \text{constant} \times \frac{T}{\eta} \quad \ldots\ldots\ldots\ldots\ldots\ 8.14$$

where T is the absolute temperature and η is the viscosity of the medium. Insertion of values of η in 44.2 mole%

H_2SO_4 over the temperature range 4.4 to 60°C, interpolated from the work of Fasullo (98), in equation 8.14 followed by a plot of $\log_{10}D$ versus 1/T leads to a value of E_D of 24.5 kJ mol^{-1}. A value of 59.2 kJ mol^{-1} for E_2 in 44.2 mole% H_2SO_4 was obtained by a calculation analogous to that described in section 8.2.2.

Since $(E_D + E_2)$ is considerably larger than E_D, the term $Dk_2 \left[HNO_3\right]_a$ increases more rapidly with temperature than K_L^2. As $Dk_2 \left[HNO_3\right]_a$ approaches K_L^2 the intermediate regime (equation 3.39) will be entered and when $Dk_2 \left[HNO_3\right]_a$ greatly exceeds K_L^2 the fast reaction diffusional regime (equation 3.38) will be entered.

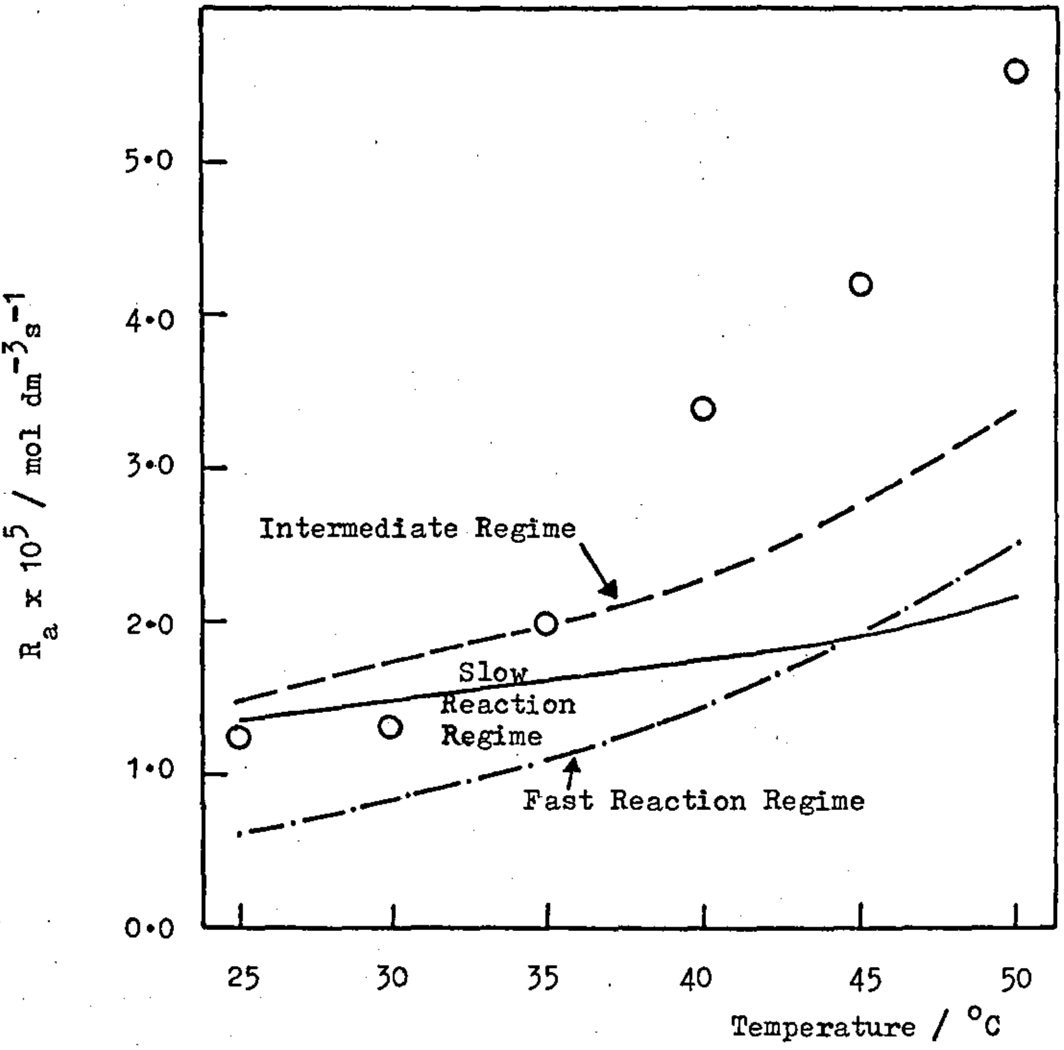
Comparison of Experimental and Predicted Rates.

The initial two phase rate of nitration of ortho-nitrotoluene in a stirred cell has been determined using the same H_2SO_4 - H_2O composition (44.2 mole% H_2SO_4) and the same nitric acid concentration (0.947 moles per dm^3 of aqueous phase) for each run. Determinations were made over the temperature range 25 to 50°C. The results obtained are shown in Table 8.6 together with rates predicted by assuming that the Slow, Intermediate and Fast Reaction Diffusional regimes (equations 3.37, 3.39 and 3.38 respectively) are observed. Figure 8.7 compares the experimental and predicted rates. The k_2, $\left[ONT\right]_a^s$ and $\left[HNO_3\right]_a$ values used to calculate the predicted rates were inter-

Table 8.6 Comparison of Measured and Predicted Rates of Nitration in the Stirred Cell in 44.2 mole% H_2SO_4

Temperature /°C	Measured Rate	Predicted Rates		
	$R_a \times 10^5$ /mol dm^{-3}s^{-1}	$(a'[ONT]^s_a K_L) \times 10^5$ /mol dm^{-3}s^{-1}	$(a'[ONT]^s_a \sqrt{K_L^2 + Dk_2 [HNO_3]_a}) \times 10^5$ /mol dm^{-3}s^{-1}	$(a'[ONT]^s_a \sqrt{Dk_2 [HNO_3]_a}) \times 10^5)$ /mol dm^{-3}s^{-1}
25	1.26	1.36	1.50	0.63
30	1.33	1.51	1.74	0.85
35	2.03	1.66	2.00	1.13
40	3.42	1.76	2.28	1.44
45	4.20	2.00	2.81	1.97
50	5.60	2.20	3.36	2.55

Figure 8.7 Comparison of Experimental and Predicted Rates of Nitration in the Stirred Cell.



