THE MECHANISM OF AROMATIC SULPHONATION.

SUMMARY

of a thesis
presented in accordance with
the regulations for the Ph.D.
Degree of the University of
Glasgow by

WILLIAM CLARKE HORNING, B.A.

The University, Glasgow. May, 1953.

It has recently been shown that in aromatic nitration and halogenation in strongly acid media the substituting agent is a positively charged ion. Although a similar attacking entity has been postulated for sulphonation, little experimental work has been done on that line. The present research is a study of the kinetics of aromatic sulphonation in fuming sulphuric acid coupled with a study of the nature of the medium and the effect of changing acid concentration on the rate of nitration.

In Part I, the ionization constants of a series of aromatic nitro-compounds are given. These were measured by a spectrophotometric method and used to determine the value of Hammett's acidity function, H_o, for the range of acid concentrations from 99% H_2SO_4 to 36% SO_3 (108.2% H_2SO_4). It is shown that the change in pK_a between nitrobenzene and various meta- and para-substituted nitrobenzenes agrees very well with the theoretical values predicted from an electrostatic model. It is also demonstrated that the acidity function H_+, defined for the addition of a proton to a positively-charged base, is a few tenths of a logarithmic unit higher than the H_o scale in anhydrous sulphuric acid and that the difference decreases in media of higher ionic strength. Finally, a comparison is made of these results and available cryoscopic measurements.

In Part II, measurements on the kinetics of sulphonation of nitrobenzene, p-nitrotoluene and p-halogen-substituted phenyltrimethylammonium ions are given for the concentration range 4 to 40% SO_3. The reactions were followed spectrometrically and were for the most part carried out at 25°C. Various additional experiments were carried out to measure the effects of change of temperature and added bases.

In Part III, a study is made of the medium effects in nitration and partition in aqueous sulphuric acid and oleums. The rates of nitration of the p-halogen-substituted phenyltrimethylammonium ions measured in 89.8% H_2SO_4 are given. These are compared with the rate constants for sulphonation in oleum and the effects of steric interference are quite markedly demonstrated. Measurements on the nitration of p-bromophenyltrimethylammonium ion in different oleums are also tabulated. The rate rises with increasing strength of SO_3, the greatest rise being in the region of 100 to 102% H_2SO_4. Finally, the results of a study made of the activity coefficients of p-nitrochlorobenzene and 2,4-dinitrochlorobenzene in concentrated sulphuric acid are given. These results are satisfactorily explained in terms of the Debye theory of salt effects, the added salt being hydroxonium bisulphate.

In the Discussion, the mechanism of sulphonation is postulated as a two-step reaction involving attack by a sulphonium ion ($SO_2.^+OH$) with the formation of an intermediate, followed by the subsequent loss of a proton. Quoted results of isotopic experiments give support to this formulation. It is postulated that the proton loss is faster than the reverse reaction, allowing the results to be interpreted in terms of the bimolecular reaction

$$Ar.H + SO_2.^+OH \rightleftharpoons ArSO_3H + H^+$$

It is shown that the concentration of sulphonium ions is given by the expression

$$\log SO_2.^+OH = -J - \log \frac{f_B . f_{SO_2.^+OH}}{f_{BH^+}} + \text{const}$$

where $J = H_0 - \log p_{SO_3}$ and the f's are the activity coefficients of the sulphonium ion, the basic indicator used to measure H_0 and its conjugate acid. The experimental first order rate constants for sulphonation are plotted against the J-function giving straight lines with slopes slightly greater than theoretical value of unity. This is attributed to the increase of an activity coefficient term which was assumed to be constant in a first approximation and a parallel is drawn with the results of the nitrations. The constants of the Arrhenius equation are evaluated for nitrobenzene and the p-chlorophenyltrimethylammonium ion.

THE MECHANISM OF AROMATIC SULPHONATION

Being a Thesis
presented in accordance with
the regulations for the
Ph.D. Degree of the
University of Glasgow,

by

WILLIAM CLARKE HORNING, B.A.(Toronto).

The University, Glasgow. May, 1953.

Acknowledgments

The author wishes to express his thanks to Dr. J.C.D. Brand who supervised this work, to Professor J.W. Cook, F.R.S. for his interest in the research and for the facilities offered in his department, and to the late Dr. J.C. James for his assistance in the conductivity measurements.

CONTENTS

Page

INTRODUCTION

THE PRESENT STATE OF THE THEORY OF AROMATIC SUBSTITUTION

EXPERIMENTAL

PART I. DETERMINATION OF THE ACIDITY FUNCTION H_o OF FUMING SULPHURIC ACID

MATERIALS

MEASUREMENTS

PART II. KINETICS OF SULPHONATION IN FUMING SULPHURIC ACID

Page

PART III. MEDIUM EFFECTS IN NITRATION AND PARTITION IN CONCENTRATED SULPHURIC ACID AND OLEUM

Nitration of p-Halogen-substituted Phenyltrimethyl ammonion Ions in Sulphuric Acid

Nitration in Fuming Sulphuric Acid

Activity Coefficients of p-Chloronitrobenzene and 2,4-Dinitrochlorobenzene in Sulphuric Acid

DISCUSSION

INTRODUCTION

INTRODUCTION.

THE PRESENT STATE OF THE THEORY OF AROMATIC SUBSTITUTION.

Position of Attack in Substitution

The replacement of hydrogen in benzene and its derivatives by a large number of substituents, constitutes one of the most important sets of reactions in organic chemistry. Very soon after Kekulé's postulation of the hexagonal structure for benzene, it became apparent that the point of replacement was determined by substituents already present in the ring. The first accurate quantitative results were obtained by Holleman (1), who determined the relative amounts of the isomerides formed in the substitution of benzene carrying one or more substituents. He showed that the proportions of the isomerides, while affected by the nature of the attacking reagent, temperature and catalysts, are primarily determined by the substituents present. These may be classified as ortho- and para-, or meta-directing and he arrived at the well known sequence:

op-directive: $OH > NH_2 > \text{Halogen} > CH_3$

m-directive: $COOH > SO_3H > NO_2$

Scheffer (2) used the temperature dependence of the isomeric proportions to show that the difference in velocity of substitution was due only to the energy of activation at the position, and that the frequency factors were very nearly the same.

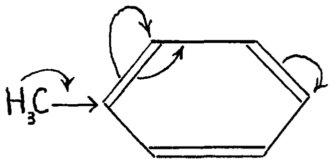
Although Holleman appreciated that op-substitution corresponded to activation and m-substitution to deactivation, it was not until Ingold and his collaborators (3) carried out competitive nitrations between benzene and its derivatives that a quantitative comparison could be made between the reactivities of the various positions in C_6H_5X relative to one of the positions in unsubstituted benzene. These results and others have given the experimental basis for the present electronic theory of substitution. This theory has developed out of two papers by Allen, Oxford, Robinson and Smith (4) and Ingold and Ingold (5).

It is customary to divide substituting reagents into two main classes, homolytic and heterolytic. The former takes over one of the electrons of the original bond, the latter may take over both or neither of the original electron pairs, and is accordingly classified as electrophilic (electron seeking) or nucleophilic (seeking a nucleus). It is readily apparent that aromatic substitution is in general electrophilic in nature. Considering nuclear chlorination as an example,

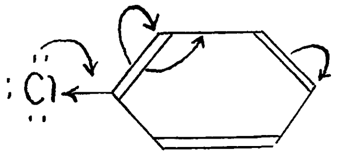
$$R - H + Cl - Cl = RCl + HCl,$$

it is evident that the chloride ion retains the original covalent pair of the chlorine molecule and the entering atom seeks additional electrons. Similar conclusions may be reached in the case of sulphonation or nitration and it follows that the most reactive positions in the benzene ring will be those having the highest electron density.

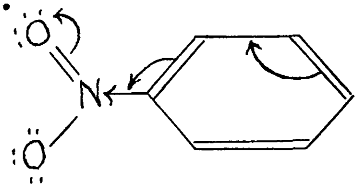
Returning to the influence of the substituents already present in the ring, it is possible to differentiate between two main effects, called by Ingold, the inductive effect (I) and the tautomeric effect (T). We can illustrate these by reference to three compounds, toluene, chlorobenzene and nitrobenzene.



In toluene, the straight arrow from the methyl group indicates a general inductive shift along the σ-bonds activating the ortho position and to a lesser degree the meta and para. By means of the mesomeric effect, shown by the curved arrows, the charge is transferred through space particularly to the ortho and para positions. The net result is general activation, but much less at the meta than at the ortho and para positions, in agreement with the experimental results. Since the methyl group is electron releasing, both effects are lumped together and it is characterized as a +I substituent.



Chlorobenzene is a -I, + T substituent. By the inductive mechanism, shown by the straight arrow, chlorine pulls electrons from the ring. The tautomerism acts in the opposite direction, one of the electron pairs of the chlorine approaching and interacting with the π -electrons of the ring. If the -I effect is greater than the +T, all positions would be deactivated, the ortho and para to a much lesser extent. This is in agreement with the experimental evidence.



Nitrobenzene is a typical example of a meta-directing compound. The nitrogen withdraws electrons from the ring giving a -I effect. The π -electrons of the nitro-group conjugate with the electrons in the ring removing them primarily from the ortho and para positions giving a mesomeric effect (-T). The overall influence is one of deactivation, the ortho and para positions being deactivated more than the meta. As a consequence the nitro-group is meta-directing and, generally, other meta-directing groups may be treated analogously.

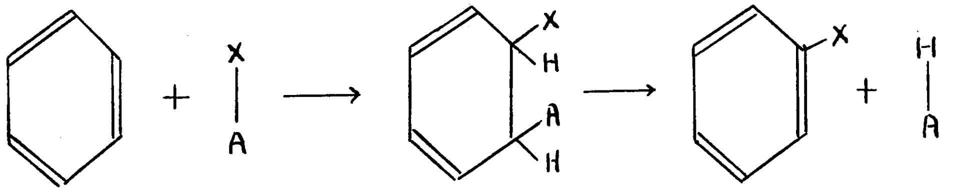
The inductive and mesomeric effects represent permanent polarizations and are manifest in dipole moment and equilibrium measurements. In addition Ingold postulates two parallel polarizations acting on the demand for an attacking heterolytic reagent. He summarizes the polar effects in the following way (6):-

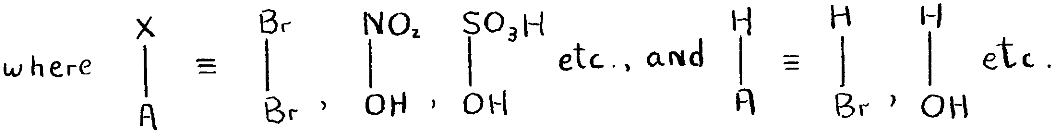
Electron mechanism	polarization	polarizability
General Inductive (I)	Inductive	Inductomeric
Tautomeric (T)	Mesomeric	Electromeric

These mechanisms explain the known facts quite adequately and predict the ease and direction of the electrophilic attack quite well. However, until quite recently very little was known about the mechanism of the replacement or the actual attacking agents and much work remains to be done on these lines.

The Mechanism of Replacement.

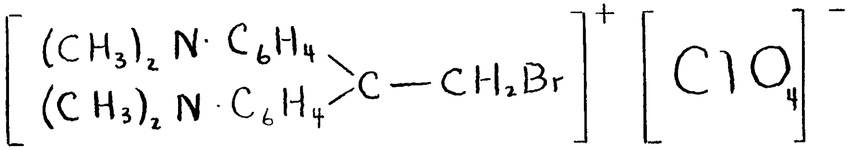
The first pictures of substitution drew an analogy between the three main types of substitution, nitration, sulphonation and halogenation, and the well known addition reactions of an olefin. The mechanism was postulated as follows:-





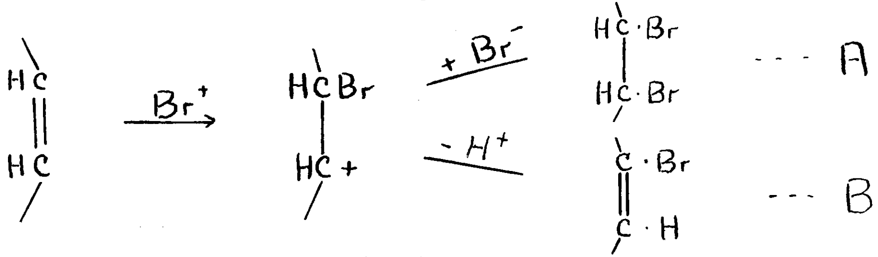
where $\overset{X}{\underset{A}{|}} \equiv \overset{Br}{\underset{Br}{|}},\ \overset{NO_2}{\underset{OH}{|}},\ \overset{SO_3H}{\underset{OH}{|}}$ etc., and $\overset{H}{\underset{A}{|}} \equiv \overset{H}{\underset{Br}{|}},\ \overset{H}{\underset{OH}{|}}$ etc.

However, it was later shown that neither HNO_3 nor H_2SO_4 reacts with olefins in this manner and the pure acids are apt to give esters (7), so that the basis for the analogy lacks experimental support. Pfeiffer and Wizinger (8), working on 1,1,di-(p-dimethylaminophenyl)-ethylene, were able to isolate an intermediate perbromide, the cation of which forms a stable perchlorate.



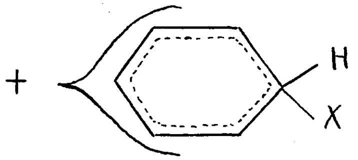
$$\left[\begin{matrix}(CH_3)_2N\cdot C_6H_4\\(CH_3)_2N\cdot C_6H_4\end{matrix}>C-CH_2Br\right]^+\left[ClO_4\right]^-$$

In the light of this they postulated bromine addition as an electrophilic attack by the bromine cation (Br^+) followed either by the addition of a bromide ion or the loss of a proton according to the following scheme:-



In the case of aromatic substitution the intermediate forms a mesomeric system and only proton elimination is possible (route B). The proposed mechanisms for sulphonation (9, 10,11) and nitration are similar.

It therefore seems probable that aromatic substitution proceeds through a more or less stable intermediate of the type proposed by Pfeiffer and Wizinger (8).



Both the entering group and the hydrogen atom are connected to the carbon by electron pair bonds and the latter has four sp^3 bonds. The four remaining π-electrons form a positively charged pentadienate system. In the case where the entering group bears no charge the complex would be unchanged. In nitration and bromination, Melander (12) has shown the existence of such an intermediate by the absence of an isotope effect, and although sulphonation does show a retardation for a heavier isotope, the formation of a similar intermediate is not excluded.

The Identity of the Substituting Agent

The true natures of the electrophilic reagents have only recently been demonstrated and much work remains to be done. The results show clearly that aromatic substitution in acid media is due to a positively-charged cation or its hydrated form.

The proof that the nitronium ion, (NO_2^+), is the nitrating agent under the usual conditions has been fully demonstrated (13,14,15,16). It is possible that the hydrated form of the cation ($H_2O.NO_2^+$) is also operative in more dilute acid solutions and with sufficiently reactive molecules.

In halogenation the situation is not quite as clear. Derbyshire and Waters (17) and Shilov and Kaniaev (18) have shown that the bromine cation or its hydrated form, (Br^+ or $H_2O.Br^+$), are the most powerful brominating agents known. They state that the action of the usual catalysts is to provide positive bromine. However, in neutral or hydroxylic solvents and with sufficiently reactive aromatic molecules, molecular bromine and hypobromous acid are the reactants. This is in accord with the most recent views of de la Mare and Robertson (19) on halogen addition to unsaturated compounds.

Hinshelwood and his co-workers (20,21,22,23) have studied the kinetics of sulphonation of a number of aromatic compounds using nitrobenzene as a solvent. With sulphur trioxide they found that the reaction was second order with respect to SO_3. It follows either that the attacking reagent is the dimer,

$$2SO_3 \rightleftharpoons S_2O_6 \;; \quad ArH + S_2O_6 \longrightarrow ArHS_2O_6$$

$$\longrightarrow ArSO_3H.SO_3 \rightleftharpoons ArSO_3H + SO_3$$

or that under the experimental conditions a second sulphur trioxide molecule is required as a proton accepter.

$$ArH + SO_3 \rightleftharpoons ArH.SO_3 \quad ; \quad ArH.SO_3 + SO_3 \longrightarrow$$
$$Ar.SO_3^- + SO_3H^+ \rightleftharpoons ArSO_3H + SO_3.$$

Working with sulphuric acid they found that the reaction is much slower than with sulphur trioxide and postulated a mechanism involving SO_3H^+ as the sulphonating agent.

Martinsen (24) and Cowdrey and Davies (25) have studied the sulphonation p-nitrotoluene in oleum and concentrated sulphuric acid. Both suggest sulphur trioxide as the sulphonating agent in oleum and the latter found that the results in 92% to 100% H_2SO_4 could best be explained by postulating SO_3H^+ as the sulphonating agent. However, Brand (26) has restudied the problem and has shown that they had neglected the ionization of the nitrotoluene. He demonstrated that the reaction in oleum is consistent with the postulation of SO_3H^+ for the attacking entity.