polated from the data shown in sections 5.1.6, 6.1.3 and 7.3. Since no data are available for the variation of K_t with temperature, $[HNO_3]_a$ was assumed to be independent of temperature. The diffusivities used to calculate the predicted rates were determined using the modified Wilke-Chang equation (3.43). The viscosities used in the determination of these diffusivities were interpolated from the data reported by Fasullo (98). The K_L value used in the prediction of the rates in the Slow and Intermediate regimes at 25°C was 5.3×10^{-4} cm s^{-1} (see Table 8.4 and section 8.3.1.(iii)). At other temperatures, K_L was calculated from equation 3.26 using values of D predicted as described above and assuming the rate of surface renewal to have the same value as at 25°C i.e. $S = K_L{}^2/D = 0.37 \ s^{-1}$. The values of k_2, $[ONT]_a^s$, D and K_L as a function of temperature, used to predict the two phase nitration rates in the stirred cell (Table 8.6), are listed in Appendix D.

The measured initial rates at 25 and 30°C are in reasonable agreement with rates predicted from equation 3.37 indicating that at these temperatures the slow reaction diffusional regime is observed. At 35°C, the measured rate is in excellent agreement with the rate predicted using equation 3.39 and thus the intermediate regime appears to be observed at this temperature. However, at the temperatures 40, 45 and 50°C, the measured rates are considerably greater than the rates predicted from equations 3.37, 3.38 or 3.39. The most likely explanation of this discrepancy is that, although the intermediate regime is observed at these temperatures, the true value of K_L at each temperature is greater than the calculated value. This leads to the experimental rate being greater than the predicted rate, as is observed.

Variation of K_L with Reaction Rate.

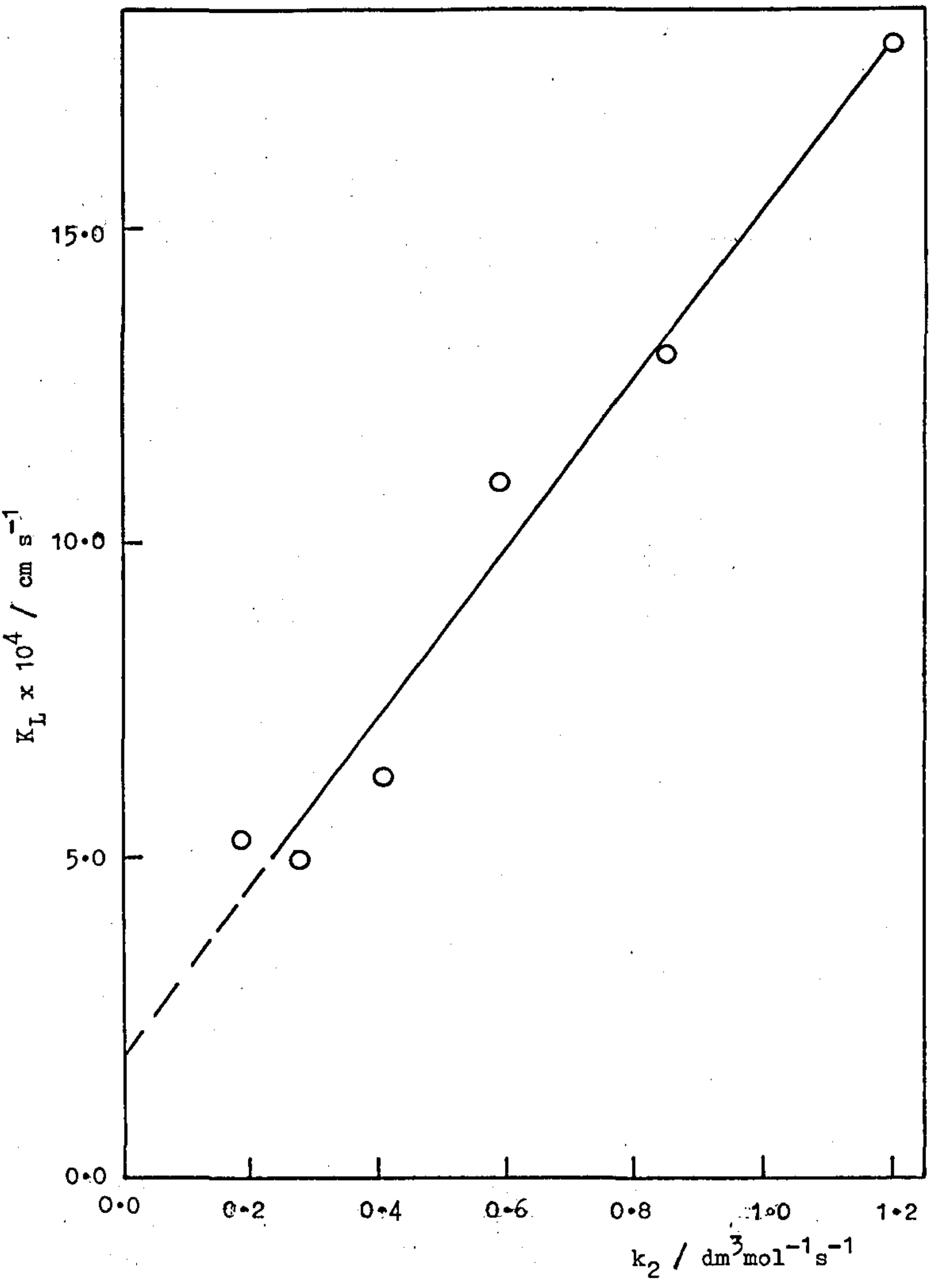
K_L has been estimated by assuming that, under the conditions described above, the initial two phase rates at 25 and 30°C observe the slow reaction diffusional regime and the rates at temperatures in the range 35 - 50°C observe the intermediate regime. A value of K_L, for each temperature, was calculated by inserting the interfacial area, a', the appropriate experimental two phase nitration rate, R_a and predicted values for the remaining variables, into equations 3.37 and 3.39. The calculated K_L values for each temperature are listed in Table 8.7 together with the corresponding predicted k_2 values.

A plot (Figure 8.8) of K_L versus k_2 appears to be linear for the limited data obtained here. The best straight line through these data was found using linear regression analysis and extrapolated to intersect the K_L axis where K_L was found to be equal to 1.91×10^{-4}cm s^{-1}. This value is in good agreement with the value of 1.73×10^{-4}cms^{-1} obtained by Chapman (25) for the mass transfer of chlorobenzene,in a stirred cell,in the absence of chemical reaction. These results indicate, as suggested earlier by Cox and Strachan (61), that in the stirred cell,chemical reaction promotes good surface renewal which the agitation alone (Reynold's Number $\approx$500) is insufficient to maintain. Hence,the interface becomes increasingly stagnant as the reaction rate falls and therefore the value of K_L decreases.

Table 8.7. Comparison of K_L and k_2 for Nitration of Orthonitrotoluene in a Stirred Cell.

Temperature /°C	$K_L \times 10^3$ /cm s^{-1}	k_2 /dm^{3}mol^{-1}s^{-1}
25	0.53	0.19
30	0.50	0.28
35	0.63	0.41
40	1.1	0.59
45	1.3	0.85
50	1.8	1.20

Figure 8.8 Comparison of Predicted Values of K_L and k_2 for the Stirred Cell.



8.4 REACTION IN THE ORGANIC PHASE DURING TWO PHASE NITRATION AT 25°C.

In the calculation of the two phase nitration rates reported here it has been assumed that nitration occurs only in the aqueous phase. Sohrabi (99) has demonstrated that the maximum rate of reaction in the organic phase, during nitration of toluene,is many orders of magnitude less than that in the aqueous phase. As confirmation that this is also true for ortho-nitrotoluene a simple experiment was carried out to establish whether or not significant reaction occurs in ortho-nitrotoluene which has been saturated with mixed acid.

In this experiment the apparatus, phase volumes and component concentrations were similar to those used in the stirred cell run in 46.7 mole% H_2SO_4 at 25°C. The experimental procedure used is described in section 4.2.2.

From the analysis of the samples withdrawn from the ortho-nitrotoluene during this experiment it was clear that, after separation of the phases,no significant reaction occurred in the organic phase. This evidence supports the assumption that reaction occurs almost exclusively in the aqueous phase during two phase nitration.

CHAPTER 9

REVIEW OF RESULTS

9.1 MUTUAL SOLUBILITY PHENOMENA

Although the published literature contains considerable information on the solubilities of aromatic compounds in aqueous sulphuric acid, the solubility of only one of the mononitrotoluenes (para-nitrotoluene) has previously been studied in detail. No data have been published for the solubilities of mononitrotoluenes in aqueous sulphuric acid as a function of temperature or for the solubilities of sulphuric acid in nitroaromatics. The solubility of ortho-nitrotoluene in aqueous sulphuric acid was determined in the present work both as a function of H_2SO_4 concentration and as a function of temperature. This information was required so that the rate of nitration of this compound under heterogeneous conditions could be predicted. The solubility of sulphuric acid in ortho-nitrotoluene was also determined so that corrections could be made to the acidity measurements obtained during the determination of the distribution of nitric acid between aqueous sulphuric acid and both ortho-nitrotoluene and nitrobenzene.

Over the range of H_2SO_4 - H_2O compositions covered in this work the solubility of ortho-nitrotoluene in aqueous sulphuric acid at $25^\circ C$ (Table 6.1) was found to be similar to that of para-nitrotoluene (79, 92), although ortho-nitrotoluene was always slightly more soluble, in a given composition, than para-nitrotoluene. At one H_2SO_4 concentration (43.1 mole% H_2SO_4) the solubility of meta-nitrotoluene in aqueous sulphuric acid at $25^{o}C$ was determined, the value obtained being similar to interpolated solubility values for both ortho-and para-nitrotoluene. It is likely that the solubilities of all three mononitrotoluenes, as a function of H_2SO_4 concentration, are similar over the whole range of H_2SO_4 - H_2O compositions.

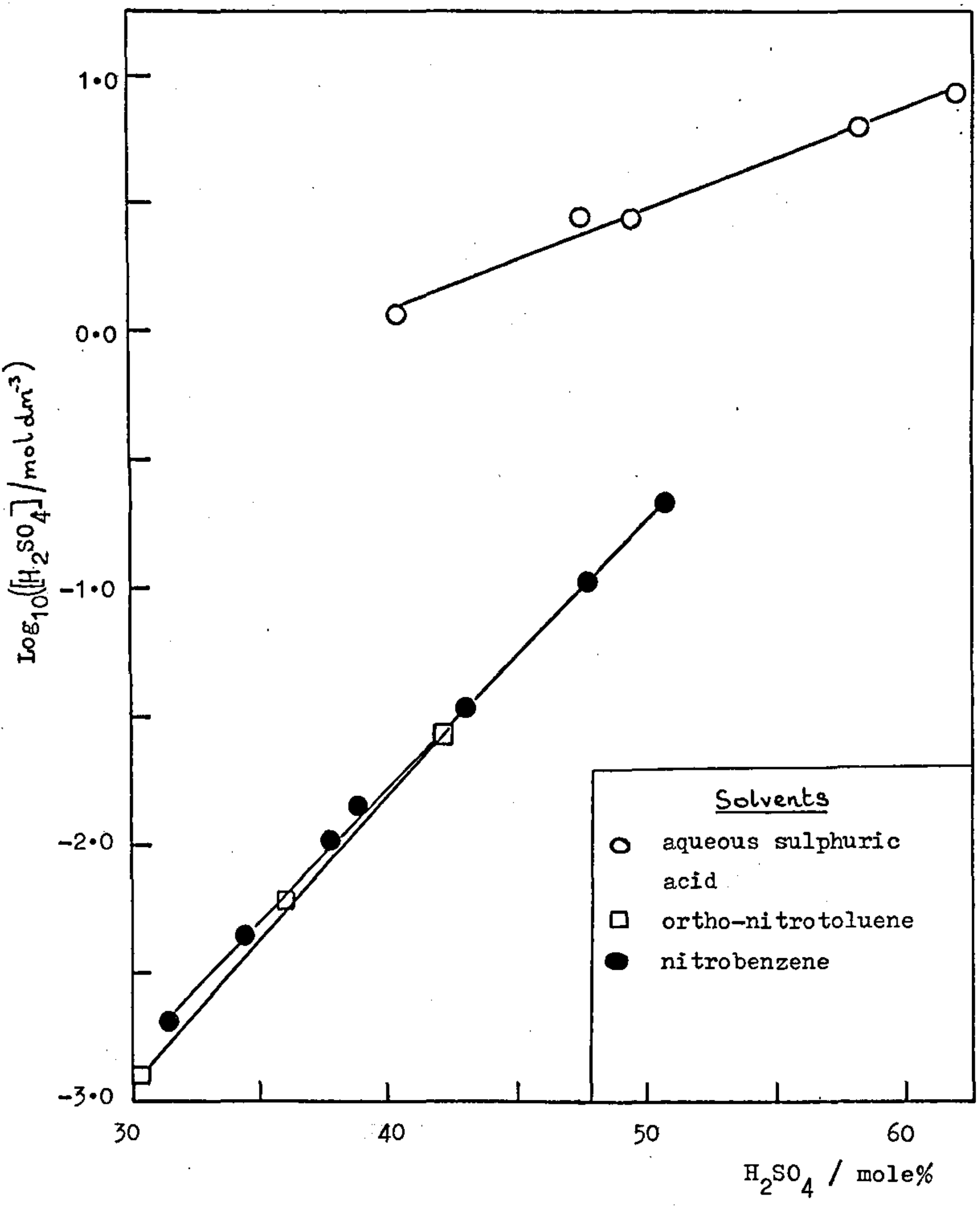
The solubility of ortho-nitrotoluene in aqueous sulphuric acid as a function of temperature has been determined for several H_2SO_4 - H_2O compositions. The heats of solution calculated from these data (Table 6.3) were found to decrease with increasing H_2SO_4 concentration. The heat of solution of meta-nitrotoluene was also determined (section 6.1.2), at one H_2SO_4 - H_2O composition, the value obtained being similar to the corresponding value for ortho-nitrotoluene.