The mechanism of sulphonation is far from clear. It is not difficult to see the similarities between the various processes of substitution but the analogy cannot be carried too far. Among the differences that are immediately apparent is the reversibility of sulphonation at fairly low temperature as exemplified by the transformation of naphthalene-1-sulphonic acid into the 2-isomer. Another point is that the product is a strong acid while aromatic nitro- and halogen-substituted products are not. It is clear that greater knowledge of reaction mechanism in solution is dependent on more precise information about the nature of the reaction medium and the trend of current investigation is in this direction.

Nature of the Work Undertaken

This work was undertaken to clarify the mechanism of sulphonation in oleum. This entailed a parallel study of the reaction medium and the effect of its change upon other reactions, notably nitration.

Part I is concerned with a determination of the ionization constants (pK_a's) of a series of aromatic nitro-compounds which are ionized in concentrated sulphuric acid and oleums. From these determinations Hammett's acidity function, (H_0), is calculated for the range of oleums in which the studies on sulphonation were carried out. It is shown that the relative values of the acidity constants can be satisfactorily calculated from an electrostatic model.

Part II is a study of the kinetics of sulphonation of nitrobenzene, p-nitrotoluene and the p-halogen-substituted phenyltrimethylammonium ions in oleum. The determinations were made over the concentration range 4% - 40% SO_3 and in the case of nitrobenzene at a number of temperatures.

Some experiments were carried out to determine the effect of added K_2SO_4 on the rate of sulphonation of nitrobenzene.

Part III is an attempt to obtain more information about the reaction medium and steric effects.

The p-halogen-substituted phenyltrimethylammonium ions were nitrated in 89.8% H_2SO_4 and their rates of nitration compared with those of sulphonation in oleum. The relative rates show the effects of steric interference in the reactions.

The rate of nitration of p-bromophenyltrimethylammonium ion was measured in different oleums. Both nitration and sulphonation are similar processes and it was hoped that the kinetic effect due to change in concentration of sulphonating agent could be separated from that due to the changing physical properties of the medium.

Finally a study was made of the activity coefficients of p-nitrochlorobenzene and 2:4-dinitrochlorobenzene in the range 90% to 100% H_2SO_4. These results are intelligible if considered as a primary salt effect, the salt being hydroxonium bisulphate.

The experimental results are followed by a discussion of the mechanism of aromatic sulphonation in oleum in the light of this and previous work.

EXPERIMENTAL

Part I

DETERMINATION OF THE ACIDITY FUNCTION, H_0 OF FUMING SULPHURIC ACID.

EXPERIMENTAL.

PART I:

DETERMINATION OF THE ACIDITY FUNCTION Ho OF FUMING SULPHURIC ACID.

General Introduction

The acidity function was first defined by Hammett (27) as a quantitative measure of the proton donating properties of strong acids. He defined the acidity function by the equation:

$$H_o = -\log \frac{a_{H^+} \cdot f_B}{f_{BH^+}} \quad \ldots\ldots\ldots\ldots\ldots \quad (I)$$

This depends only on the hydrogen ion activity and on the activity coefficients of a neutral base and its conjugate acid. He also showed that ratios of the form $f_B . f_{CH^+} / f_{BH^+} . f_C$ have the value unity, indicating that f_B/f_{BH^+} is the same for all bases, and hence the acidity function is independent of the base used in measuring it.

By combining (I) with the equation:

$$pK_a = -\log \frac{a_{H^+} \cdot a_B}{a_{BH^+}} \quad \ldots\ldots\ldots\ldots\ldots \quad (II)$$

$$= -\log \frac{a_{H^+} \cdot f_B}{f_{BH^+}} - \log \frac{C_B}{C_{BH^+}}$$

We get:

$$H_o = pK_a + \log \frac{C_B}{C_{BH^+}} \quad \ldots\ldots\ldots\ldots\ldots \quad (III)$$

Therefore if we know the pKa of a colorimetric indicator, by adding it to the acid solution and determining the ratio C_B/C_{BH^+}, the value of the acidity function may be determined for the range of acidity over which the indicator is ionized. Conversely, the pKa of a basic indicator may be obtained from the acidity function and the ionization ratio. By stepwise determination of the acidity function and pKa's of weak organic bases, Hammett and Deyrup (28) and Hammett and Paul (29) have determined the acidity function of sulphuric acid solutions from dilute aqueous acids up to 100% sulphuric acid.

All mononitro-derivatives of benzene behave as weak bases in concentrated fuming sulphuric acids. As a class they are the weakest bases about which there is any quantitative information. Their basicity was discovered cryoscopically by Hantzsch in 1908 (30) and approximate ionization constants have been evaluated by this method (31,32). Their ultra-violet absorption spectrum is modified radically in a characteristic way by the transfer of a proton (33). Hence they were chosen as appropriate bases for this study.

Both cryoscopic and optical methods have limitations. The former can be used in sulphuric acid containing a trace of water or sulphur trioxide, but it is limited to a narrow range of solvent concentration. This was unfavourable, as bases weaker than nitrobenzene are only slightly ionized in such media. The optical method has free choice of medium composition, but suffers from the disadvantage that it is necessary to know the spectrum of the conjugate ion. The very feebly basic trinitro compounds are too incompletely ionized even in the strongest medium available to be quantitatively treated. In addition, the physical effects of a change of medium on the spectra present quite serious difficulties. These disadvantages are offset by the access to information about the acidic properties of the range of media where sulphonation of aromatic compounds is most frequently carried out.

The characteristic spectral effect of the addition of a proton to an aromatic nitro-compound is the movement of the principal absorption band between 6000 and 9000 cm.$^{-1}$ towards lower frequencies, simultaneously increasing the value of ε_{max}. nearly twice (Figures 1 to 6). Weaker bands on the long wave-length side are also displaced and may remain prominent or disappear depending on the other substituents and their positions in the molecule. The main band obviously represents the same transition in the ion and the uncharged molecule both of which have the same electron configuration. The suggestion has been made by Doub and Vanderbelt (34) and by Platt (35) that the transition corresponds to the formally forbidden 50,000 cm.$^{-1}$ ($'A_{1g}$ - $'B_{1u}$) transition in benzene.

However, there are several features of the spectra which indicate that this transition is localized in the nitro-group. Firstly, the addition of a second and third nitro-group increases the intensity of the base absorption by a factor of almost exactly two and three respectively. Secondly, the ionizations of 2,4-dinitrotoluene and 2,4-dinitrochlorobenzene are similar, but both quite different from that of a simple mono-nitro compound, for the absorption at the maximum of the base falls only to a value equal to that of the unionized mono-nitro compounds. Thus we have for the di-nitro compounds two absorption bands, at about 3500 Å and about 2650 Å, one due to the ionized, the other to the unionized nitro-group. The fundamental difference can be easily seen from the absorption curves (Figs. 5, 6).

This gives fairly conclusive evidence for the interpretation of the transition as being localized in the nitro-group. This suggestion has been previously advanced by Matsen and Hastings to account for the photochemical formation of nitrosobenzene (36). This means that the transition becomes $a_2.b_2$, $({}^{e}A_1 - {}^{e}B_1)$, allowed by the selection rules with polarization perpendicular to the symmetry axis and in the plane of the molecule. Mixed transitions between the upper filled ($2a_2$) level of the nitro-group and the unfilled benzene levels may account for the weaker bands on the long wave-length shoulder of the nitro-band, where two and possibly more weak bands can be observed. These transitions are allowed by the symmetry rules but weakened by small overlap.

MATERIALS

Preparation of Media

The oleums were prepared, in an all-glass Pyrex apparatus, by distilling sulphur trioxide from B.D.H. oleum into a weighed flask containing a known weight of B.D.H. "AnalaR" concentrated sulphuric acid, until the desired strength was approximated. The media so prepared were then transferred into storage flasks with ground glass cones at the neck and ground glass caps as stoppers. The oleums were prepared and stored in 500 cc. to one litre quantities. Under these conditions even the strongest media maintained a remarkably constant composition over periods up to six months or longer. Oleums stronger than 30% sulphur trioxide showed a tendency to crystallize due to the rather wide temperature fluctuations of the atmosphere and to overcome this they were stored in a thermostat at 25°. By this means, oleums containing up to 41% SO_3 could be maintained and used without freezing occurring.

Sulphur dioxide absorbs in the region 3100 - 2500 Å (37). It was eliminated by either of two methods, both of which seemed efficient. The sulphur dioxide in the oleum was oxidized by adding chromium trioxide and allowing to stand 24 hours before distillation, or by adding potassium persulphate and warming gently for an hour before distilling.

In the latter method the strength of the oleum should not exceed 30% sulphur trioxide for the complete removal of sulphur dioxide. Under these conditions the prepared media showed no absorption traceable to sulphur dioxide.

Aqueous acids were prepared by diluting B.D.H. 'AnalaR' sulphuric acid (99.1% - 98.8%) with the requisite amount of water. As the quantities were of the order of 2 to 2½ litres, they were stored in Winchesters. The strength varied little over periods of three months or longer.

Analysis of Concentrated Sulphuric Acid

The oleums were analysed by titration with water using Brand's method (38). A weighed amount of oleum in a glass stoppered flask was cooled in an ice bath to below 10°. Distilled water was added from a 5 cc. micro-burette graduated to read to 0.01 ml. After each addition the fume was absorbed by shaking and cooling. Fuming diminished rapidly near the end of the titration. The end point was marked by a cessation of fuming at the surface of the liquid, when a jet of air was blown into the flask. For the detection of last traces of fume it was necessary to carry out the titrations in bright daylight.

Aqueous acids were analysed by adding a weighed excess of an oleum of known strength to a weighed amount of acid and titrating the excess sulphur trioxide as above.

The strengths of aqueous acids were also determined by diluting a weighed portion with water and titrating with standard alkali or potassium iodate. The various methods gave the same values to within 0.1%, the limits of accuracy of the volumetric glassware. The water titration, however, gave results which agreed to within 0.02% (of the strength as sulphuric acid).

Since the acidity changes rapidly with composition in the range 99% to 100% sulphuric acid, the strengths of these media were checked independently by a conductometric method.

Conductivity of Sulphuric Acid

The conductivities of the various acids were measured at (25 ±.005°) in a U-shaped cell with bright platinum electrodes using the screened A.C.-bridge of James and Knox (39). The measuring frequency was 1000 - 3000 cycles per second and the measurements were steady and reproducible for several days. The cell was standardized with Jones and Bradshaw's (40) 0.1 m. potassium chloride solution.

The existing conductivity measurements of sulphuric acid (41, 42, 43, 44) are in very poor agreement with one another. As a result it was first necessary to determine the conductivity over the range from 99.20% to 100.40% sulphuric acid. For this the special apparatus shown in

Figure 7 was constructed. It consisted of a U-shaped conductivity cell using the same bright platinum electrodes. A large capillary tube led from the bottom of the cell to a 100 cc. reservoir. A stoppered semi-microburette, with a glass tube joining top and bottom to maintain equality of pressure, was fitted to the reservoir. A side-arm fitted with a glass stop-cock led from just above the reservoir through successive drying trains of phosphorous pentoxide and sulphuric acid to a nitrogen cylinder. The tops of both sides of the conductivity cell were joined through a stop-cock to another similar train free to the atmosphere. The apparatus was immersed in a constant temperature bath during the measurements.

A weighed amount of oleum, strength by water titration 100.295%, was put in the reservoir. The burette was filled with 90.07% sulphuric acid. The apparatus was assembled and allowed to come to equilibrium in the thermostated bath. By regulation of the nitrogen pressure the oleum was forced into the conductivity cell. The conductivity was measured and the acid was allowed to run back into the reservoir. This was repeated over various intervals of time during two days giving the same results for the resistance as Table 1 shows.

Table 1.

Oleum 130.93 g.

Filling	Time	Resistance Ohms.	Filling	Time	Resistance
1	0	790.4	4	3 hrs. 15 min.	790.3
2	10 min.	790.3	5	3 hrs. 25 min.	790.4
3	20 min.	790.3 -	6	2 days	790.5 - 790.54
	held in cell 3 hr. & 5 min.	790.1			

The constancy of the cell having been demonstrated, the addition of 90.07% sulphuric acid was started. A measured volume was added to the oleum in the reservoir to the cell until the resistance remained constant for two successive fillings, indicating that mixing and equilibration of temperature were complete. When the additions had covered the desired range of concentrations, the apparatus was removed from the thermostat, washed with conductivity water and dried. The cell constant was determined using Jones and Bradshaw's 0.1 m. potassium chloride solution. The specific conductivity was plotted against the volume of 90.07% acid and the minimum taken as 100.00% sulphuric acid. The results are tabulated in Table 2.

The values of the conductivity (Figure 8) agree, within a few units %, with those of Bergius (42) for fuming acids, and Lichty (43) for aqueous acids, but there is no

Table 2. Conductivity of Sulphuric Acid:

(temp. 25±.005°, cell constant = 14.208)

Added H_2SO_4 90.07%	D_4^{20} 1.815	Total H_2SO_4	Successive fillings resistance					Specific conductivity $ohm^{-1}cm^{-1}$	H_2SO_4 (90%) from 100%	%H_2O
ccs.	g.	g.		ohms					g.	g.
0.0	0.0	130.93	790.5	790.54				.017973	-4.10	-0.311
0.54	0.98	131.91	-	873.3	876.6$_5$			.016263	-3.12	-0.235
1.07	1.94	132.87	-	983.9	985.4			.014419	-2.16	-0.161
1.62	2.94	133.87	-	-	1154.1			.012311	-1.16	-0.086
1.98	3.59	134.52	1257	1291.1	1292.7	1293.2		.010987	-0.51	-0.038
2.28	4.14	135.07	1306	1372.9	1373.1			.010347	0.04	0.003
2.57	4.66	135.59	1258	1263.9	1262.1			.011257	0.56	0.041
3.11	5.65	136.58	912	892.8	888.2	885.7	885.4	.016047	1.55	0.113
3.67	6.66	137.59	673	-	660.1			.021524	2.56	0.185
4.37	7.93	138.86	511	507.1	506.0			.028074	3.83	0.274
5.06	9.19	140.12	422	418.83	418.58			.033943	5.09	0.360
5.88	10.67	141.60	355	358.0	357.84			.039705	6.57	0.461
6.68	12.11	143.04	318	317.4	317.26			.044783	8.01	0.556
7.86	17.28	145.21	279.5	277.97	277.50			.05120	10.18	0.695

agreement with Reinhardt (44) or Hantzsch (4).

Recently Giauque and Kunzler (45) have shown that the minimum of conductivity does not coincide exactly with the maximum freezing point. Assuming that the latter represents 100.00% sulphuric acid, the minimum of conductivity occurs at 99.996%. This slight correction is of too small a magnitude to make any difference to these results. Since this work was completed Gillespie and Wasif (88) have published the results of a new conductivity determination. Their values are about 1% higher than these in more aqueous acids but for the most part the agreement is excellent, the value of the specific conductivity of H_2SO_4 at 25°, 0.1034 ohm^{-1} cm^{-1} agreeing with their value of 0.1033 ohm^{-1} cm^{-1} to within the limits of experimental error of the two methods.

The values of the conductivities were used to determine the concentrations of the acids used. They were all made from an oleum of known strength by adding a calculated volume of water from a microburette. The agreement between the concentrations determined from the conductivity and water titration is very satisfactory (Table 3) although the former method is the more accurate.

Table 3. Comparison of the acid analysis:

% water		% water	
Water titration	Conductivity	Water titration	Conductivity
-0.30	-0.31	0.15	0.15
-0.20	-0.21	0.25	0.26
-0.11	-0.11	0.34	0.35
-0.10	-0.09	0.45	0.47
-0.04	-0.03	0.56	0.58
0.04	0.04	0.70	0.73
0.04	0.05		

Preparation of Nitro-compounds

Nitrobenzene was prepared according to the directions of Masson (46) from fractionally crystallized benzene, freezing point 5.53°. The nitrobenzene was frozen to constant melting point, 5.71 - 5.72°. It was almost colourless and did not perceptibly darken on standing several years in a glass-stoppered flask.

m-Nitroaniline, m.p. 110.8°, crystallized several times from aqueous ethanol, gave bright yellow needles. 2,4-Dinitrotoluene, m.p. 70.5°, was crystallized from aqueous ethanol. *p*-Chloronitrobenzene, m.p. 83.0°, was obtained in white cubes by recrystallization alternately from 50% nitric acid and aqueous alcohol. p-Nitrotoluene, m.p. 52.2°, was recrystallized in white needles from ethanol, 2,4-di-Nitrochlorobenzene, m.p. 51.5°, was recrystallized in pale yellowish-white cubes from ethanol.

The nitro-compounds were dissolved in 90% sulphuric acid at concentrations of from 10^{-2} to 10^{-3}m., and stored in a refrigerator in bottles with inverted stoppers. No change in concentration of acid, or reaction of nitro-compounds was detectable over periods of six months.