Combination of the solubility and heat of solution data for ortho-nitrotoluene allowed determination of the entropy of interaction, $\triangle S_I$, in this solute-solvent system, as a function of H_2SO_4 - H_2O composition. The entropy of interaction was found to be almost independent of H_2SO_4 -

H_2O composition (Table 6.4). This indicated that, although interactions between ortho-nitrotoluene and one or more of the species present in aqueous sulphuric acid do occur, the marked changes in the solubility of ortho-nitrotoluene,with H_2SO_4 concentration,are unlikely to be explained by changes in solute-solvent interactions.

The solubility of H_2SO_4 in ortho-nitrotoluene and nitrobenzene,as a function of H_2SO_4 - H_2O composition,was also investigated. The logarithm of the solubility of sulphuric acid in each of these compounds increased almost linearly with mole% H_2SO_4 (Figure 6.5). The solubility of sulphuric acid in an aromatic compound is likely to be related to the concentration of undissociated H_2SO_4 in the aqueous phase with which it is contacted because this is the species most likely to be extracted into the organic phase. Figure 9.1 compares the logarithms of the solubilities of sulphuric acid in nitrobenzene and ortho-nitrotoluene with logarithims of the concentrations of undissociated H_2SO_4 in aqueous sulphuric acid,as a function of H_2SO_4 - H_2O composition (100). Although there is insufficient overlap,between the organic and aqueous phase data,to assess whether any direct correlations exist, it appears that increases in the concentration of undissociated H_2SO_4 in the aqueous phase favour increases in the solu-

Figure 9.1 $\mathrm{Log}_{10}[H_2SO_4]$ in Various Solvents versus Mole% H_2SO_4.



bility of sulphuric acid in nitrobenzene and ortho-nitrotoluene.

The mutual solubility of sulphuric acid and nitroaromatic compounds is not entirely unexpected since,if complex formation (which promotes solution) between the nitroaromatic and one of the species present in aqueous sulphuric acid occurs in the aqueous phase,it might also be expected to occur in the organic phase. At high H_2SO_4 concentrations,the mutual solubility may increase to such an extent that the phases become totally miscible.

The solubilities of ortho-nitrotoluene in aqueous sulphuric acid determined in this work (Chapter 6) were subsequently used (Chapter 8) to predict the two phase rates of nitration of ortho-nitrotoluene in mixed acid containing a low nitric acid concentration (approximately 2 mole% HNO_3). Although the agreement between experimental and predicted rates was not exact,it was close enough to suggest that the solubility of ortho-nitrotoluene in H_2SO_4 compositions is not very different from that in mixed acids containing low nitric acid concentrations.

In this thesis the theories which relate to the solubility behaviour of aromatic compounds,in aqueous sulphuric acids,have been discussed in some detail. Because of the extremely complex nature of these media and the lack of knowledge about the solute-solvent interactions which may occur in them, it is not yet possible to predict, quantitatively, the solubilities of nitroaromatics in aqueous sulphuric acid solutions. The three component system (H_2SO_4 - HNO_3 - H_2O), in which most large scale nitrations are carried out, is even less well understood, although Field (95) has recently made considerable progress in this area. Clearly more work on this topic is desirable.

9.2 INFLUENCE OF REACTION CONDITIONS ON PRODUCTS OF NITRATION.

In Chapter 1 it was stated that, for some applications, it is desirable to produce dinitrotoluenes containing a high proportion of the 2, 4 - isomer. For most applications, it is also desirable to minimise the proportion of the 3, 5-; 3, 4-; 2, 3- and 2, 5-isomers (usually called "meta" isomers because they arise almost exclusively from nitration of meta-nitrotoluene) in the dinitrotoluene product. The product mixture obtained using conventional, large scale, commercial techniques usually contains approximately 77% 2, 4-dinitrotoluene and about 4% of the "meta" dinitroisomers. A method of producing up to 89% 2, 4-dinitrotoluene and as little as 1.5% of the "meta" dinitroisomers has been reported in the literature (33) (see Table 2.5). However, this method involves nitrating toluene directly to dinitrotoluene at low temperatures (-5 to -35°C). To use this method on a large scale the nitration plant would have to incorporate refrigeration systems. The price differential,between different quality dinitrotoluenes, is probably not sufficient to justify the cost of operating nitration plants below ambient temperature. However, dinitration plants are often operated at temperatures well above ambient and a sufficient improvement in the product might be achieved by running them,instead,at ambient temperature. One of the aims of the work described here was to determine the factors which influence the rates and products of nitration of mononitrotoluenes so that operators of nitration plants will be able to assess whether improved products can be manufactured, by slight modification of the reaction conditions, using existing processes.

The major factors which are likely to influence the proportion of 2, 4-dinitrotoluene and/or the proportion of "meta" isomers in the dinitrotoluene product are:

(i) the relative proportions of the nitrotoluene isomers formed during mononitration of toluene;

(ii) the rate of nitration of para-nitrotoluene relative to the rates of nitration of ortho- and meta-nitrotoluene;

and (iii) the ratio of products formed by nitration of ortho-nitrotoluene.

Table 2.2 shows that, although changes in acid phase composition do not significantly influence the nitrotoluene isomer distribution, decreases in reaction temperature appear to increase the percentage of para-nitrotoluene and decrease the percentage of meta-nitrotoluene formed. Since, on further nitration, para-nitrotoluene yields exclusively 2, 4-dinitrotoluene and meta-nitrotoluene yields a mixture of the 2, 3-; 2, 5-; 3, 4- and 3, 5- isomers, a decrease in temperature during mono-nitration will tend to produce a "better quality" dinitrotoluene product.

Table 5.5 compares relative rates of nitration of mono-nitrotoluenes determined in the present work with those reported in the literature. The values shown in this table were determined over a wide range of H_2SO_4 - H_2O compositions and a limited temperature range. The relative rates of nitration do not appear to be significantly affected by large changes in H_2SO_4 concentration or small changes in temperature.

Nitration of ortho-nitrotoluene leads to the formation of a mixture of 2, 4- and 2, 6-dinitrotoluene. The variation of the ratio of these products as a function of temperature and H_2SO_4 concentration is shown in Table 5.7. The proportion of 2, 4-dinitrotoluene formed from nitration of ortho-nitrotoluene appears to be slightly increased by decreasing the reaction temperature and increasing the H_2SO_4 concentration of the mixed acid.

The above discussion suggests that the reaction conditions used in the manufacture of dinitrotoluenes could be modified to increase the yield of 2, 4-dinitrotoluene and decrease the yield of the "meta" isomers by:

(a) using a low reaction temperature during mononitration of toluene;

(b) using a low reaction temperature and high H_2SO_4 concentration during the dinitration stage of the process.

Whether commercial plants for the manufacture of dinitrotoluenes can be operated economically,at ambient temperature and using high H_2SO_4 concentrations in the dinitration stage,depends on a number of factors. These include: the influence of reaction conditions on the side reactions which compete with nitration and the influence of reaction conditions on the heterogeneous rate of nitration of toluene and mononitrotoluenes.

The influence of reaction conditions on the heterogeneous nitration of toluene has been discussed extensively in the literature (see Chapter 3) and will not be discussed further here. The other factors are, however, discussed below.

9.3 HETEROGENEOUS NITRATION.

Considerable effort, both in this laboratory (25, 59) and elsewhere,has been devoted to studies of the macrokinetics of heterogeneous nitration of toluene. As a result, operators of plants designed for the production of mono-, di- or trinitrotoluenes should be able to model the first nitration stage (from toluene to a mixture of mononitrotoluenes) with reasonable confidence. However, the same is not true for the second nitration stage (from mononitrotoluenes to dinitrotoluenes) and is probably not true for the third stage (from dinitrotoluenes to trinitrotoluenes). One of the aims of the work described here was to provide operators of toluene nitration plants with sufficient information to enable them to model the rate of nitration in their dinitrators. In order to achieve this aim it was necessary to measure the two phase rates of nitration of mononitrotoluenes for a range of reaction conditions and investigate whether the measured rates were in agreement with rates predicted using established rate models (see section 3.1.4).

Two phase nitration runs were carried out here only for one of the mononitroisomers, namely ortho-nitrotoluene. However,the solubility and homgeneous rate data obtained both in this work and previously by other workers indicate that the three mononitrotoluenes behave quite similarly. Hence, the two phase nitration behaviour of para- and meta-nitrotoluene are likely to be quite similar to that of ortho-nitrotoluene.

To use the established rate models, a knowledge is required of several reaction parameters as a function of temperature and the H_2SO_4 - H_2O composition of the aqueous phase. The data used to predict k_2, $[ONT]_a^s$, $[HNO_3]_a$ and D, under the conditions of the two phase nitration experiments, are shown in Chapters 5, 6 and 7 and Appendix E. In the calculation of values of $[HNO_3]_a$ it was assumed that the plot of K_t versus mole% H_2SO_4 (Figure 7.2) is linear over the range of H_2SO_4 - H_2O compositions considered here. In addition, for the prediction of two phase rates of nitration, at elevated temperatures, it was assumed that K_t (and hence $[HNO_3]_a$) is independent of temperature.

9.3.1. The Stirred Reactor

The two phase rate of nitration of ortho-nitrotoluene in a stirred batch reactor, for low nitric acid concentrations, was found to be kinetically controlled under all conditions in which it was possible to measure the nitration rate (section 8.2). It was not possible to observe the transition from kinetic to mass transfer control in the stirred batch reactor because this transition would occur at rates of nitration which would be too fast to follow using the sampling technique employed here. In future work it might be possible to observe this transition by diluting the ortho-nitrotoluene in an inert solvent as was done by Cox (59) for toluene. The concentration of ortho-nitrotoluene in the organic phase would then be much lower than with the technique used here. Since the concentration of ortho-nitrotoluene in the aqueous phase would then also be lower, both the kinetic and mass transfer rates would be reduced without altering the competition between them. The degree of dilution could be adjusted so that the overall rate would be sufficiently slow to be followed by the sampling method used here. The major difficulty in adopting this procedure would be in finding a solvent that would be both considerably less reactive than ortho-nitrotoluene and reasonably transparent at the wavelengths at which both ortho-nitrotoluene and its nitration products absorb.

9.3.2. The Stirred Cell

The rate of nitration in a two phase system is mass transfer controlled when $k_2 [HNO_3]_a \gg a'K_L$ (see section 3.1). Hence, the use of a stirred cell (for which a' is relatively low) has the advantage that the rate will sometimes be mass transfer controlled at overall reaction rates which can be followed. This is in contrast to the stirred reactor (for which a' is relatively high) where the rate is often mass transfer controlled only at overall rates which would be too fast to follow with the sampling technique used here. The rate of nitration in the stirred cell was, in fact,mass-transfer controlled under all conditions investigated (section 8.3).

The initial two phase rate of nitration of ortho-nitrotoluene was determined,at a constant temperature (25°C), for a range of H_2SO_4 - H_2O compositions. The slow reaction diffusional regime was easily identified because of the relative insensitivity of the rate to changes in H_2SO_4 - H_2O composition in this regime. The fast reaction diffusional regime was identified by comparison of the measured rates with those predicted from equation 3.38. A Danckwerts plot of the data yielded average values of D and K_L for the range of conditions investigated. The value of D determined by this method was in reasonable agreement with the values calculated from the modified Wilke-Chang equation (62). The value of K_L,determined from the Danckwerts plot,was similar to the values calculated from the rate data for the H_2SO_4 - H_2O compositions in which the slow reaction diffusional regime (where $K_L = R_a/a' [ONT]_a^s$, see Table 8.4) was observed. This value was, however, much lower than the values determined previously for toluene and chlorobenzene (59).