MEASUREMENTS

General

The extinction coefficients, ϵ (cm. mole $l^{-1})^{-1}$, were measured with a 'Unicam' photoelectric spectrophotometer, with an absorbing path of 1 cm. 'AnalaR' sulphuric acid is transparent at wavelengths above 2000 Å. Oleums absorb at the shorter wave-lengths (47). With a set minimum of 50% solvent transmission, 36% oleum is transparent above 2400 Å and 65% oleum above about 2850Å. Sulphur dioxide absorbs in the region 3100 - 2500Å (37) and was removed as described in the preparation of the media.

All the solutions were made up by weight from the stock solutions of nitro-compound in 90% sulphuric acid and the required oleum. The dilution of the oleum was calculated and found to be negligible in most cases, but was corrected for. The parent oleum was used as the reference solvent. Oleums were prepared in the range 0 - 36% and 60 - 65% of "free" sulphur trioxide. The intermediate acids crystallized too easily at room temperature.

The temperature was not accurately controlled and results refer to $18^{\circ} \pm 2^{\circ}$. Dependence of ε on temperature was small over this range. Value of $(1/\varepsilon)\,(d\varepsilon/dt)$ for p-nitrotoluene in 99.9% sulphuric acid was +0.0005 at 3650Å (48).

Determination of the ionization ratios

The ratio of concentration of base to ion was calculated from the equation (IV)

$$\frac{(\text{Base})}{(\text{Ion})} = \frac{(\varepsilon_{\text{ion}} - \varepsilon)}{(\varepsilon - \varepsilon_{\text{base}})} \qquad \text{(IV)}$$

Aside from the experimental error in the measurement of ε, which is relatively small, there are two major sources of error which are as follows:-

(I) The spectrum of the ion (ε_{ion}) was difficult to determine. There is little doubt that nitrobenzene and p-nitrotoluene are completely ionixed in 36% oleum. They both sulphonated at appreciable speeds and the value of ε was extrapolated to the time of mixing. p-Chlorobenzene is incompletely ionized in 36% oleum and the reference spectrum was determined in 64.5% oleum. 2,4-Dinitrotoluene, 2,4-dinitrochlorobenzene and the m-nitroaniline cation were not completely ionized even in the strongest medium.

(II) The increase of concentration of sulphur trioxide shifts the reference spectrum of base and acid towards longer wave-lengths (49). There is little alteration of the shape or value of ε max. The effect of this shift can be minimized, either by working at the wave-length of the absorption maximum where $d\varepsilon/d\lambda$ is smallest, or, since all curves should theoretically have one point in common, by shifting them until all are coincident at one point. However, it is questionable if a simple medium effect causes the major shift in strong oleum (65%) since the formation of $Ar.NO_2SO_3$ as well as $Ar.NO_2H^+$ is possible.

Measurements were made at the maximum of the ion as the change of ε is greatest and all media were highly transparent. The values of the ionization ratios were plotted as a function of medium composition (Figure 9) and the acidity function of the fuming sulphuric acid (Figure 10) determined from this group of almost parallel curves. The numerical values are based on the figure pKa = -10.34 for the p-toluylnitracidium ion in slightly aqueous media. This is consistent with the H_0 data obtained by Hammett and Deyrup (28) with the indicator 2,4,6-trinitroaniline.

The results are all self-consistent and their relative accuracy quite high. However, in view of the long stepwise determination of H_0, it is probable that the absolute accuracy is low. The results are collected in Tables 4 to 10. Individual cases are dealt with separately.

Nitrobenzene The extinction coefficients at 3650Å were reported by Brand (33). Since the wavelength falls on a sloping part of the curve, the error in the ε's due to displacement is appreciable in more concentrated acids, and they have been redetermined at the maximum of absorption of the ion (Table 4). Nitrobenzene reacted at higher concentrations and the absorption was extrapolated to the time of mixing.

p-Nitrotoluene The pKa of p-nitrotoluene was determined by Brand (33) at 3650Å. As this is on a sloping part of the absorption curve it was redetermined at the maximum of the ion, 3750Å - 3800Å. Since p-nitrotoluene was used as a basis for determining the acidity function in oleum from Hammett and Deyrup's and Hammett and Paul's figures (28, 29) in aqueous acids, the analyses of the media from 99.25% to 100.40% sulphuric acid were checked both by water titration and conductometrically. The results (Table 5) are 0.06 of a unit higher than the previous values. The values in the oleum are extrapolated to the time of mixing because sulphonation occurs in the more concentrated media.

<u>p-Chloronitrobenzene</u> The original conclusion (Brand, 33) that ionization was complete in 25% oleum has been revised. The pK_a (Table 6) obtained using the value of the extinction coefficient at 3900Å is 0.08 unit higher than the previous value. To clarify the medium effect in strong oleums the acidity constant was also calculated from the extinction coefficient of the maximum absorption of the base at 3050Å (Table 6a). Because the change of the extinction coefficient on ionization is only half that at the maximum of the ion, the measurements are not as precise. This latter value is in agreement with Brand's figure. The difference, which is not explicable if ionization is incomplete in 65% oleum, can be explained, if in the stronger oleums the medium effect is more complex than in more dilute media. It would appear that in addition to the shift of wavelength there is an increase in the extinction coefficient, leading to values of ε_{ion} which are several units percent too high. The effect is also found with <u>m</u>- and <u>p</u>-fluoronitrobenzene and <u>m</u>-chloronitrobenzene and appears to be general (48). This increase in intensity has the largest effect on the ionization ratio calculated from the maximum of absorption of the ion. However, this exaltation of intensity would also increase the absorption of the ion at the wavelength of the base maximum giving values of log ($^{Base}/Ion$) which were too low. Also,

calculation from H_o and pK_a shows that ionization is about one percent incomplete in 65% oleum, which would partially compensate for this exaltation. It is notable that in weaker oleums where the value log ($^{Base}/Ion$) is relatively insensitive to changes of ε ion, the two tables are in good agreement. This coupled with the fact that the precision is greater at the maximum of the ion than the maximum of the base, tends to show that the former is correct to within at least 0.02 of a unit and leads to its adoption.

m-Nitroaniline cation From the curves in Figure 4 the second stage ionization of *m*-nitroaniline must be incomplete in 65% oleum. Rough calculations from approximate values of pK_a and H_o for 65% oleum indicate about 60% ionization. Because the NH_3^+ group is remarkable for its small influence on the ultra-violet spectra, the value of ε ion is assumed to be the same as that for the phenylnitracidium cation. The support for this, aside from the excellent agreement obtained (Table 7), is as follows:-

(1) The values of ε_{max} of the *m*-nitroaniline cation and unionized nitrobenzene are very nearly equal in concentrated sulphuric acid.

(2) Doub and Vandenbelt (34) have shown that in aqueous solution several pairs of compounds differing by a *p*-NH_3^+ group gave values of ε max varying by only 1000

units on the average. The cation always absorbed more strongly. However, a difference of this magnitude would only raise the ionization ratio by less than 0.05 units and in the m-series closer agreement is likely.

A plot of ε against $(\varepsilon - \varepsilon_{base})/h_o$ gives the same value for ε_{ion} to within a few hundred units, and confirms the assignment.

<u>2,4-Dinitrotoluene and 2,4-Dinitrochlorobenzene</u> Both bases are incompletely ionized in the strongest media. In order to calculate pK_a and ε_{ion} the ionization ratio (IV) is rewritten as:

$$\frac{(\text{Base})}{(\text{Ion})} = \frac{\varepsilon_{ion} - \varepsilon}{\varepsilon - \varepsilon_{base}} = \frac{K_a}{h_o} \quad ; \quad H_o = -\log h_o$$

$$\text{hence} \quad \varepsilon_{ion} - \varepsilon = K_a \left\{ \frac{\varepsilon - \varepsilon_{base}}{h_o} \right\} \qquad (V)$$

The factor $\left\{ \frac{\varepsilon - \varepsilon_{base}}{h_o} \right\}$ is tabulated in Tables 8 and 9 and K_a and ε_{ion} are evaluated by the method of least squares. The values of ε_{ion} calculated in this manner gave consistent results when used for determination of pK_a by means of H_o and the ratio $(\varepsilon_{ion} - \varepsilon)/(\varepsilon - \varepsilon_{base})$.

Table 4. Ionization ratios and acidity constant of nitrobenzene

$\varepsilon_{ion} = 15700$ $\varepsilon_{base} = 900.$

Medium		ε mean	$\varepsilon - \varepsilon_{base}$	$\varepsilon_{ion} - \varepsilon$	Log	H_o	pK_a
H_2SO_4%	SO_3%	(λ 3500 Å)			(base/ion)		
93.3	-	900	-	-	-	-	-
95.65	-	975	75	14730	2.29	-	-
96.84	-	1008	108	14690	2.13	-	-
98.20	-	1167	267	14530	1.74	-	-
98.98	-	1223	323	14480	1.65	9.61	11.26
99.32	-	1350	450	14350	1.50	9.79	11.29
99.54	-	1411	511	14290	1.45	9.94	11.39
99.84	-	2260	1360	13440	1.00	10.29	11.29
99.95	-	3430	2530	12270	0.69	10.60	11.29
99.96	-	3870	2970	11830	0.60	10.70	11.30
100.28	1.25	8970	8070	6730	-0.08	11.40	11.32
100.54	2.40	10675	9775	5025	-0.29	11.56	11.27
100.76	3.38	11340	10440	4360	-0.38	11.63	11.25
100.99	4.40	11570	10670	4130	-0.41	11.70	11.29
101.63	7.25	12530	11630	3170	-0.59	11.86	11.27
102.40	11.0	13350	12450	2350	-0.72	12.06	11.34
103.15	14.0	14050	13150	1650	-0.90	12.20	11.30
103.16	14.0	14000	13100	1700	-0.89	12.20	11.34
104.70	20.9	14700	13800	1000	-1.14	12.45	11.31
105.33	23.7	15300	14400	400	-1.56	-	-
106.74	30.0	15700	-	-	-	-	-
107.33	32.6	15640	-	-	-	-	-
108.49	37.7	15700	-	-	-	-	-

mean: 11.30±.03.

Table 5. Ionization ratios and acidity constant of p-nitrotoluene

Medium		ε mean	$\varepsilon - \varepsilon_{base}$	$\varepsilon_{ion} - \varepsilon$	Log	$-H_o$	$-pK_a$
H_2SO_4%	SO_3%	(λ3750-3800Å)			(base/ion)		
93.53	-	1460	-	-	-	-	-
96.65	-	2245	785	16845	1.33	8.97	10.30
98.98	-	4370	2910	14720	0.70	9.60	10.30
99.27	-	5380	3920	13710	0.55	9.75	10.30
99.42	-	5750	4290	13340	0.49	9.85	10.34
99.53	-	6400	4940	12690	0.41	9.93	10.34
99.65	-	7360	5900	11730	0.30	10.04	10.34
99.73	-	8200	6740	10890	0.21	10.14	10.35
99.85	-	10100	8640	8990	0.02	10.32	10.34
99.94_5	-	13700	12240	5390	-0.36	10.69	10.33
99.95	-	13760	12300	5330	-0.36	10.70	10.34
100.04	0.18	16370	14910	2720	-0.74	11.09	10.35
100.09	0.40	16670	15210	2420	-0.80	11.16	10.36
100.11	0.49	16810	15350	2280	-0.83	11.19	10.36
100.21	0.93	17280	15820	1810	-0.94	11.32	10.38
100.31	1.38	17650	16190	1440	-1.05	11.41	10.36
102.16	9.60	19050	17590	40	(-3.64)	(11.99)	10.35
103.43	10.8	19090	17630	-	-	-	-

Mean 10.34±.02.

Table 6. Ionization ratios and acidity constant of p-chloronitrobenzene

$\varepsilon_{ion} = 22200$ $\varepsilon_{base} = 390$

Medium		ε_{mean} (λ3850-3900Å)	$\varepsilon - \varepsilon_{base}$	$\varepsilon_{ion} - \varepsilon$	Log (base/ion)	$-H_0$	$-pK_a$
H_2SO_4%	SO_3%						
97.8	-	390	-	-	-	-	-
99.56	-	724	334	21475	1.82	-	-
99.79	-	1053	653	21160	1.51	-	-
100.19	0.84	8425	8035	13775	0.24	11.32	11.56
100.53	2.36	10920	10530	11280	0.03	11.55	11.58
100.61	2.71	11400	11010	10800	-0.01	11.58	11.57
100.89	3.95	12650	12260	9550	-0.11	11.67	11.56
101.47	6.53	14650	14260	7550	-0.28	11.82	11.54
101.64	7.28	14850	14460	7350	-0.29	11.85	11.56
102.24	9.95	16090	15700	6110	-0.41	12.00	11.59
102.42	10.70	16250	15860	5950	-0.42	12.05	11.62
104.21	18.75	18400	18010	3800	-0.68	-	-
105.47	24.3	19450	19060	2750	-0.84	-	-
107.33	33.0	20090	19700	2110	-0.97	-	-
114.2	63.0	22200	-	-	-	-	-

Mean: 11.57 ± 0.03.

Table 6a. Ionization ratios and acidity constant of p-chloronitrobenzene at maximum of base

$\varepsilon_{ion} = 685$ $\varepsilon_{base} = 10350$

Medium		ε_{mean}	$\varepsilon_{base} - \varepsilon$	$\varepsilon - \varepsilon_{ion}$	Log (base/ion)	$-H_o$	$-pK_a$
H_2SO_4%	SO_3%	(λ 3050Å)					
97.8	-	10350	-	-	-	-	-
99.56	-	10350	-	-	-	-	-
99.79	-	10340	-	-	-	-	-
100.19	0.84	6895	3455	6210	0.26	11.32	11.58
100.21	0.93	6890	3460	6205	0.25	11.33	11.58
100.61	2.71	5210	5140	4525	-0.06	11.58	11.52
100.89	3.95	4540	5810	3855	-0.18	11.67	11.49
101.47	6.53	3590	6760	2905	-0.37	11.82	11.45
101.64	7.28	2960	7390	2275	-0.51	11.86	11.35
102.24	9.95	2880	7470	2195	-0.53	12.00	11.47
102.42	10.70	2540	7810	1855	-0.62	12.05	11.43
104.21	18.75	1530	8820	845	-1.02	12.38	-
105.47	24.3	1380	8970	695	-1.11	12.56	-
107.30	33.0	685	-	-	-	-	-
114.2	63.0	(685)	-	-	-	-	-

Mean: 11.49 ± 0.07

Table 7. Second ionization constant m-nitroaniline

Medium		ε_{mean} (λ 3200 - 3250Å)	$\varepsilon - \varepsilon_{base}$	$\varepsilon_{ion} - \varepsilon$	Log (base/ion)	$-H_o$	$-pK_a$
H_2SO_4%	SO_3%						
99.1	-	600	-	-	-	-	-
101.26	5.60	1035	435	14065	1.51	11.75	13.26
102.73	12.1	1600	1000	14400	1.16	12.10	13.26
104.24	18.8	2570	1970	13430	0.83	12.38	13.21
105.85	26.0	3690	3090	12310	0.60	12.61	13.21
107.30	32.4	5500	4900	10500	0.33	12.85	13.18
114.5	64.5	12050	11450	3950	-0.46	13.67	13.21

$16000 = \varepsilon_{ion}$

Mean: 13.21 ± .03.

Table 8. Ionization constant of 2,4-dinitrotoluene

Medium		ε mean					
H_2SO_4%	SO_3%	(λ 3300-3350Å)	$\varepsilon - \varepsilon_{base}$	$-H_o$	$h_o \times 10^{-11}$	$\frac{\varepsilon - \varepsilon_{base}}{h_o} \times 10^{11}$	
99.0	-	1700	-	-			
101.64	7.3	3400	1700	11.89	7.76	219	$-pK_a = 12.6_8 \pm 0.05$
102.74	12.2	4170	2470	12.12	13.2	187	
104.23	18.8	5870	4170	12.39	24.6	170	
105.46	24.3	7060	5360	12.58	38.0	141	
106.07	27.0	7790	6090	12.68	47.9	127	
107.30	32.4	9220	7520	12.85	70.8	106	
114.2	63.0	12550	10850	13.7	501	21.6	

ε_{ion} = 13,800

Table 9. Ionization constant of 2,4-dinitrochlorobenzene

Medium		ε mean					
H_2SO_4%	SO_3%	(3360-3700Å)	$\varepsilon - \varepsilon_{base}$	$-H_o$	$h_o \times 10^{-11}$	$\frac{\varepsilon - \varepsilon_{base}}{h_o} \times 10^{11}$	
90.7	-	350	-	-	-	-	$-pK_a = 13.5_5 \pm 0.05$
99.1	-	350	-	-	-	-	
101.25	5.55	480	130	-	-	--	
102.73	12.1	920	570	12.12	-	-	
104.25	18.8	1480	1130	12.39	24.6	43.8	
105.10	22.7	2100	1750	12.53	33.9	50.0	
107.35	32.6	4000	3650	12.86	72.4	49.7	
114.2	63.0	12300	11950	13.7	501	23.8	

ε_{ion} = 19,600

DISCUSSION

The values of the acidity constants for a number of substituted arylnitro-compounds are collected in Table 10. The pK_a's refer to a standard state in water, since in the determination of the H_o function it is assumed that in a particular medium (excluding media of low dielectric constant) the ratio f_b/f_{BH^+} (the f's referring to an ideally dilute, aqueous solution) has the same value for all bases. Therefore the K_a's are thermodynamic dissociation constants, $K_a = \frac{a_{H^+} \cdot a_B}{a_{BH^+}}$, the activities referring to a standard state in water. Therefore, although the measurements are made in sulphuric acid, the activity coefficients automatically allow for any change in solvent. The assumption involved is supported by the demonstration that the acidity constant is independent of the solvent used for its determination (28, 29). However, this has not been verified in $H_2SO_4 - H_2O$ mixtures more concentrated than 70% H_2SO_4.