The initial two phase rate of nitration of ortho-nitrotoluene was also determined, as a function of temperature, using a constant H_2SO_4 - H_2O composition (section 8.3.2). At the higher temperatures the measured rates were greater than predicted. This discrepancy could be a consequence of the assumption that $[HNO_3]_a$ was constant over the temperature range employed in these experiments. Thus, in future work, it would be desirable to investigate the effect of temperature on K_t so that this uncertainty can be resolved. It is more likely, however, that the discrepancy arises because K_L does not remain constant as the temperature is increased, as assumed in the prediction of the two phase rates. To investigate this possibility, the experimental two phase rate data were combined with predicted values of k_2, $[ONT]_a^s$, D and $[HNO_3]_a$ and the known value of a' in order to calculate values of K_L from equations 3.37 and 3.39. The values of K_L, calculated in this way, were found to increase with temperature. A plot of K_L versus k_2 for each temperature was approximately linear (Figure 8.8). It is considered that the agitation in the stirred cell is not, alone, sufficient to promote efficient surface renewal and thus, in the absence of rapid chemical reaction, interfacial stagnation, which inhibits mass transfer, can occur. However, it is thought that chemical reaction influences surface renewal and thus, as k_2 increases, stagnation is reduced and K_L increases. Therefore, care should be exercised when using the stirred cell technique to predict mass transfer coefficients for rapidly stirred systems such as those used for the manufacture of nitroaromatics, since, in rapidly stirred systems, interfacial stagnation is less likely to occur. Cox and Strachan (61) determined K_L values for chlorobenzene using both the stirred reactor and the stirred cell. The values of K_L (2.10×10^{-3} and 2.29×10^{-3} cms^{-1} respectively) that they obtained were very similar. This suggests that k_2 was sufficiently high to promote good surface renewal at the stirred cell interface and that the rate of surface renewal in the stirred cell was similar to that in the stirred reactor. It is recommended that, in future work, the stirred cell experiments performed here are extended to higher temperatures. Values of K_L may then be calculated as described in section 8.3.2. If chemical reaction does indeed influence the rate of surface renewal, the calculated K_L values should increase with temperature (and k_2) until good surface renewal is achieved. K_L should then remain relatively constant as the temperature is further increased. The value of K_L, in this "plateau" region, might be expected to be similar to that prevailing in rapidly stirred systems such as those used for commercial production of dinitrotoluenes.

All the rate measurements presented in this work were obtained during the early stages of the nitration of mononitrotoluenes. Thus, throughout the two phase runs, the organic phase consisted predominantly of the unreacted mononitrotoluene and the aqueous phase remained relatively unchanged. In large scale, commercial systems the degree of conversion is close to 100% and so the compositions of both phases change considerably during the course of the reaction. Hence, in order to predict the rate throughout the reaction, it is necessary to be able to predict the variation of the parameters k_2, $[ONT]_a$, $[HNO_3]_a$, K_L and D as a function of phase composition. Recent work by Field (95) and Schiefferle and co-workers (88) has made some progress in this direction but considerable work is still needed before a complete knowledge of the two phase rates of nitration of mononitrotoluenes can be obtained.

9.4. SIDE REACTIONS OF MONONITROTOLUENES

Although aromatic nitration has been studied in considerable detail, comparatively little is known about the oxidation processes that accompany it. Recently, Hanson and co-workers (101) and Ross and Kirshen (102) investigated the side reactions that occur during the nitration of toluene and dinitrotoluenes respectively but little work has been published on the side reactions which accompany the nitration of mononitrotoluenes.

In the work described here,the prime intention was to study the nitration of mononitrotoluenes but some consideration of the side reactions which accompany nitration, is necessary because of the difficulties encountered in determining true homogeneous nitration rates (section 5.1.3). Surprisingly,no such difficulties were encountered during heterogeneous nitration experiments.

In section 5.1 it was shown that when ortho-nitrotoluene is nitrated in excess nitric acid,deviations from pseudo-first-order kinetics were observed during the early stages of each run. Similar deviations were observed for meta- and para-nitrotoluene but the effect was less marked. It was considered that these effects might be caused either by oxidation of the mononitrotoluene being nitrated (the oxidation products formed might then be nitrated) or by oxidation of the dinitrotoluenes formed. The use of excess nitric acid was thought to be likely to contribute to oxidation of the dinitrotoluenes and therefore,subsequent experiments were performed using equal concentrations of the reactants. Although this precaution enabled values of

k_2 for the nitration of ortho-nitrotoluene to be determined, it did not appear to eliminate side-reactions completely since considerable variation in the A_∞ values, for runs at different temperatures, was observed, indicating that some competition between oxidation and nitration still occurred and that the relative rates of the processes involved are temperature dependent. However, in order to use the measured k_2 values for the prediction of two phase nitration rates, it was assumed that k_2 (nitration) $\gg$ k_2 (oxidation) so that the measured values could be considered as those for true nitration rate constants.

Recent work in this laboratory (91) has shown that nitrous acid is formed in significant quantities when all three mononitrotoluenes are nitrated to dinitrotoluenes. The nitrous acid formation parallels the dinitrotoluene formation and hence appears to result from oxidation of mononitrotoluenes rather than from oxidation of dinitrotoluenes. The rate of nitration, under certain conditions, was about fifty times the rate of formation of nitrous acid and hence, providing the latter is a measure of the rate of oxidation of mononitrotoluenes, the above assumption that k_2 (nitration) $\gg$ k_2 (oxidation) is probably justified. The ratio $[HNO_2]/[DNT]$ in the reaction mixture was found to decrease with increased sulphuric acid concentration and to increase with increased temperature. Thus, the suggestion in section 9.2 that dinitrators should be operated at high sulphuric acid concentrations and low temperatures could, as well as leading to an improved dinitrotoluene product, minimise oxidation of the reactant mononitrotoluenes.

It is clear from the preceding discussion that a complete understanding of the factors affecting the rates of nitration of mononitrotoluenes will not be possible until the oxidation reactions which compete with nitration are better understood.

CONCLUSIONS

1. To increase the yield of 2, 4 - dinitrotoluene and decrease the yield of the remaining dinitrotoluene isomers, reactors used for nitration of mononitrotoluene mixtures should, within the constraints imposed by economic factors, be operated using as low a temperature and as high an H_2SO_4 concentration as possible. Such conditions may also favour a decrease in the side reactions which occur during dinitration of mononitrotoluenes.

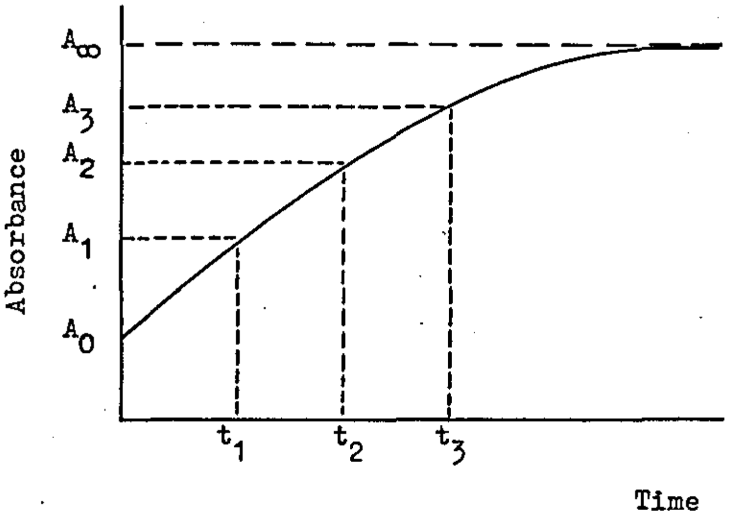
2. The entropy of interaction for solution of ortho-nitrotoluene in aqueous sulphuric acid is almost independent of H_2SO_4 - H_2O composition. Although interactions between ortho-nitrotoluene and species present in aqueous sulphuric acid do appear to occur, the marked changes in the solubility of ortho-nitrotoluene with H_2SO_4 concentration are unlikely to be explained by changes in these solute-solvent interactions.

3. The initial two phase rate of nitration of ortho-nitrotoluene in a small stirred batch reactor (stirring speed 2500 ± 25 r.p.m.) is kinetically controlled in mixed acids having a low nitric acid concentration (0.56 mol dm^{-3}) and H_2SO_4 concentrations up to 38.5 mole% H_2SO_4 at 25°C.

4. The initial two phase rate of nitration of ortho-nitrotoluene in a stirred cell (stirring speed 55 ± 1 r.p.m., interfacial area 0.2 cm^{-1}) is mass transfer controlled for mixed acids having a low nitric acid concentration (0.56 mol dm^{-3}) and H_2SO_4 concentrations in the range 43.3 - 49.0 mole% H_2SO_4. Under these conditions Danckwerts' Surface Renewal Theory is observed. The value of K_L,calculated from a Danckwerts plot of the observed data,is lower than that previously observed for other systems and this suggests that, in the stirred cell, agitation alone is not sufficient to prevent interfacial stagnation. Values of K_L, calculated from data for the temperature range 25 - 80°C in a constant H_2SO_4 - H_2O composition, appear to increase almost linearly with k_2. This suggests that chemical reaction increases the rate of surface renewal and reduces interfacial stagnation.

Appendix A

Roseveare's Method of Calculating Second Order Rate Coefficients



Roseveare's method (90) enables the second order rate constant, k_2, to be evaluated for reactions in which the concentrations of the components at infinite time are unknown or inaccessible. The method requires that concentration measurements should be taken in groups of three, adjacent pairs of measurements being separated by a constant time interval t. If the concentrations are determined by spectrophotometric means, a given absorbance value is related to its corresponding concentration C as follows:-

$$A = A_\infty - \alpha C \qquad \text{A.1.}$$

therefore $$C = \frac{A_\infty - A}{\alpha} \qquad \text{A.2.}$$

and $$C_o = \frac{A_\infty - A_o}{\alpha} \qquad \text{A.3.}$$

where A_o and A_∞ are the respective absorbances at zero and infinite time, C_o is the concentration of the reactants at zero time and α is a proportionality constant.

The method assumes that the initial reactant concentrations are equal. The equation governing second order kinetics under these conditions is as follows:-

$$\frac{1}{C} - \frac{1}{C_o} = kt \text{ .... A.4}$$

therefore $$\frac{1}{A_\infty - A} - \frac{1}{A_\infty - A_o} = kt \text{ .... (5.1)}$$

Hence, for measurements A_1, A_2 and A_3 at reaction times t_1, t_2 and t_3 where $t_3 - t_2 = t_2 - t_1 = t$ the following equations hold:-

$$\frac{1}{A_\infty - A_1} - \frac{1}{A_\infty - A_o} = \frac{k_2 t_1}{\alpha} \text{ .... A.5}$$

$$\frac{1}{A_\infty - A_2} - \frac{1}{A_\infty - A_o} = \frac{k_2 (t_1 + t)}{\alpha} \text{ ..... A.6}$$

$$\frac{1}{A_\infty - A_3} - \frac{1}{A_\infty - A_o} = \frac{k_2 (t_1 + 2t)}{\alpha} \text{ .... A.7}$$

Subtracting A.5 from A.7

$$\frac{1}{A_\infty - A_3} - \frac{1}{A_\infty - A_1} = \frac{2k_2t}{\alpha} \quad \ldots\ldots\ldots\ldots \text{A.8}$$

Subtracting A.5 from A.6

$$\frac{1}{A_\infty - A_2} - \frac{1}{A_\infty - A_1} = \frac{k_2t}{\alpha} \quad \ldots\ldots\ldots\ldots \text{A.9}$$

Multiplying A.9 by 2 and comparing with A.8 we have.-

$$\frac{1}{A_\infty - A_3} - \frac{1}{A_\infty - A_1} = 2\left\{\frac{1}{A_\infty - A_2} - \frac{1}{A_\infty - A_1}\right\} \ldots\ldots \text{A.10}$$

and hence

$$A_\infty = \frac{A_1A_2 + A_2A_3 - 2A_1A_3}{(A_2 - A_1) - (A_3 - A_2)} \quad \ldots\ldots\ldots\ldots \text{(5.3)}$$

Subtracting A.6 from A.7

$$\frac{1}{A_\infty - A_3} - \frac{1}{A_\infty - A_2} = \frac{k_2t}{\alpha} \quad \ldots\ldots\ldots\ldots \text{A.11}$$

therefore $(A_3 - A_2)\dfrac{\alpha}{k_2t} = A_\infty^2 - (A_2 + A_3)A_\infty + A_2A_3 \ldots\ldots$ A.12