The absolute values are probably not accurate to better than 0.3 to 0.5 of a unit, owing to the long stepwise determination of the acidity function. However, the relative acidity constants are probably precise to within better than 0.05 of a unit, and are limited by the difficulty in correcting for the physical effects of the medium.

The new values of H_o are higher in oleum than those published by Brand (38). The difference is small in weak oleums but increases with rising strength of acid and is due to the reassessment of the extinction coefficients of the ions at their maxima. This minimizes the medium effect, which is greatest over the middle range of oleum concentration where the value of the acidity function changes slowly with composition.

The change of the acidity function, H_o, with composition is shown in Figure 10. The analogy to the pH change in aqueous solution is immediately obvious. This analogy is natural since water, a strong base, is "neutralized" by disulphuric acid, a weak acid, in solvent sulphuric acid. The change of acidity is measured with colorimetric indicators and the 'neutral' point is at the composition H_2SO_4.

The values of the acidity constants (pK_a's) for a number of nitro-compounds are tabulated in Table 10. The Table is from the paper by Brand, Horning and Thornley (48). The values in column four for the acidity constant relative to the nitrobenzene are calculated by the method of Kirkwood and Westheimer (50,51) and Sarmousakis (52). The organic molecule is treated as a uniform cavity of low dielectric constant, approximated by an oblate spheroid. This is surrounded by a medium of high dielectric constant and the field of the dipole acts partially through the medium and partially

Table 10. Influence of substituents on the acidity constant of nitrobenzene

Substituent	Acidity constant $-pK_a$	$\Delta pK = pK_a^o - pK_a$	
		obs.	calc.
p - Bu^t	10.2 *	-1.1	-0.27
p - Me	10.34	-0.95	-0.13
m - Me	10.84*	-0.45	-0.21
H	11.29	0.0	0.0
p - F	11.50*	0.21	0.58
p - Cl	11.57	0.28	0.50
m - F	12.15*	0.86	0.87
m - Cl	12.15*	0.86	0.83
m - NO_2, p - Me	12.6_8	1.4	1.4
m - NO_2	-	-	1.5
m - NH_3^+	13.2_1	1.9	1.8
m - NO_2, pCl	13.5_5	2.3	2.0
3,5-di-NO_2, 4-Me and 3,5-di-NO_2	too weak to be measured.		

---

*Brand et al. (48).

through the cavity. The acidity constant relative to nitrobenzene is the equilibrium constant of equation (VI) where $\Delta pK = \log K$ and is given by equation (VII)

$$X.C_6H_4.NO^{+}.OH + C_6H_5.NO_2 \xrightleftharpoons{K} X.C_6H_4.NO_2 + C_6H_5.NO^{+}.OH \qquad (VI)$$

$$\Delta G^{o} = -2.3kT.\ \Delta pK = \frac{e\mu_{\xi}\cos(\mu_{\xi}, r)}{r D_{\xi}^{2}} + \frac{e\mu_{\phi}\cos(\mu_{\phi}, r)}{r D_{\phi}^{2}} \qquad (VII)$$

where μ_{ξ} and μ_{ϕ} are the components of the substituent dipole μ along the radius and tangent of the focal circle respectively, and D_{ξ} and D_{ϕ} are the corresponding "effective" dielectric constants, determined by the dielectric constants of the solvent and cavity, r being the distance from the dipole to the acid group. The net electrostatic work is assumed to be equal to the standard free energy change. Other details of the calculation are given in the paper (48).

The results are quite satisfactory for m-derivatives. However, the results for p-fluoro- and p-chloronitrobenzene are much lower and this is due to the resonance between the substituents, with a greater resonance energy for p-fluoro- than for p-chloro. This type of resonance is well known from the exaltation of the dipole moment (53, 54).

The anomalous values for the p-alkyl substituents are clearly not due to hyperconjugation alone. They probably arise from solvent solute interaction which has previously been assumed to be constant. The variations although small are of the same order as the electrostatic energy differences. Calculation of the entropies of the ionization of p-fluoronitrobenzene and p-nitrotoluene (48) show that the latter has a ΔS^{o} of 3-4 cal.deg.$^{-1}$ mole^{-1} higher than the expected small negative value, whereas the former is small if not zero as expected. Therefore, in the case of p-nitrotoluene it is no longer justifiable to equate ΔG^{o} with the net electrostatic work.

The pK_a value of m-nitroaniline was evaluated using the H_o scale. This is equivalent to the assumption that the dipolar positive ion (m-$NH_3^+.C_6H_4.NO^+OH$) behaves in the same way as the ion of a univalent electrolyte: or, in other words, the ratios log (fB/f_{BH^+}) and log.$(f_{B^+} / f_{BH^{++}})$ are taken to be equal. This assumption is permissible in aqueous solutions of high ionic strength (55, 56, 57, 58).

The application to sulphuric acid and oleums, where the ionic strength is uncertain, is hypothetical. It is, however, possible to calculate the ratios of the activity coefficients on the basis of spherical symmetry of charge and estimate if in a real case it will be serious to neglect this factor. From the definition of the acidity function (equation I)

$$H_+ = -\log \frac{a_{H^+} f_{B^+}}{f_{BH^{++}}} \quad ; \quad H_o = -\log \frac{a_{H^+} f_{B^+}}{f_{BH^+}}$$

$$H_o - H_+ = \log \frac{f_B}{f_{BH^+}} \cdot \frac{f_{BH^{++}}}{f_{B^+}} \qquad \text{(VIII)}$$

Assuming inverse square law attraction and Maxwell-Boltzmann distribution for the ionic atmosphere, the solution of the Poisson equation leads to the following expression for the potential, $\psi_j(r)$, at a distance r from the j'th ion in a medium of dielectric constant D:

$$\psi_j(r) = \frac{z_j e}{Dr} - \frac{z_j e}{D} \cdot K \qquad \text{(IX)}$$

where $K = \frac{4\pi e^2}{DkT} \cdot \sum_{j=1}^{s} n_j z_j^2$

and z is the charge on the j'th ion, k the Boltzmann constant, e the electronic charge and T the absolute temperature (59). The first term on the right is the potential due to the ion itself and the second term is that due to its ionic atmosphere. Following the general Debye-Hückel development (see Harned and Owen, 59), but retaining both terms for the potential, we obtain the expression for the activity coefficient of the j'th ion,

$$\ln f_j = \frac{z_j^2 e^2}{2DkTa_j} - \frac{z_j^2 e^2}{2DkT} \cdot \frac{K}{1+Ka_j} \qquad \text{(X)}$$

where a_j is the distance of the closest approach to the j'th ion. This equation is merely a combination of two other well known ones: the first term being the primary medium effect derived by Born (60) and is independent of concentration, the second, the usual Debye-Hückel expression for the change in activity coefficient with ionic concentration. Referred to a standard state in water, dielectric constant D_o, the expression becomes:

$$\ln f_j = \frac{z_j e^2}{2kTa_j}\left\{\frac{1}{D} - \frac{1}{D_o}\right\} - z_j^2\left\{\frac{\pi N e^6}{1000(kT)^3}\right\}^{\frac{1}{2}} \cdot \sqrt{w} \times \left[\frac{1}{D^{\frac{3}{2}}} \cdot \frac{1}{1 + \frac{35.57\,\mathring{a}_j}{(DT)^{\frac{1}{2}}} \cdot \sqrt{w}} - \frac{1}{D_o^{\frac{3}{2}}} \cdot \frac{1}{1 + \frac{35.57\,\mathring{a}_j}{(D_oT)^{\frac{1}{2}}}\sqrt{w}}\right] \qquad \text{(XI)}$$

where $W \equiv \sum_{j=1}^{s} c_j z_j^2$ is the total "ional concentration".

Consider the medium 100.0% H_2SO_4. The maximum concentration of any of the indicator ions is 10^{-4} m/l and the maximum ional concentration due to dissociation of indicator is 5×10^{-4}. However, there is a large contribution from the self dissociation of the solvent. Gillespie (61), from the rounding of the freezing point curve, has estimated that the total ional concentration is 0.043 molal, or 0.0792 m/l. Hence the contribution due to dissolved base is negligible.

Taking Gillespie's value for the ional concentration and assuming the radii (r) of B, BH^+, B^+ and BH^{++} are all equal, and equal to a_j, we obtain by substituting (XI) in (VIII):

$$H_o - H_+ = -\frac{e^2}{2.3kTa_j}\left\{\frac{1}{D} - \frac{1}{D_o}\right\} + \frac{2}{2.3}\left(\frac{\pi Ne^6}{1000\,k^3}\right)^{\frac{1}{2}} .079 \times \left[\frac{1}{(DT)^{\frac{3}{2}}} \cdot \frac{1}{1 + \frac{35.5\overset{o}{a}_j\sqrt{.079}}{(DT)^{\frac{1}{2}}}} - \frac{1}{(D_oT)^{\frac{3}{2}}} \cdot \frac{1}{1 + \frac{35.5a_j\sqrt{.079}}{(D^oT)^{\frac{1}{2}}}}\right] \tag{XII}$$

Introducing the values $D_o = 80$, $D = 110$ (62), $a_j = 4\overset{o}{A}$, and remembering that T refers to 18°C, we obtain from this equation:

$$H_o - H_+ = 0.28 - 0.03 = 0.25$$

$$\text{or } H_+ = H_o - 0.25 = -11.2.$$

This agrees with the observation of Michaelis and Granick (63) that the acidity scale established with multipolar bases is a few tenths of a unit more negative than Hammett's H_o. The above calculation containing only ratios of the f_j's, minimizes the effect of non-electrostatic factors. It also refers to a spherical symmetry of charge and magnifies the effect for unsymmetrically charged ions. Finally, the two factors, due to the ion and its atmosphere, are opposite in sign and in media of greater ional concentration the difference between the scales lessens considerably. Hence, as it is about half the uncertainty of the absolute value of the acidity function, we conclude that it could be safely neglected.

The value of ΔpK of m-nitroaniline in Table 10, col.4 is calculated from the equation (52)

$$2.3\ kT.\quad \Delta\ pK = \frac{e^2}{rD_{effective}}$$

in which the symbols have the same meaning as equation VII and the parameters r and $D_{effective}$ are evaluated by similar conventions.

Comparison with Cryoscopic Results

The only results available for comparison are the cryoscopic measurements of Gillespie (32). These are expressed as basic dissociation constants:

$$K_b = \frac{[ArNO^{+}.OH]\,[HSO_4^-]}{[ArNO_2]}$$

where the brackets refer to concentrations. Retaining the former assumption that the ratio f_B/f_{BH^+} is equal for all bases in a single medium then log (K_b^o/K_b) has the same thermodynamic significance as Δ pK in Table 10. The base strengths are in the same order, but quantitative agreement is poor. This is not due to temperature effects which are negligible.

Table 11. Comparison of Δ pK from cryoscopic and spectrometric measurements

Base	log $(K_b{}^o/K_b)_{9^oC}$	pK_{18^oC}
$p\text{-}CH_3.C_6H_4.NO_2$	-0.84	-0.95
$C_6H_5.NO_2$	(0.0)	(0.0)
$m\text{-}H_3\overset{+}{N}.C_6H_4.NO_2$	0.31	1.9_2
$CH_3.C_6H_2(NO_2)^3$	0.63	3.0

It is more instructive to compare Gillespie's calculated ν-factors with the ν-factors obtained from the spectrometric results (Table 12). In the latter case the ν-factor is measured directly. It is apparent that the cryoscopic results are higher and the concentration differences would have the effect of making them higher still.

Table 12. Number of solute particles produced per mole of solute (ν-factor)

Solute	Medium		$-H_o$	ν-Factor from	
	H_2O molality	H_2SO_4 %		F.P. (0.1m.)	Spectrum (10^{-3}-10^{-4}m.)
$p.MeC_6H_4NO_2$	0.061	99.89	10.45	1.63*	1.56
$C_6H_5.NO_2$	0.059	99.89	10.45	1.26	1.13
$m.NH_3^+.C_6H_4.NO_2$	0.052	99.91	10.54	2.10	2.00
$C_7H_5(NO_2)^3$	0.074	99.87	10.40	1.09	1.00

*Slight variation with concentration.

In the calculation of K_b it is factor $\nu -1$ (or $\nu -2$ in the case of m-nitroaniline) that is important and it is apparent that the best agreement is obtained with p-nitrotoluene where this factor is relatively large. In the cases of m-nitroaniline and trinitrotoluene, there was no spectral evidence of the ionization of the nitro-group in anhydrous sulphuric acid. As the limit of spectrometric detection is about 0.05g.-ion %, the degree of ionization of these bases is much less than the analysis of the cryoscopic data indicates. The reason for this is that the calculation of ν-factors from the freezing point depression involves assumptions of considerable weight. First, all solutions are assumed to be ideal. Secondly, all solutes are assumed to be solvated; therefore, the osmotic coefficient may differ from unity unless the molalities are calculated with respect to 'free' solvent. Finally, solutions of electrolytes are assumed to require a correction for the influence of added HSO_4^- ions on the dissociation of water (equation XIII), and the autoprotolysis of the solvent (equation XIV):

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad \text{(XIII)}$$

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad \text{(XIV)}$$

The effect of these corrections is at once apparent. We take the cases of m-nitroaniline and trinitrotoluene as examples and quote from Gillespie's results (32).

Table 13. Freezing points of trinitrotoluene and m-nitroaniline in H_2SO_4.

Molality		F.P.	ν-Factor			
H_2O	T.N.T.		Solvation number of			
0.074	-	9.691°	0*	1	3	4
"	0.0222	9.554	1.12	1.09	1.06	1.04
"	0.0385	9.437	1.12	1.09	1.05	1.03
"	0.0537	9.337	1.12	1.09	1.04	1.02
"	0.0721	9.215	1.12	1.09	1.04	1.02
"	0.0963	9.064	1.11	1.07	1.02	1.00

Molality			ν - Factor	
H_2O	m-nitro aniline	F.P.	Corrected**	Uncorrected**
0.052	-	9.959	-	-
"	0.01045	9.834	2.08	1.98
"	0.02536	9.654	2.11	1.99
"	0.03191	9.569	2.10	2.02
"	0.03712	9.509	2.10	2.02

$K_f = 5.98$ (deg.mole^{-1} Kg.)

* The reaction of water with sulphuric is written

$$H_2O + 2H_2SO_4 \rightleftharpoons H_3\overset{+}{O}.H_2SO_4 + HSO_4^-$$

except in this column where solvation of H_3O^+ is omitted.

** This refers to the supposed effect of added HSO_4^- ions on the equilibria XIII and XIV.

In the case of *m*-nitroaniline if the correction for added HSO_4^- ions is dropped, the ν-factor falls from 2.10 to 2.00. The question whether *m*-nitroaniline is basic or not depends entirely upon a correction to the freezing point. It is basic but not to any detectable degree in anhydrous sulphuric acid.

In the case of trinitrotoluene the correction for added HSO_4^- ions is negligible, as no ionization is detectable in anhydrous sulphuric acid. However, there are real differences between sulphuryl chloride and trinitrotoluene (64). If we retain the convention that sulphuryl chloride is a perfect non-electrolyte, it means that the osmotic coefficient (g) of a dilute solution of trinitrotoluene is 1.12. If we must assume that all solutions are ideal, then g-1 must represent the solvation correction. From Table 13 we see that this is achieved if the solvation number is 4 or 5, which is not impossible since there are three nitro-groups.

The fact of primary importance is that from cryoscopic data (thermodynamically), we may obtain g or i or f, but not ν. Therefore, until all the processes occurring in the solutions are better understood, small differences of ν from an integer cannot be quantitatively interpreted.

Part II

KINETICS OF SULPHONATION IN FUMING SULPHURIC ACID.

PART II:

KINETICS OF SULPHONATION IN FUMING SULPHURIC ACID

General Introduction

Several methods are available for the rate determinations. The earliest due to Martinsen (24) is dependent on the fact that the unsulphonated material is quantitatively nitrated at low temperatures. The excess nitric acid may be determined with ferrous sulphate. Due to the need for appreciable concentrations of aromatic material there is some decomposition due probably to local heating during mixing. There is also the possibility of non-reversible oxidation during the addition of nitric acid.