Similarly from A.9

$$(A_2 - A_1)\frac{\alpha}{k_2t} = A_\infty^2 - (A_1 + A_2)\,A_\infty + A_1A_2 \quad \ldots\ldots \text{A.13}$$

Subtracting A.13 from A.12 and rearranging we have:-

$$A_\infty = A_2 - \frac{(A_3 - A_2) - (A_2 - A_1)}{A_3 - A_1}\cdot\frac{\alpha}{k_2t} \quad \ldots\ldots\ldots \text{A.14}$$

Equating (5.3) and A.14 we have

$$\frac{k_2}{\alpha} = \frac{\left\{(A_2 - A_1) - (A_3 - A_1)\right\}^2}{2t\,(A_3 - A_1)(A_3 - A_2)(A_2 - A_1)} \quad \ldots\ldots \quad (5.4)$$

Appendix B

Comparison of Reproducibility of Relative Response Factors Based on Peak Area (A) and Peak Height (h) Ratios.

$A_{2,4}$ /cm^2	$A_{2,6}$ /cm^2	$h_{2,4}$ /cm	$h_{2,6}$ /cm	Relative Response Factors	
				$1.777A_{2,6}/A_{2,4}$	$1.777h_{2,6}/h_{2,4}$
46.1	27.9	15.25	13.30	1.08	1.55
44.4	24.0	14.60	12.30	0.96	1.50
61.6	33.4	19.60	16.55	0.96	1.50
53.4	31.0	17.40	14.65	1.03	1.50
53.2	30.1	17.30	14.20	1.01	1.46
62.9	35.2	20.20	17.15	0.99	1.51
45.0	26.7	14.90	12.45	1.05	1.49
40.2	22.8	13.40	11.35	1.01	1.50
40.1	22.6	13.45	11.20	1.00	1.48
43.9	26.3	14.50	12.20	1.06	1.49
54.5	32.0	18.35	15.20	1.04	1.47
47.8	26.5	15.70	13.20	0.99	1.49
48.7	27.8	15.75	13.30	1.01	1.50
44.5	25.6	14.40	12.00	1.02	1.48
60.1	32.8	19.20	16.15	0.97	1.49
36.6	-	12.50	10.50	-	1.49
56.6	33.0	18.20	15.30	1.04	1.49
55.5	31.9	17.95	15.10	1.02	1.49

<u>Notes</u>: (1) For each run,a mixture of dinitrotoluenes dissolved in toluene (ca.0.1 mol dm^{-3}) was employed. The ratio of dinitrotoluenes,in each case,was:- 2, 4 - DNT/2,6 - DNT = 1.777.

(2) Peak areas were measured by planimetry.

(3) Peak height measurement was made using an accurate steel rule.

APPENDIX C

Predicted Reaction Parameters for Nitration of Ortho-nitrotoluene in a Stirred Cell at 25°C.

H_2SO_4 /mole%	$[ONT]_a^s$ /mol dm^{-3}	k_2 /$dm^3mol^{-1}s^{-1}$	$[HNO_3]_a$ /mol dm^{-3}	D x 10^7 /$cm^2 s^{-1}$
43.3	0.100	0.12	0.43	7.74
44.2	0.117	0.19	0.42	7.60
45.6	0.155	0.42	0.42	7.59
46.7	0.200	0.74	0.41	7.64
47.8	0.251	1.2	0.41	7.61
48.6	0.309	1.9	0.41	7.60
49.8	0.457	3.3	0.40	7.63

APPENDIX D

Predicted Reaction Parameters for Nitration of Ortho-nitrotoluene in a Stirred Cell in 44.2 mole% H_2SO_4.

Temperature /°C	$[ONT]_a^s$ /mol dm^{-3}	k_2 /$dm^3 mol^{-1} s^{-1}$	$D \times 10^7$ /$cm^2 s^{-1}$	$K_L \times 10^4$ /cm s^{-1}
25	0.128	0.19	7.60	5.3
30	0.131	0.28	8.95	5.8
35	0.133	0.41	10.5	6.2
40	0.136	0.59	11.3	6.5
45	0.138	0.85	14.2	7.3
50	0.140	1.20	16.5	7.8

Appendix E

Diffusivity of Ortho-nitrotoluene in Mixed Acid

Diffusivities of ortho-nitrotoluene in various H_2SO_4 - H_2O - HNO_3 solutions at 25°C were calculated using equation 3.43 and these are shown in Table E.1. Values of $\bar{\phi}\bar{M}$ for each composition were calculated using the linear mixing rule (equation 3.44) which can be rewritten in the more appropriate form

$$\overline{\phi}\,\overline{M}_{(\text{mixture})} = (\phi\, MX)_{H_2SO_4} + (\phi\, MX)_{H_2O} + (\phi\, MX)_{HNO_3} \qquad \text{.......... E.1.}$$

M and X are molecular weight and mole fraction respectively. The ϕ values used were those calculated by Cox (59), namely, $\phi_{H_2SO_4} = 2.00$, $\phi_{H_2O} = 2.60$ and $\phi_{HNO_3} = 1.05$.

The molar volume, V_{ONT}, of ortho-nitrotoluene calculated from its density was 118 $cm^3 mol^{-1}$.

The viscosities shown in Table E.1. were interpolated from the data of Fasulo (98) for H_2SO_4 - H_2O mixtures. These data do not take into account the presence of nitric acid but are unlikely to differ greatly from the true values since the mole fraction of HNO_3 in the mixtures is never greater than 0.02.

Table E.1

MOLE FRACTION (X)			ϕ MX			$\overline{\phi}\ \overline{M}$ MIXTURE	Viscosity /cp	D x 10^7 /$cm^2 s^{-1}$
H_2SO_4	H_2O	HNO_3	H_2SO_4	H_2O	HNO_3			
0.433	0.550	0.017	84.94	25.74	1.12	111.8	16.6	8.02
0.442	0.541	0.017	86.70	25.32	1.12	113.1	16.8	7.97
0.456	0.526	0.018	89.45	24.62	1.19	115.3	17.0	7.95
0.467	0.515	0.018	91.61	24.10	1.19	116.9	17.2	7.90
0.478	0.504	0.018	93.76	23.59	1.19	118.5	17.4	7.88
0.486	0.495	0.018	95.33	23.17	1.19	119.7	17.5	7.87
0.498	0.484	0.019	97.68	22.65	1.26	121.6	17.7	7.84

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