Cowdrey and Davis (25) determined the rate of sulphonation of p-nitrotoluene by extraction of the unreacted material with benzene. They estimated the nitrotoluenesulphonic acid by addition of excess titanous sulphate and back titrating with ferric alum.

Brand (26) used Martinsen's method, determining the excess nitric acid by potentiometric titration with ferrous sulphate. He also did some preliminary rate measurements using a dilatometer to measure the change of volume of the reactants. The change of volume was found to be difficult to measure due probably to the high viscosity of media. Another method explored was the change in light absorption during reaction. With aromatic nitro-compounds there is a twenty-fold decrease of absorption at 3600Å on sulphonation.

The latter method was chosen because of several apparent advantages. The light absorption of the system can be measured continuously without withdrawing samples. The absorption can be measured with a considerable degree of accuracy. The concentration of aromatic reagents is of such an order (10^{-4} m.), that first order coefficients may be directly determined. Also, due to the small concentration of organic reagent, decomposition due to heat of mixing is minimized. Although the method is of general application, wherever there is an approximately ten-fold change in absorption between reagents and products, this does not always occur at easily measurable wave-lengths. Therefore, an indirect method which quantitatively introduced a nitro-group into any unsulphonated reagent was employed for p-halogen-substituted phenyltrimethylammonium salts.

p-Nitrotoluene and the p-halogen-substituted phenyltrimethylammonium ions give 100% m-substitution. In the case of nitrobenzene it is claimed that sulphonation is over 98% in the meta-position (65) but there are good reasons for suspecting this figure since in nitration Pounder and Masson (88) found that nitrobenzene gave 90.1% of the m-nitrated product. In addition, Brand and Rutherford (89) have shown that the phenyltrimethylammonium ion gives 78% of the m-sulphonated product. Therefore it would be surprising if nitrobenzene sulphonated exclusively in the m-position and more experimental investigation is required on this point. However, the main product is m-nitrobenzenesulphonic acid and the actual proportions of the various isomerides are not vital to the analysis of the kinetics.

Materials The preparation, analysis and storage of the oleums have been described in Part I. Solutions of oleums containing potassium sulphate were prepared by adding a weighed amount of dried B.D.H. 'AnalaR' potassium sulphate to a known weight of oleum.

Nitrating media were prepared by adding a weighed amount of dried B.D.H. 'AnalaR' potassium nitrate to a known weight of sulphuric acid. Where the actual medium strength was not required to be known, as in the quantitative nitration of unsulphonated material, sufficient was added to a Winchester of 85% sulphuric acid to make it approximately 0.1 m. in potassium nitrate. In this case the same medium sufficed for all experiments.

The preparation of nitrobenzene, p-nitrotoluene and p-nitro-tert-butylbenzene is described in Part I.

p-Fluorophenyltrimethylammonium methyl sulphate was prepared from p-fluorodimethylaniline and excess dry methyl sulphate in acetone. It was recrystallized from acetone to which sufficient ethanol had been added to just dissolve the salt at the boiling point, giving white needles, m.p. 104.5°. Found: C, 45.1; H, 5.9; N, 5.4%. $C_{10}H_{16}O_4NFS$ requires: C, 45.3; H, 6.1; N, 5.3%.

p-Chloro-, p-bromo-, and p-iodophenyltrimethylammonium methyl sulphate, prepared from the corresponding dimethylanilines in the same manner as the fluorine analogue, had:

Formula	Found %			Requires %			
	C	H	N	C	H	N	M.P.
$C_{10}H_{16}NClS$	42.5,	5.7,	5.2	42.6,	5.7,	5.0	143.5°
$C_{10}H_{16}NBrS$	36.9,	4.6,	4.3	36.8,	4.9,	4.3	139.5° (also 122°)
$C_{10}H_{16}NIS$	32.4,	4.3,	3.9	32.2,	4.3,	3.75	184.5° dec.

Apparatus For the aromatic nitro-compounds, the reactions were carried out in the specially made optical cells, (depth 1 cm.), fitted with side-arms and ground stoppers. The cells were fixed in a carriage which fitted into a small tank through which water circulated at 25°. The tank was provided with glass windows and sat in the cell compartment of a Hilger 'Spekker' absorptiometer. The light source of the absorptiometer was a mercury arc lamp fitted with suitable filters to give a radiation of 3650Å only.

The small tank was supplied by siphon from a large thermostat tank. The water was returned to the main tank by means of a small electric pump. The rate of flow was of the order of one gallon per minute. There was a slight cooling in the transfer from the reservoir to the small tank which was compensated for by slight heating in the water pump, so that the main thermostat remained at equilibrium very readily. As this meant that small tank was about 0.02° lower in temperature than the main supply, the thermostat was easily adjusted to give the required temperature in the small tank. Temperatures were constant to within ±0.01°C. The cells and apparatus are shown in Figure 11.

Measurements The aromatic nitro-compounds (nitrobenzene, p-nitrotoluene, p-nitro-tert-butylbenzene) were dissolved in 94% sulphuric acid and stored in a refrigerator in small bottles with inverted ground stoppers. The above compounds do not react in this medium at low temperatures.

For reaction, 0.2 to 0.5 g. of the stock solution was weighed into a glass-stoppered flask and set in the large thermostat along with the appropriate oleum. When both had reached the reaction temperature they were withdrawn and 50 to 60 gm. of oleum was added to the solution. The reaction mixture was shaken vigorously and the optical cells were filled and placed in the small thermostat. After the temperature had been allowed to equilibrate readings of the optical density were taken over two half-reactions or more. The interval between readings varied from 30 secs. to 3 hrs. depending on the reaction rate. The reference density ($\ln I_0$) was either a cell filled with solvent or a piece of plate glass of approximately the same optical density. The reaction was allowed to proceed to constant optical density, giving the infinity absorption. No secondary or back reaction could be detected in any experiment. Because of this it was unnecessary to know the exact initial concentration of nitro-compound and the handling of reagents was speeded up. The whole sequence from removal of the oleum from the thermostat to the time of the first reading of absorption took less than five minutes. As a result the cooling during handling was negligible and the first reading could be taken two minutes after mixing.

The quaternary ammonium ions were weighed as the solid methyl sulphates. The medium was added directly to the solid in a stoppered flask which was shaken and placed in the thermostat. The heat of the mixture was negligible, due to the small amount of solid, (10^{-4} - 10^{-5} m/l.), added. Aliquot portions of the reaction mixture were withdrawn by pipette, and run into equal volumes of solutions of potassium nitrate in 89% sulphuric acid. The 2 cc. sampling pipettes were widened at the tips and one minute was allowed for drainage. The nitrating mixture was measured in a semi-microburette, allowing the same drainage time for each successive addition. Tests showed that both methods delivered volumes of solution reproducible to several parts per thousand by weight. The sulphonation was arrested and the unreacted material nitrated slowly but quantitatively, while the sulphonation product was unattacked. The samples were analysed for nitro-compound on a 'Unicam' spectrophotometer by means of the transmission of the solution in the spectral region (3200Å - 3400Å). The nitro-group absorbed strongly but the other constituents of the solution were transparent. The optical density was proportional to the concentration of the unsulphonated material and the first order rate constants could be evaluated directly.

In order to determine the region in which the quarternary nitro-compounds absorbed most strongly while the product of sulphonation was transparent, the absorption spectra of all the products was determined. Each of the compounds was quantitatively sulphonated and nitrated in the appropriate medium. No attempt was made to isolate the products. The spectra were determined directly from the reaction mixtures whose concentrations were known accurately. The results are shown in Figures 12, 13, 14. The iodo-compound decomposed immediately on addition to either oleum or nitrating mixture and gave free iodine and an entirely different resultant spectrum. As a result of this no sulphonation or nitration rates could be determined for it.

Attempts were made to sulphonate the p-tert-butyl-derivatives of both nitrobenzene and the phenyltrimethylammonium ion. In neither case was the reaction successful. Kinetics measurements gave extraneous results and numerous attempts to carry out the reactions on a quantitative scale yielded no recognizable product.

Results For a reaction in which the compounds obey Beer's law

$$\ln\left(\frac{I_o}{I}\right)_t = (\varepsilon_N C_N + \varepsilon_S C_S)\ell = \left[\varepsilon_S(C_{N_o} - C_N) + \varepsilon_N C_N\right]\ell \quad \ldots\ldots \text{(I)}$$

$$\text{and} \quad \ln\left(\frac{I_o}{I}\right)_{t_\infty} = \varepsilon_S C_{S_o}\ell = \varepsilon_S C_{N_o}\ell \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(II)}$$

where C_N, C_S, ε_N, ε_S are the concentrations and molar extinction coefficients of unreacted nitro-compound and sulphonation product. The I's are intensities and the subscripts refer to time.

Combining (I) and (II) we get

$$\ln\left(\frac{I_o}{I}\right)_t - \ln\left(\frac{I_o}{I}\right)_{t_\infty} = C_N(\varepsilon_N - \varepsilon_S) \quad \ldots\ldots\ldots\ldots\ldots \text{(III)}$$

since $\ell = 1$ for cells 1 cm. in depth.

For a first order reaction

$$\ln\left(\frac{C_{N_o}}{C_N}\right) = k_1 t$$

or converting to decadic logarithms

$$\log C_N = -0.4343\ k_1 t + \text{const.} \quad \ldots\ldots\ldots\ldots\ldots \text{(IV)}$$

Substituting (III) in (IV) gives

$$\log \left[\ln \left(\frac{I_o}{I}\right)_t - \ln \left(\frac{I_o}{I}\right)_{t_\infty} \right] = -0.434\ k_1 t + \text{const.} \ldots \text{(V)}.$$

For compounds which are ionized, only the unionized fraction reacts. Therefore, in the case of nitrobenzene and nitrotoluene, plotting $\log \left[\ln \left(\frac{I_o}{I}\right)_t - \ln \left(\frac{I_o}{I}\right)_{t_\infty} \right]$ graphically against time and determining the slope, the apparent velocity coefficients, k_a, were obtained (Figure 15). The true first order coefficients, k_1, were calculated from the ionization data (Part I) and refer to the concentrations of unionized nitrobenzene and p-nitrotoluene. These results are collected in Table 14 and refer to measurements at 25°. The rate constants determined by Brand (26) for p-nitrotoluene in weaker oleums are included for comparison. These results were obtained by Martinsen's method (24) of quantitative nitration of unreacted material and the titration of excess nitric acid by ferrous sulphate. The two sets refer to greatly differing initial concentrations of nitrotoluene, 10^{-1} to 10^{-2} molal for the analytical and 10^{-4} to 10^{-5} molal for the spectrometric method and the good agreement attests the validity of the two methods.

As the quantity of unsulphonated material was determined directly for the quaternary ammonium ions, the first order coefficients were evaluated by plotting the logarithm of the transmission, $\log \left[\ln \left(\frac{I_o}{I} \right)_t - \ln \left(\frac{I_o}{I} \right)_{t_\infty} \right]$, against the time. This was done for each of three wavelengths and the average value of the slope was taken. The rate constants are given in Table 15, each value being the mean of two determinations.

Additional experiments were performed on nitrobenzene and p-chlorophenyltrimethylammonium ion to determine the effects of temperature on the rate of reaction (Table 16). The Arrhenius activation energies were also determined and are given in the general discussion on the mechanism. For nitrobenzene only the apparent first order rate constants are available. Although the plots of log $(10^3 k_a)$ against $^1/_T$ showed the expected linearity the situation is complicated since the proportion of unionized nitrobenzene is also a function of the temperature. The calculation of the 'true' activation energy would require values of k_1 at the various temperatures of reaction. This necessitates use of the temperature variation of the extinction coefficient, since

$$\frac{d\left[\frac{B}{B + BH^+}\right]}{dT} = \frac{d\,\frac{\varepsilon_{ion} - \varepsilon}{\varepsilon - \varepsilon_{base}}}{dT} = -\frac{1}{\varepsilon_{ion} - \varepsilon_{base}} \cdot \left(\frac{d\varepsilon}{dT}\right)$$

where $[B] / [B + BH^+]$ is the fraction of unionized nitrobenzene and ε, ε_{ion} and ε_{base} have their usual meanings, it being assumed that the spectra of the ion and base are independent of temperature over small ranges.

Several additional experiments were performed on nitrobenzene in order to show the effect of added base on the rate of sulphonation and the mean values are collected in Table 17. The values of H_o and k_a in columns five and six are calculated in the following manner. It was assumed that, on ionizing, one mole of K_2SO_4 removed the same amount of SO_3 as two moles of water. The strength of the acid was corrected and the equivalent value of the acidity function taken. The calculated value of k_a was then read off the graph of log k_a against H_o. A comparison of columns four and six gives the effect of added base KHS_2O_7.

Further consideration of the results is given in the general discussion on the mechanisms involved.

Table 14. Influence of medium on the rate of sulphonation of nitro-compounds (25°)

Medium		10^3k_a (min^{-1})	$-H_o$	Fraction of union-ized nitro-compound	10^3k_1 (min^{-1})	-J
H_2SO_4%	SO_3%					
		Nitrobenzene	pK_a =	-11.30		
101.27	5.66	.305	11.78	0.248	1.23	11.89
102.77	12.3	1.07	12.12	0.131	8.16	12.62
104.77	21.2	3.16	12.48	0.062	51.0	13.37
106.07	27.0	5.29	12.67	0.041	129	13.83
106.75	30.0	7.25	12.75	0.034	211	14.04
107.33	32.6	8.60	12.84	0.028	370	14.25
108.22	36.6	12.8	12.96	0.020	640	14.54
		p-Nitrotoluene	pK_a =	-10.34		
100.48	2.14	2.49*	11.53	.0606	41.0	11.32
100.93	4.12	5.54	11.69	.0428	129	11.71
101.85	8.24	15.6	11.93	.0251	621	12.21
103.00	13.36	33.4	12.16	.0153	2180	12.74
103.54	15.76	45.3	12.27	.0117	3870	12.95
104.53	20.16	73	12.43	.00813	8980	13.29
103.43	15.25	43.9+	12.25	.0121	3630	12.90
104.70	20.9	70.6	12.46	.0076	9280	13.34
106.74	29.9	78.3	12.76	.0038	20600	14.04

*Analytical results, Brand (26).
+Spectrometric results.

Table 15. Influence of medium on the rate of sulphonation of p-Hal. $C_6H_4.NMe_3^+$ (at 25°)

Medium		10^3k_1 (min^{-1}) for			
H_2SO_4%	SO_3%	F	Cl	Br	-J
104.18	18.6	-	-	0.959	13.17
104.70	20.9	2.12	1.45	-	13.35
105.00	22.2	2.66	-	1.92	13.45
105.81	25.9	6.10	4.59	4.63	13.73
106.54	29.1	11.1	8.60	-	13.98
106.76	30.1	-	10.5	11.6	14.05
106.89	30.6	-	13.2	-	14.08
107.45	33.1	28.3	19.9	21.2	14.29
108.88	39.5	50.2	45.1	50.7	14.78
109.23	41.0	64.9	52.3	-	14.86

Table 16. Effect of temperature variation on the velocity of sulphonation

Medium		10^3k_a - nitrobenzene			
H_2SO_4%	SO_3%	20°	25°	30°	35°
102.77	12.3	-	1.07	-	3.17
104.77	21.2	-	3.16	5.53	9.39
105.85	26.0	2.65	-	-	-
106.00	26.7	-	-	9.44	16.5
106.07	27.0	2.95	5.95	-	-
108.22	36.6	6.97	12.8	20.7	35.7

		10^3k_1 - p-Cl.C_6H_4.NMe_3SO_4Me	
		25°	50°
106.75	30.1	10.5	70.5
106.89	30.6	13.2	94.0

Table 17. Effect of added base on velocity of sulphonation of nitrobenzene

Medium			10^3k_a exptl.	$-H_o$	10^3k_a calc.
H_2SO_4%	SO_3%	K_2SO_4 molality			
104.77	21.2	0.000	3.16	12.48	3.16
104.77	21.2	0.100	2.80	12.42	2.70
104.77	21.2	0.200	2.12	12.36	2.24

Part III.

MEDIUM EFFECTS IN NITRATION AND PARTITION IN CONCENTRATED SULPHURIC ACID AND OLEUM.

PART III:

MEDIUM EFFECTS IN NITRATION AND PARTITION IN CONCENTRATED SULPHURIC ACID AND OLEUM

Nitration of p-Halogen-substituted Phenyltrimethylammonium Ions in Sulphuric Acid

Introduction

The relative rates of nitration of organic compounds in sulphuric acid are not greatly influenced by changes of medium concentration in acids of the composition 90% H_2SO_4 or higher. In both nitration and sulphonation of *p*-halogen-substituted phenyltrimethylammonium ions the substituting agents, nitronium and sulphonium ions respectively, react quantitatively at the position ortho to the halogen atom. A comparison of the relative rates of sulphonation and nitration of a particular compound should therefore give some indication of the part played by the neighbouring halogen in the substitution.

The rates of nitration of the *p*-bromo- and *p*-chloro-derivatives in 89.8% H_2SO_4 have previously been determined by Brand and Paton (66). These experiments were repeated and the nitration of the *p*-fluoro- and *p*-iodo-compounds was included.

Velocity Measurements

The nitrations were carried out in the same optical cells, (depth 1 cm.), and using the same apparatus as that used for the measurements on the rate of sulphonation of nitrocompounds. The nitration velocities were determined from the rate of increase of optical density at 3650Å. One single medium (90.84% H_2SO_4) was used throughout all the experiments. Potassium nitrate was dissolved in this acid, the relatively low concentration of potassium hydrogen sulphate having no appreciable effect on the nitration velocity (67). The p-halogen derivatives of phenyltrimethylammonium ion were added directly to the nitrating mixture as the solid methyl sulphate, the initial concentration being 10^{-2} to 10^{-3} molar. The flask was shaken vigorously and the contents were poured into the optical cell. Heat of mixing was negligible and the first measurements could be taken two to three minutes after the initial addition. All compounds reacted smoothly with the exception of the p-iodo analogue which decomposed in sulphuric acid immediately upon addition. The reactions were invariably first order, the nitric acid concentration being in large excess. The absorption rose to a high constant value which did not change over several days, indicating that under the experimental conditions no secondary reactions occur.

Results

The first order coefficients were determined from the slope of $\log\left[\ln\left(\frac{I_o}{I}\right)_{t_\infty} - \ln\left(\frac{I_o}{I}\right)_t\right]$ against time by both graphical (Figure 16) and half-table methods, the two values agreeing to better than 1%. The results are collected in Table 18.

Table 18. Nitration of p-halogen substituted derivatives of $Ph.NMe_3^+$

Expt. No.	Medium H_2SO_4%	Medium KNO_3 moles/l	ArH	k_1 (min^{-1})	$k_2 = \frac{k_1}{[HNO_3]}$ ($min^{-1}.mole^{-1}$ l.)
92	90.84	.0835	p-F	.00522	0.0625
94	"	.0835	p-F	.00516	0.0618
97	"	.0840	p-Cl	.0287	0.343
99	"	.0840	p-Cl	.0289	0.344
93	"	.0835	p-Br	.0550	0.657
96	"	.0840	p-Br	.0565	0.660
95	89.8	.0824	p-Br	.0455	0.552
98	90.84	.0840	p-I	decomposed	

The values of k_2 in 89.8% H_2SO_4 determined by Brand and Paton (66) were 0.340 (p-Cl) and 0.71 (p-Br). The agreement is excellent for the p-chloro-compound but not as good for the p-bromo-derivative and duplication of the medium does not explain the difference. A comparison of the rates with those of sulphonation is given in the general section on the mechanism involved.

Nitration of Fuming Sulphuric Acid

Introduction

It became apparent in the investigation that increase of sulphonium ion concentration did not wholly explain the increase in reaction rate on going to stronger oleums. It was postulated that this variation was due to a medium effect of the solvent. In a medium such as sulphuric acid which provides both reagent and solvent it is fundamentally impossible to separate primary effects due to changing reagent concentration and secondary effects due to changing physical properties of the solvent. It was thought that a study of the effect of the same range of solvent concentration on the rate of nitration would give an indication of the sign of the medium effect on the speed of sulphonation.

Nitration is particularly well adapted for this purpose. The nitrating agent, either nitric acid or metal nitrate, dissolved in concentrated sulphuric acids and oleum with quantitative formation of nitronium ion according to the formal equations;

$$KNO_3 + H_2SO_4 \rightleftharpoons K^+ + HSO_4^- + HNO_3 \qquad (I)$$

$$HNO_3 + 2\ H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2\ HSO_4^- \qquad (II)$$

both equilibria lying quantitatively to the right (13, 67, 68, 69). Allowance must be made for the fact that each mole of added bisulphate immobilizes one mole of sulphonium ion. Therefore from equations (I) and (II), $KNO_3 \equiv 3\ HSO_4-$ and $HNO_3 \equiv 2\ HSO_4^-$ and a correction must be made for the drop in sulphonating agent due to the addition of potassium nitrate or nitric acid, (column 3, Table 19).

The formation of nitronium ion being complete, any change in the second order rate constant must be due to the changing physical properties of the medium. Therefore, since the mechanisms are similar both in kinetic form and type of attacking reagent, the magnitudes and signs of the medium effects should be the same. Although both sulphonation and nitration proceed with appreciable speeds in the media in question it is possible to distinguish between the two reactions.

Consider a sulphonation and a nitration occurring simultaneously and competing for a small amount of organic reactant. Then the rate or disappearance of organic reagent is given by the equation

$$-\frac{dC}{dt} = (k_n + k_s)\left[C\right]$$

where C is the concentration of organic material and k_n and k_s are the first order rate constants for nitration and sulphonation respectively.

Integrating we get:

$$\ln \frac{C_t}{C_o} = (k_n + k_s)\ t \qquad \text{..........} \quad \text{(III)}$$

Now $C_o = N_\infty + S_\infty$ and $C_t = N_t + S_t$, where N and S are the concentrations of nitrated and sulphonated products respectively and the subscripts refer to time. Substituting for C_o and C_t in (III) and converting to common logarithms gives

$$\log \frac{(N_\infty + S_\infty) - (N_t + S_t)}{(N_\infty + S_\infty)} = 0.4343\ (k_n + k_s)t$$

and since $\frac{N_t}{S_t} = \frac{N}{S} = \frac{k_n}{k_s}$

$$\log \frac{(N_\infty - N_t)(1 + \frac{k_s}{k_n})}{N_\infty \quad (1 + \frac{k_s}{k_n})} = 0.4343\ (k_n + k_s)t \ \ldots\ldots \text{(IV)}$$

If the product of sulphonation does not absorb at the wavelength of measurement then Beer's law gives:

$$\ln\left(\frac{I_o}{I}\right)_t = \varepsilon_n N_t$$

Substituting in (IV) we get

$$\log \left\{ \frac{\ln\left(\frac{I_o}{I}\right)_{t_\infty} - \ln\left(\frac{I_o}{I}\right)_t}{\ln\left(\frac{I_o}{I}\right)_{t_\infty}} \right\} = 0.4343\ (k_n + k_s)\ t$$

$$\text{or } \log \left\{ \ln\left(\frac{I_o}{I}\right)_{t_\infty} - \ln\left(\frac{I_o}{I}\right)_t \right\} = 0.4343\ (k_n + k_s)\ t \ \ldots\ \text{(V)}.$$

This equation, (V), is identical in form with that derived for the sulphonation of aromatic nitro-compounds.

Velocity Measurements

p-Bromophenyltrimethylammonium ion was chosen for reaction for several reasons. Firstly, its rate of sulphonation was known. Secondly, it has the highest relative rate of nitration compared with sulphonation of any of the p-halogen-substituted phenyltrimethylammonium ions. As a result of this the correction to the measured rate due to the simultaneous sulphonation was small and the rate of nitration could be determined with considerable precision.

The reaction media were prepared by dissolving a weighed amount of potassium nitrate into a weighed sample of oleum of known strength. This was allowed to equilibrate to the reaction temperature in the thermostat. A weighed sample, 10 to 20 mg., was dissolved in approximately 20 to 30 cc. of the reaction media in a glass stoppered flask, shaken vigorously, and poured into the absorption cell. The cell carriage was placed in the small thermostat and the absorption at 3650Å was measured continuously as previously described.

All experiments gave first order reactions up to five half reactions and reached a final value that was constant over several days indicating the absence of secondary reactions. The experimental rate constants, $(k_n + k_s)$, were determined graphically and by half table methods, both procedures giving identical values. Duplicate experiments were reproducible to better than one percent. The experimentally determined values of the first order rate constants for sulphonation, (k_s), were subtracted giving k_n. The second order velocity constants were obtained by dividing by the strength of dissolved nitrating agent. The results are collected in Table 19. The interpretation of the results is included in the general section on the mechanism of sulphonation.

Table 19. Nitration of p-bromophenyltrimethyl ammonium ion in oleums

Medium						
H_2SO_4%	KNO_3 (molar)	H_2SO_4% (corr.)	$k_n + k_s$ (min^{-1})	k_s	k_n	$k_2 = \frac{k_n}{(HNO_3)}$
100.29	.1001	100.11	.0174	$<10^{-5}$	.0175	0.174
"	"	"	.0174	"	.0174	0.174
101.66	.1000	101.47	.0212	$<10^{-4}$	.0212	0.212
"	"	"	.0212	"	.0212	0.212
103.17	.1048	102.99	.0297	.0003	.0294	0.281
"	"	"	.0296	.0003	.0293	0.280
104.18	.0999	104.00	.0301	.0008	.0293	0.293
"	"	"	.0298	.0008	.0290	0.290
105.00	.0996	104.82	.0293	.0017	.0276	0.277
"	"	"	.0298	.0017	.0281	0.282

Activity Coefficients of *p*-Chloronitrobenzene and 2,4-Dinitro-Chlorobenzene in Sulphuric Acid

Introduction

The determination of the activity coefficient of a neutral molecule in a salt solution may be most easily made from solubility determinations or from partition measurements. It is usual to take the standard state in a saturated solution in pure water. Extensive work has been done on the salt effects of added electrolytes on the activity coefficients of dissolved gases, weak acids, and organic compounds. The work has been reviewed by Randall and Failey (70), and other later references may be found in Harned and Owen's book on the "Physical Chemistry of Electrolytic Solutions" (71).

The activity coefficients of *p*-chloronitrobenzene and 2,4-dinitrochlorobenzene have been determined in 90% to 100% sulphuric acid by means of partition between cyclohexane and the particular acid. The concentrations were determined spectrophotometrically and the results may be interpreted as a "salting out" of the organic compounds by added water. This effect will be shown to parallel the aqueous case both qualitatively and quantitatively.

Experimental

The cyclohexane used was B.D.H. spectrometric grade. This was further purified by shaking 24 hours with concentrated sulphuric acid, washing with water and distilling from calcium oxide, the first and last 50 ccs. being discarded. It was used immediately after purification. The sulphuric acids were all prepared by adding the calculated volume of distilled water to an oleum of known strength. The oleum was prepared by the method already described in Part I. The details of the purification of p-nitrochlorobenzene and 2,4-dinitrochlorobenzene have also been given previously.

A weighed sample of the organic compound was dissolved in cyclohexane and made up volumetrically. The concentration of the stock solution was checked spectrometrically throughout the experiments. The partition was measured by adding 5 ccs. of cyclohexane solution to a similar volume of sulphuric acid in a glass-stoppered test-tube. This was shaken for fifteen minutes on a mechanical shaker in a constant temperature room ($20^{o}\pm2^{o}$). Preliminary trials showed that equilibrium was obtained in ten minutes. The cyclohexane layer was withdrawn and the concentration of organic compound was determined on a 'Unicam' spectrophotometer by measuring the absorption over the range 2600Å -

2750Å. Each experiment was carried out in duplicate. A sample of pure cyclohexane also underwent the same shaking and was used as the solvent in the spectrometric determinations. The concentration of organic compound in the sulphuric acid was obtained by difference. In several experiments a direct determination of the concentration in the acid layer gave the same values as those obtained by calculating the loss in the cyclohexane layer. The deliveries of the pipettes were checked by weighing and were found to give 5.00 ± 0.005 ccs. of cyclohexane and 4.94 ± 0.008 ccs. of sulphuric acid, allowing one minute drainage for the latter because of the higher viscosity of the sulphuric acid. Several experiments were carried out to test the concentration dependence of the partition. Twice the amount of the cyclohexane solution was shaken with the same amount of sulphuric acid. In every case the partition coefficient was independent of the relative amounts of the two solvents and the concentration of organic solute.

In the strongest acids p-chloronitrobenzene was partially ionized and the partition was calculated with respect to the unionized portion from the known values of the acidity function and the ionization constant.

The absorption spectrum of p-chloronitrobenzene has been determined in ethanol (72) and water (34). For the purpose of these experiments it was determined in cyclohexane along with that of 2,4-dinitrochlorobenzene (Figure 17).

Discussion

For the equilibrium partition of a substance between two phases the chemical potential in each phase must be equal. This means in the present case that

$$\mu_c = \mu_s$$

$$\text{or} \quad \mu_c^o + RT\ln a_c = \mu_s^o + RT\ln a_s$$

where μ_c, μ_c^o μ_s and μ_s^o are the chemical potentials of the compound, the subscripts c and s referring to cyclohexane and sulphuric acid respectively, and the subscript o referring to the standard state. We may choose a common standard state making $\mu_c^o = \mu_s^o = \mu^o$, and

$$a_c = a_s \quad ; \quad f_c c_c = f_s c_s$$

$$\text{or} \quad f_s = \left(\frac{c_c}{c_s}\right) f_c \qquad \text{(VI)}$$

where the c's stand for concentration and the f's are the molar activity coefficients. In the experiments carried out the value of the partition coefficients were independent of the concentration of organic material over the small concentrations employed (10^{-4} - 10^{-5} molar). Therefore f_c may be taken as constant. Finally we may choose our standard state as that in pure sulphuric acid (100% H_2SO_4) then $f_{s(100\%)} = 1.0$ and (VI) becomes:

$$f_{s\,(x\%)} = \left(\frac{c_c}{c_s}\right)_{x\%} \Big/ \left(\frac{c_c}{c_s}\right)_{100\%} \qquad \text{........ (VII)}$$

In the actual case the standard state was taken in 99.78% H_2SO_4. There were three reasons for this. At the concentration of pure sulphuric acid, due to decomposition, there is possibly a certain amount of sulphur trioxide present which would be partitioned changing the nature of the cyclohexane layer. Secondly, the correction for the ionization of the organic material would become large enough to lessen the accuracy of the determination of the partition, due to the decreasing amount of unionized material. Finally, at this concentration the added water has depressed the self ionization of the sulphuric acid. The results are tabulated in Table 20.

Table 20. Activity Coefficients of p-Nitrochlorobenzene and 2,4-diNitrochlorobenzene in Sulphuric Acid (20° ± 0.2°)

p-Nitrochlorobenzene

Medium				
H_2SO_4%	H_2O molar	$\frac{C_{cyclohexane}}{C_{H_2SO_4}}$	f_s	log f_s
99.78	0.068	0.0705	1.00	0.000
98.97	0.315	0.0874	1.23	0.089
97.50	0.773	0.123	1.74	0.240
95.99	1.26	0.180	2.55	0.406
94.50	1.78	0.259	3.68	0.565
93.00	2.28	0.383	5.43	0.735
91.50	2.83	0.574	8.14	0.911
90.05	3.37	0.923	13.08	1.117

2,4-diNitrochlorobenzene

H_2SO_4%	H_2O molar	$\frac{C_{cyclohexane}}{C_{H_2SO_4}}$	f_s	log f_s
99.78	0.068	0.00943	1.00	0.000
98.97	0.315	0.0108	1.14	0.058
97.51	0.773	0.0133	1.40	0.149
96.00	1.26	0.0183	1.95	0.290
94.50	1.78	0.0240	2.55	0.406
93.01	2.28	0.0338	3.59	0.555
91.50	2.83	0.0481	5.10	0.708
90.01	3.37	0.0785	7.49	0.875

Debye and MacAulay (78) have developed a theory for the salting effect of added electrolyte on the activity coefficient of a neutral molecule. They obtain the equation

$$\ln f_s = \frac{\bar{\beta}}{2kTD_o} \sum_1^s \frac{n_j e_j^2}{b_j} \qquad \ldots\ldots\ldots \text{(VIII)}$$

where D_o is the dielectric constant of the pure medium, k the Boltzmann constant, T the temperature, n_j the number, e_j the charge and b_j the radius of the j'th ion. The constant $\bar{\beta}$ is characteristic of the non-electrolyte and may be either positive or negative corresponding to salting out or salting in. This equation is similar in form to the empirical one suggested by Setchénow (74).

$$\log \frac{s^o}{s} = k_s c \qquad \ldots\ldots\ldots\ldots\ldots \text{(IX)}$$

where s^o and s are the solubilities of the neutral molecule in pure solvent and salt solution, respectively, c is the molar concentration of salt and k_s is a constant. A comparison of (VIII) and (IX) leads to the relation

$$\log f_s = k\mu \qquad \ldots\ldots\ldots\ldots\ldots \text{(X)}$$

μ being the ionic strength and k a constant since

$$\sum_1^s \frac{n_j e_j^2}{b_j} = \frac{Ne^2}{1000} \sum_1^s \frac{c_j z_j^2}{b_j}$$

which for a 1:1-electrolyte gives

$$\frac{Ne^2}{1000} \cdot \frac{1}{b} \times 2c = \frac{Ne^2}{1000} \cdot \frac{1}{b} \times 2d_o\mu$$

where 'N' is Avogadro's number, 'e' the electronic charge, 'b' the mean radius and 'd_o' the density of the solvent.

Equation (X) represents the data reasonably well over fairly large changes in ionic strength but the role of the ionic radius is confused (75) and values obtained from different salts which should be proportional to b_j do not agree with those derived from crystallographic radii. A further development by Debye (76) gives a close agreement in all respects but its validity is restricted to very dilute salt solutions.

Considering the solvent sulphuric acid, the addition of water, a strong base, is equivalent to the addition of a salt to water since

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \quad .... \text{(XI)}$$

the equilibrium being almost quantitatively to the right. If we take the standard state as 99.78% H_2SO_4, self-dissociation is completely depressed and the freezing point curve is linear to quite high dilutions. This means that the ionic strength is directly proportional to the concentration of added water and that a constant major fraction of this added water is dissolved as the salt hydroxonium bisulphate. Since the organic compounds lower the dielectric constant of sulphuric acid they should be 'salted out' (the activity coefficients should rise with increasing concentration of water). This prediction is experimentally verified. A plot of log f_s against the concentration of water is linear with a positive slope (Figure 18).

Gold and Tye (77) and Plattner, Heilbronner and Weber (78) have performed similar experiments with hydrocarbons in more aqueous sulphuric acids. They found that log.f_s was a linear function of H_o. This does not agree with these results and the possible explanation is as follows. The acidity function is nearly linear with respect to the concentration of water over the range of acids which they studied. Also the fact that each compound was only investigated over a small change in the acidity function (0.4 to 0.8 of a unit) would heighten the supposed linearity. The present results are approximately linear with respect to H_o in acids of strength less than 97% H_2SO_4 and had limiting slopes of close to unity, but the effect is almost certainly due to the changing ionic strength and not to the acidity function. A further verification of this contention is found in the results of Hammett and Chapman (79). On the addition of sulphuric acid organic oxygen compounds have their solubility in water decreased until a fairly high concentration of acid is reached, then the solubility increases rapidly in the region 70 - 90% H_2SO_4. If the effect was caused by the increasing acidity of the medium it should not have a minimum but should rise continuously with increasing concentration of H_2SO_4.

DISCUSSION.

DISCUSSION

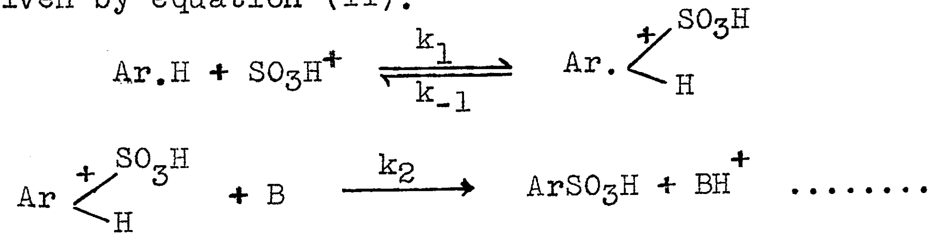
Mechanism of Sulphonation

Sulphonation in fuming sulphuric acid is always strictly first order with respect to the concentration of aromatic compound. The apparent first order coefficients, k_1, rise steeply with increasing concentration of sulphur trioxide in the medium. This behaviour has been noted by previous investigators (25, 26) for comparatively dilute oleums and no great differences have been observed in these determinations in more concentrated media. The results are consistent with the mechanism

$$Ar.H + SO_2.OH^+ = ArSO_2.OH + H^+ \qquad .... \text{(I)}$$

and the variation of k_1 with medium concentration is essentially determined by the change in concentration of the $SO_2.OH^+$ cation.

A survey of the proposed mechanisms for aromatic substitution leads to two possibilities, either a bimolecular mechanism (S_E2) as shown in equation (I) or a stepwise reaction involving the formation of an intermediate complex given by equation (II).



$$Ar.H + SO_3H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar.\overset{+}{<}{}^{SO_3H}_{H}$$

$$Ar\overset{+}{<}{}^{SO_3H}_{H} + B \xrightarrow{k_2} ArSO_3H + BH^+ \qquad .... \text{(II)}$$

Although the sulphonation kinetics are consistent with the simple bimolecular reaction, there are good reasons for postulating the second mechanism and the two are fundamentally similar. Writing the stationary state condition for the transition complex gives the following expression for the rate of stepwise reaction

$$-\frac{d[ArH]}{dt} = \frac{k_1k_2[B]}{k_{-1}+k_2[B]} \cdot [ArH][SO_3H^+] \frac{f_{ArH} \cdot f_{SO_3H^+}}{f_{\ddagger}} \quad .... \quad (III)$$

where $f_{\ddagger}$ stands for the activity coefficient of the transition complex. In the event that $k_2[B] \gg k_{-1}$ or no base, B, is required for the removal of a proton, this reduces to (IV)

$$-\frac{d[ArH]}{dt} = k_1[ArH][SO_3H^+] \frac{f_{ArH} \cdot f_{SO_3^+H}}{f_{\ddagger}} \quad .... \quad (IV)$$

Even in the case where the second step is rate determining it may not be possible to distinguish between (I) and (II) due to the lack of knowledge about the species responsible for proton removal.

As mentioned in the introduction, experimental work using isotopic hydrogen has shown that in nitration and bromination the rate is identical for the normal and isotopic species within the limits of experimental error (12, 80). This shows unequivocally that these reactions proceed with the formation of a transition complex, the first step being rate determining. The results for sulphonation are less clear, there being a definite isotope effect, with the deuterium- and tritium-substituted compounds reacting more slowly. From these results either bimolecular, (S_E2), or a stepwise reaction is possible.

Recent measurements on the sulphonation of deuteronitrobenzene using the same apparatus and method as in Part II gave the following results (Table 21).

Table 21. Rate of Sulphonation of $C_6H_5NO_2$ and $C_6D_5NO_2$ (temp.25°)

% H_2SO_4	10^3k_D min^{-1}	10^3k_H min^{-1}	k_D/k_H
103.25	0.85 *	1.47	0.58
104.97	2.05	3.40	0.60
107.23	5.46	8.35	0.65
108.19	8.79	12.1	0.72

* (ref.81)

The k's are the experimental first order rate constants, the subscripts referring to the isotopic species.

The fact that there is no isotopic effect in nitration quite definitely proves that the first step is slow and the second fast. Theoretically, however, it is impossible to predict that (k_D/k_H) should be exactly unity and it might well have been as low as 0.8. In experiments where the rate determinating step is known to be the removal of a proton or deuteron, it has been found that k_D/k_H = 0.1 (82) and theoretical predictions give values of the same magnitude. The values of (k_D/k_H) for sulphonation vary from 0.58 to 0.72 with an apparently regular dependence on medium. From these figures it is impossible to definitely choose between the two mechanisms, but since the isotopic effect is small compared with the normal case and the two stage mechanism has definitely been proved for nitration and halogenation, it seems natural to argue that the mechanisms are the same. This being accepted, it seems reasonable to assume that since there is no isotope effect in the first step in nitration there should be none in sulphonation. This being the case, the experimental results show that the decomposition of the intermediate complex to form the product is faster than the loss of SO_3H^+. Actual numerical calculation shows that $k_1/k_2 = 1/17$ and k_{-1} is neglected in the subsequent analysis of the results in terms of the acidity function and the vapour pressure, as it is within the accuracy of these results. This mechanism of sulphonation seems to be consistent with the facts but contains several fairly strong assumptions. Moreover the explanation of the variation of k_D/k_H with % H_2SO_4 is not clear and more knowledge about the nature of oleum solutions and proton loss from the intermediate is required.

The Concentration of Sulphonium Ion ($SO_2^+.OH$)

The concentration of $SO_2^+.OH$ can be deduced from the value of the acidity function and the vapour pressure. If we consider the formal equilibrium

$$HO.SO_2.O.SO_2.OH + H^+ \overset{K_1}{\rightleftharpoons} HO.SO_2.OH + SO_2^+.OH \quad .. \text{(V)}$$

the equilibrium constant, K_1 is given by the equation

$$K_1 = \frac{\{SO_2.OH^+\}\{H_2SO_4\}}{\{H_2S_2O_7\}\{H^+\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(VI)}$$

where the braces $\{\ \}$ denote activities, referred to a standard state in sulphuric acid. The term $\{H^+\}$ may be replaced by introducing the value of the acidity function,

$$H_o = A - \log \{H^+\} . \frac{f_B}{f_{BH^+}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(VII)}$$

where BH^+ and B are the acid-base pair used in the measurement of H_o and the f's refer to the standard state in sulphuric acid. The term A is constant at constant temperature and allows for the fact that H_o is usually defined with reference to a standard state in water (27). The circumstance that a simple constant will transfer from one standard state to another is implicit in the original assumption that the ratio f_B/f_{BH^+} has the same value in a given medium for all neutral bases ionizing to form the conjugate acid and the experimental evidence for this is given by Hammett (27). The activities of H_2SO_4 and $H_2S_2O_7$ are related by the equations

$$H_2SO_4 + SO_3 \overset{K_2}{\rightleftharpoons} H_2S_2O_7$$

$$K_2 = \frac{\{H_2S_2O_7\}}{\{H_2SO_4\}\{SO_3\}} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(VIII)}$$

Substitutiong (VII) and (VIII) in (VI) gives the following expression (IX) for the concentration of $SO_2.^+OH$:

$$\log\left[SO_2.^+OH\right] = \log\left\{SO_3\right\} - H_o - \log({}^{f_B}/_{f_{BH^+}}).f_{SO_2{}^+OH} + A + \log K_1K_2 \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(IX)}$$

We may define the activity of sulphur trioxide in sulphuric acid to be equal to its vapour pressure and write J = $H_o - \log(p_{SO_3})$. This expression is analogous to the J_o-function for aqueous sulphuric acid introduced by Gold and Hawes (83). Because the vapour pressure of sulphur trioxide in dilute oleums is too small (Tables 14, 15) for accurate measurement at 25°, the J-function was evaluated from the vapour pressure measurements at 50° (84). This treatment is justified because the gradient of the plot of log (p_{SO_3}) against composition is independent of the temperature at which the measurements are made. Therefore relative values of J are independent of the temperature to which the vapour pressure measurements refer, provided they always refer to the same temperature. The J-function is then purely relative and no significance is attached to the absolute values. A similar consideration led to the definition of the activity of sulphur trioxide as equal to the logarithm of the vapour pressure rather than the ratio log (p/p_o), (where p and p_o are the vapour pressures of SO_3 for the medium and pure sulphuric acid respectively), since the vapour pressure of SO_3 over 100% sulphuric acid is too small to be measured accurately.

With this substitution equation (IX) becomes

$$\log (SO_2^+OH) = -J - \log \frac{f_B . f_{SO_2^+OH}}{f_{BH^+}} + A + \log K_1K_2 \ldots \quad (X)$$

Correlation of the Theory with the Experimental Results

On the basis of equation (IV) the velocity of sulphonation was given by

$$-\frac{d(ArH)}{dt} = k(ArH)(SO_2^+OH) \frac{f_{ArH} . f_{SO_2^+OH}}{f_\ddagger}$$

$f_\ddagger$ denoting the activity coefficient of the transition state. From the fact that the reaction is experimentally first order it follows that

$$-\frac{d(ArH)}{dt} = k_1(ArH) \ ; \ k_1 = k(SO_2^+OH) \frac{f_{ArH} . f_{SO_2^+OH}}{f_\ddagger} \ldots \quad (XI)$$

Combining (X) and (XI) gives equation (XII),

$$\log k_1 = -J + \log \frac{f_{ArH} . f_{BH^+}}{f_\ddagger . f_B} + (\log k + \log K_1K_2 + A) \ .. \quad (XII)$$

which expresses the variation of the experimentally determined rate constants, k_1, with medium composition, in terms of the J-function (Figure 10) and an activity coefficient term of approximately symmetrical form. The final term in equation (XII) is constant at a fixed temperature since k_1, K_1 and K_2 are thermodynamical constants.

The values of log 10^3k_1 from Tables 14 and 15 in Part II are plotted against the J-function (Figure 19). If the activity coefficient term is constant the points should fall on a straight line of unit slope. The experimental results fall on straight lines with slopes slightly greater than unity. These slopes vary from 1.03 for nitrobenzene and 1.07 for p-nitrotoluene to 1.14 for the p-halogen-substituted and 1.16 for the unsubstituted phenyltrimethylammonium ion (26). The results cover an effective variation of velocities of several powers of ten and provide a fairly comprehensive test of the theory. The deviation from unit slope probably does not greatly exceed the experimental error in J.

The vapour pressure results used to calculate J refer to 50° and although it was stated that the graphs of log p_{SO_3} against composition were to a good approximation parallel for various temperatures, closer comparison of results at 50° and 70° reveals a slight decrease in slope at the lower temperature (84). A similar decrease between 50° and 25° would improve the results. However, although there are good reasons for believing that the change in the activity coefficient term is small, it is probably too simple, considering the large change in medium composition, to assume that it is zero.

Medium Effects in Sulphonation and Nitration

In explaining the medium effect it is necessary to distinguish between two different reaction intermediates. Nitrobenzene and p-nitrotoluene give a singly-charged transition state whereas the phenyltrimethylammonium ions give a doubly-charged dipolar ion. It can be shown (Part I) that the activity coefficient terms in both cases vary in a similar way in a solvent of high dielectric constant, but it is apparent from the difference in the slopes of the sulphonation curves that this similar variation is not exact.

Considering the nitro-compounds first, it is obvious that the slopes are nearer unity and if the previously mentioned decrease in slope of the vapour pressure curve is allowed for, it makes the agreement even better. There are two main reasons for this better agreement. Firstly, the acidity function scale which is the least certain of the experimental quantities, enters twice into the correlation of log k_1 and J, so that errors in H_0 tend to cancel out. Secondly, the activity coefficient term, $\frac{f_{ArH} \cdot f_{BH^+}}{f_{\ddagger}^{(+)} \cdot f_B}$ is symmetrical with respect to charge and f_B and f_{ArH} refer to the same compounds since nitrobenzene and p-nitrotoluene were used to determine the acidity function. Therefore when these considerations are allowed for, it is probable that the true deviation of the slope of log k_1 against J from unity is very small. This near constancy of activity coefficient term has also been recently demonstrated (85) for the nitration of unionized p-nitrochlorobenzene in oleum although the symmetry of the f's is not exactly the same in that case.

In the case of the quaternary ammonium ions there is no acid-base type of equilibrium and the errors in H_o do not tend to cancel. Also, the activity coefficient term is not completely symmetrical with respect to charge and is given by log $\frac{f_{ArH^+} \cdot f_{BH^+}}{f_{\ddagger}^{(2+)} \cdot f_B}$. However, it was shown in Part I that the ratios $f_{B^+}/f_{BH}^{(2+)}$ and f_B/f_{BH^+} vary in a similar way in solvents of high dielectric constant. It can be argued therefore that $f_{ArH}/f_{\ddagger}$ should be approximately the same for a charged and uncharged reactant. Support for this is given by the fact that the relative velocity of nitration of $C_6H_5.NMe_3^+$ and $C_6H_5.NO_2$ is practically constant over the medium range 90 to 97% H_2SO_4 (86). This must mean that the ratios $f_{Ph.NMe_3^+}/f_{\ddagger}^{(2+)}$ and $f_{PhNO_2}/f_{\ddagger}^{(+)}$ vary in the same way with medium composition. However, it has been recently shown by Gillespie that this is not always true in stronger media (85). Therefore if the activity coefficient term is not constant for sulphonation, it is difficult to say whether it is positive or negative. The nitrations of p-bromophenyltrimethylammonium ion in oleum were carried out to try to determine the sign and magnitude of this effect. The experimental results in Part III show that the term $(f_{ArH}/f_{\ddagger}^{(2+)}).f_{NO_2^+}$ rises with increasing strength of oleum and similar results have just been published for the p-chloro-analogue (88). It is not completely analogous to sulphonation but it does not seem unreasonable that $\log (f_{ArH}(+)/f_{\ddagger}(2+)).(f_{BH^+}/f_B)$ should also be positive and the slopes of the lines in Figure 18 slightly greater than unity. It may also be noted that the greatest rise in nitration rate occurs in 100 to 102% media and that this is the same region of composition that the points in Figure 18 tend to deviate from linearity.

Possible Alternative Sulphonating Agents

The correlation of $\log k_1$ with J shows that the velocities are consistent with the proposed mechanism, but it cannot be regarded as an unequivocal proof of mechanism. Some alternatives may be immediately eliminated. Neither SO_3 (velocities correlated with partial pressure), nor H_3SO_4 (correlation with H_o), are possible reactants. However, because H_o and $\log p_{SO_3}$ are almost parallel functions of medium concentration (83,86), $\log k_1$ could be successfully correlated with $2\ H_o$ or $2 \log (p_{SO_3})$, as well as with

J. The first possibility, ($2\ H_o$), corresponds to sulphonation by $H_4SO_4^{++}$ which can be immediately rejected. The second ($2 \log p_{SO_3}$) corresponds to sulphonation by S_2O_6. The reason for preferring $SO_2.OH^+$ to S_2O_6 is that it explains the exceptional power of sulphuric acid as a sulphonating medium in terms of its high proton-activity. Otherwise the presence of sulphuric acid is unfavourable because the equilibrium

$$SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7$$

causes a large proportion of the sulphur trioxide to be stored as unreactive disulphuric acid. However, there is evidence that in aprotic solvents S_2O_6 is the active sulphonating agent (20, 21, 22) and S_2O_6 is analogous to $SO_3.OH^+$ in the general system of acids and bases. A parallel may be drawn between Br_2 and Br^+ as brominating agents in aqueous and strongly acid media respectively.

Steric Retardation in Sulphonation

The relative velocity of sulphonation of derivatives of $C_6H_5.NMe_3^+$ is practically independent of the composition of the medium. This condition is also satisfied for nitration in sulphuric acid (85, 86). It seems reasonable to suppose that, apart from the steric factor, the influence of the halogens should be qualitatively of the same order in both nitration and sulphonation.

The results from Part II and Part III are collected in Table 22.

Table 22. Relative velocities of substitution of p-Hal.-$C_6H_4.NMe_3^+$ in sulphuric acid (25°)

Substituent	H	F	Cl	Br
Nitration	1.0	0.030	0.165	0.32
Sulphonation	1.0	0.026	0.020	0.022

With the exception of the unsubstituted compound the point of attack is ortho to the halogen substituent and a comparison of sulphonation and nitration gives a clear indication of steric compression in the transition state of sulphonation of the chloro- and bromo-derivatives (Figure 20). A fluoro-substituent does not impede sulphonation appreciably. This is supported by the fact that the iodo-compound reacted with decomposition and all attempts to sulphonate *p*-nitro-*tert*-butylbenzene and *p*-*tert*-butylphenyltrimethylammonium ion were unsuccessful.

Effect of Added Bases on the Rate of Sulphonation

The effect of added potassium sulphate on the rate is explained by the assumption that one mole of K_2SO_4 is equivalent to two moles of water, the equations involved being:

$$K_2SO_4 + 2H_2S_2O_7 = 2K\,HS_2O_7 + H_2SO_4 \quad \ldots\ldots\ldots \quad (XII)$$

$$2H_2O + 2H_2S_2O_7 = 4H_2SO_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (XIII)$$

In the case of nitrobenzene this explains the results as may be seen in Table 17 by a comparison of columns 4 and 6. The reason for this apparently simple explanation is two-fold. Firstly, the presence of $HS_2O_7^-$ generated by the addition of potassium sulphate depresses the concentration of sulphonium ion according to equation (XV)

$$SO_3H^+ + HS_2O_7^- \rightleftharpoons H_2S_2O_7 + SO_3 \quad \ldots\ldots \quad (XV)$$

Secondly, the concentration of unionized nitro-compound is increased (XVI)

$$BH^+ + HS_2O_7^- \rightleftharpoons B + H_2S_2O_7 \quad \ldots\ldots\ldots\ldots \quad (XVI)$$

where BH^+ represents the ionized nitro-compound. Therefore the failure of the hydrogen pyrosulphate ions to retard sulphonation is only apparent and the decrease in concentration of sulphonium ion is offset by the increase in concentration of unionized nitro-compound, the two effects cancelling each other. This supports the view that the sulphonating agent is SO_3H^+ and the same has been observed by Brand (26) in the case of p-nitrotoluene. His results also show that in the case of the phenyltrimethylammonium ion, where the loss of sulphonium ion is not compensated for, the hydrogen pyrosulphate ions have a strong retarding effect on the rate. However, the results do not at present lend themselves to a quantitative analysis.

Influence of the Temperature

The influence of temperature on the velocity coefficients of nitrobenzene and p-chlorophenyltrimethylammonium ion is shown in Table 16. For a specific medium plots of log 10^3k_a against 1/T gave straight lines for nitrobenzene and Brand (26) has found the same behaviour for p-nitrotoluene and p-tolyltrimethylammonium and phenyltrimethylammonium ions. The constants of Arrhenius equation were evaluated and are given in Table 23.

Table 23. Constants of the Arrhenius Equation $k_1 = Ae^{-\frac{E}{RT}}$ *

Medium H_2SO_4%	SO_3%	E	log A
	nitrobenzene		
102.77	12.3	19.7_5	11.07
104.77	21.2	19.6_5	11.47
106.00	26.7	20.1	12.10
108.22	36.6	19.5	11.88
	p-chlorophenyltrimethylammonium ion		
106.75	30.1	14.6	7.94
106.89	30.6	15.0	8.37

*k_a was used in the case of nitrobenzene; the k's were expressed in sec.$^{-1}$ at 25° for the calculation of log A.

The apparent heat of activation of nitrobenzene agrees with that of p-nitrotoluene (26) in being considerably higher than any of the quaternary ions. This gives further evidence for the existence of an ionized and unionized form in solution. In this case the energy of activation is composite, containing an additional factor corresponding to the heat of ionization of nitrobenzene.

The relative rates of sulphonation of nitrobenzene and p-nitrotoluene bear no relation to the difference in the activation energies which is small. This is to be expected since the overall process is the loss of a proton and the addition of a sulphonium ion. These two steps are consecutive and conditioned by the same electrostatic factors. Therefore differences tend to cancel and the measured heats of activation are very nearly the same. In the case of the p-chlorophenyltrimethylammonium ion the two steps cannot be considered as two mutually compensating ionizations and the picture is not so clear. The activation energies of the p-chloro-substituted quaternary ion and the unsubstituted quaternary ion (26) are very nearly the same, although the relative rates are quite different. This may be influenced by steric effects but the activation energies are probably composite and interpretation is difficult.

BIBLIOGRAPHY.

Bibliography.

1. Holleman, Chem.Rev. (1924/25), 1, 187.
2. Scheffer, Proc.Akad.Wet.Amsterdam (1912/13), 15, 1118.
3. Ingold and Shaw, J.Chem.Soc. (1949), 575, also previous refs.
4. Allan, Oxford, Robinson and Smith, J.Chem.Soc. (1926), 401.
5. Ingold and Ingold, J.Chem.Soc. (1926), 1310.
6. Ingold, Chem.Rev. (1934), 15, 225.
7. Michael et al., J.Am.Chem.Soc. (1935), 53, 1142; (1936), 58, 294.
8. Pfeiffer and Wizinger, Ann. (1928), 461, 132.
9. Lantz, Bull.Soc.Chim. France (5), 1945, 12, 1004.
10. Baddeley, Holt and Kenner, Nature (1944), 154, 361.
11. Hughes, Ingold and Reed, J.Chem.Soc. (1950), 2400.
12. Melander, Arkiv För Kemi, (1950/51), 2, 211.
13. Bennett, Brand and Williams, J.Chem.Soc. (1946), 869, 875.
14. Hughes, Ingold and Reed, Nature (1946), 158, 448.
15. Chédin, Chim. et Ind., (1946), 56, 7.
16. Westheimer and Kharasch, J.Amer.Chem.Soc. (1946), 68, 1871.
17. Derbyshire and Waters, J.Chem.Soc. (1950), 564.
18. Shilov and Kaniaev, Compt.rend. (Doklady) Acad.Sci. U.R.S.S. (1939), 24, 890; C.A. (1940), 34_2, 4062.
19. de la Mare and Robertson, J.Chem.Soc. (1950), 2838.
20. Vicary and Hinshelwood, J.Chem.Soc. (1939), 1372.
21. Wadsworth and Hinshelwood, J.Chem.Soc. (1944), 469.

22. Dresel and Hinshelwood, J.Chem.Soc. (1944), 649.

23. Stubbs, Williams and Hinshelwood, J.Chem.Soc. (1948), 1065.

24. Martinsen, Z.physikal.Chem. (1908), 62, 713.

25. Cowdrey and Davies, J.Chem.Soc. (1949), 1871.

26. Brand, J.Chem.Soc. (1950), 1004.

27. Hammett, Chem.Reviews (1935), 16, 67.

28. Hammett and Deyrup, J.Amer.Chem.Soc. (1932), 54, 2721.

29. Hammett and Paul, J.Amer.Chem.Soc. (1934), 56, 827.

30. Hantzsch, Z.Physikal.Chem. (1908), 65, 41.

31. Hammett, J.Chem.Physics (1940), 8, 644.

32. Gillespie, J.Chem.Soc. (1950), 2542.

33. Brand, J.Chem.Soc. (1950), 997.

34. Doub and Vandenbelt, J.Amer.Chem.Soc. (1947), 69, 2714.

35. Platt, J.Chem.Physics (1951), 18, 101.

36. Matsen and Hastings, J.Amer.Chem.Soc. (1948), 70, 3514.

37. Gold and Tye, J.Chem.Soc. (1950), 2932.

38. Brand, J.Chem.Soc. (1946), 585.

39. James and Knox, Trans.Faraday Soc. (1950), 46, 254.

40. Jones and Bradshaw, J.Amer.Chem.Soc. (1933), 55, 1780.

41. Hantzsch, Z.physikal.Chem. (1907), 61, 257.

42. Bergius, Z.physikal.Chem. (1910), 72, 338.

43. Lichty, J.Amer.Chem.Soc. (1908), 30, 1834.

44. Reinhardt, J.Amer.Chem.Soc. (1950), 72, 3359.

45. Giaque and Kuntzler, J.Amer.Chem.Soc. (1952), 74, 804.

46. Masson, Nature (1931), 128, 726.

47. Fajans and Goodeve, Trans.Faraday Soc. (1936), 32, 511.

48. Brand, Horning and Thornley, J.Chem.Soc. (1952), 1374.

49. Flexser, Hammett and Dingwall, J.Amer.Chem.Soc. (1935), 57, 2103.

50. Kirkwood and Westheimer, J.Chem.Physics (1938), 6, 503,513; (1939), 7, 437.

51. Kirkwood and Westheimer, Trans.Faraday Soc. (1947), 43, 77.

52. Sarmousakis, J.Chem.Physics,(1944), 12, 277.

53. Groves and Sugden, J.Chem.Soc. (1937), 1782.

54. Hurdis and Smith, J.Amer.Chem.Soc. (1942), 64, 2212.

55. Bjerrum, Z.Physikal.Chem. (1923), 104, 147.

56. Güntelberg and Schöidt, Z.Physikal.Chem. (1938), 135, 393.

57. Fuoss and Edelson, J.Amer.Chem.Soc. (1951), 73, 269.

58. Fuoss and Chu, J.Amer.Chem.Soc. (1951), 73, 949.

59. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, 1943, Chaps. 2, 3.

60. Born, Z.Physik. (1920), 1, 45.

61. Gillespie, J.Chem.Soc. (1950), 2493.

62. Brand, James and Rutherford, J.Chem.Physics (1952), 20, 530.

63. Michaelis and Granick, J.Amer.Chem.Soc. (1942), 64, 1861.

64. Gillespie, Hughes and Ingold, J.Chem.Soc. (1950), 2473.

65. Amiantov and Titkov, Anilinokrasochnaya Prom. 2, (1932), 8, 9, 24; C.A. (1933), 27, 5315.

66. Brand and Paton, J.Chem.Soc. (1952), 281.

67. Bennett, Brand, James, Williams and Saunders, J.Chem.Soc. (1947), 474.

68. Brand, J.Chem.Soc. (1946), 880.

69. Gillespie, Graham, Hughes, Ingold and Peeling, J.Chem.Soc. (1950), 2504.

70. Randall and Failey, Chem.Rev. (1927), 4, 291.

71. Harned and Owen, Chap.12, page 397.

72. Morton and McGookin, J.Chem.Soc. (1934), 901.

73. Debye and MacAulay, Physik.Z. (1925), 26, 23.

74. Setchénow, Ann.Chim.Phys. (1892), [6], 25, 225.

75. Scatchard, Trans.Faraday Soc. (1927), 23, 454.

76. Debye, Z.Physikal.Chem. (1927), 130, 55.

77. Gold and Tye, J.Chem.Soc. (1952), 2181.

78. Plattner, Heilbronner and Weber, Helv.Chem.Acta, (1944), 32, 574.

79. Hammett and Chapman, J.Amer.Chem.Soc. (1934), 56, 1282.

80. Bonner, Bowyer and Williams, J.Chem.Soc. (1952), 3274.

81. Brand, unpublished results.

82. Wynne-Jones, J.Chem.Phys. (1934), 2, 381.

83. Gold and Hawes, J.Chem.Soc. (1952), 2102.

84. Brand and Rutherford, J.Chem.Soc. (1952), 3916.

85. Gillespie and Norton, J.Chem.Soc. (1953), 971.

86. Bonner, James, Lowen and Williams, Nature, (1949), 163, 955.

87. Lewis and Bigeleisen, J.Amer.Chem.Soc. (1943), 65, 1144.

88. Gillespie and Wasif, J.Chem.Soc. (1953), 204.

89. Pounder and Masson, J.Chem.Soc. (1934), 1352.

90. Brand and Rutherford, J.Chem.Soc. (1952), 3927.

FIGURE 1. ABSORPTION SPECTRA of NITROBENZENE in SULPHURIC ACID

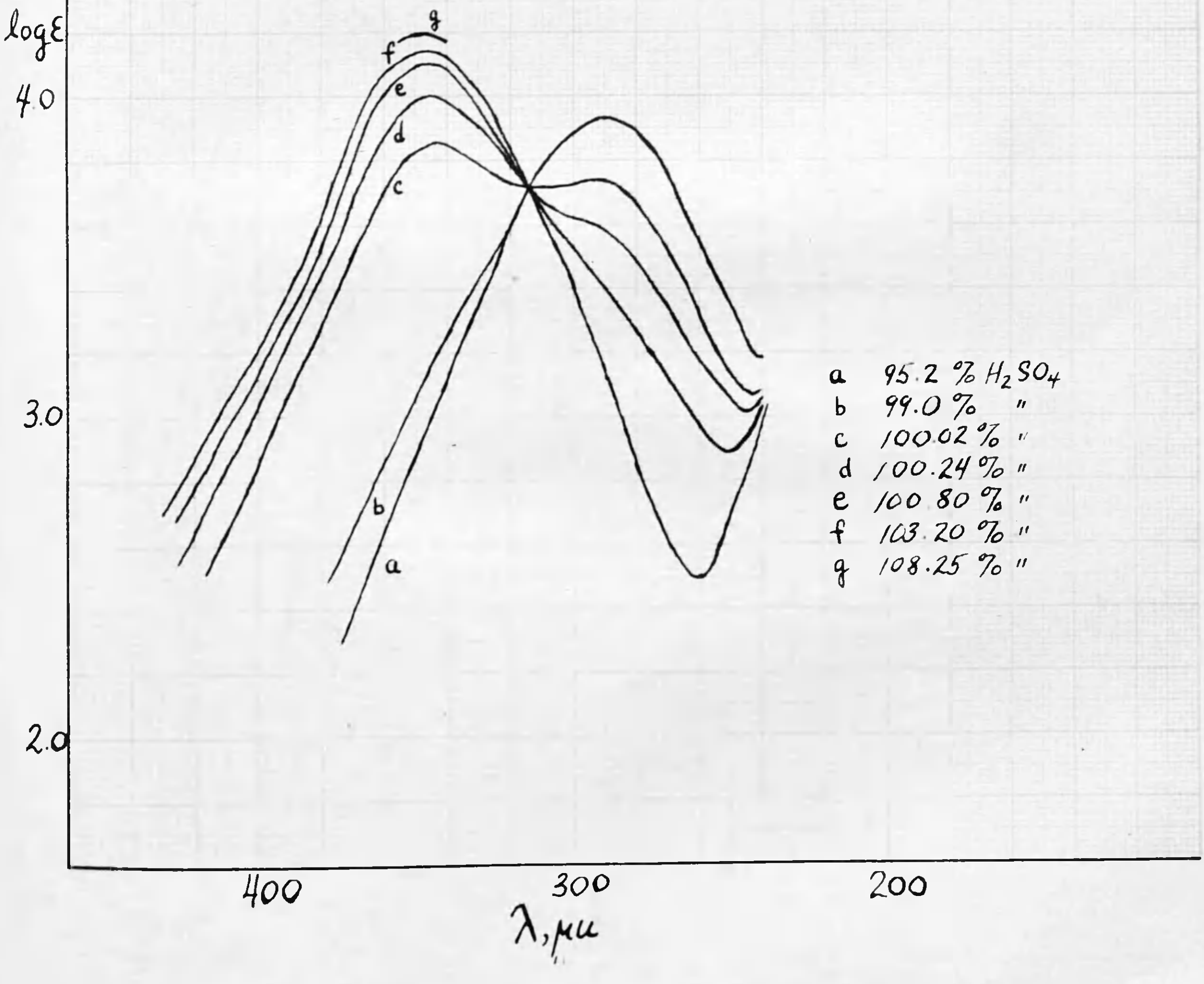
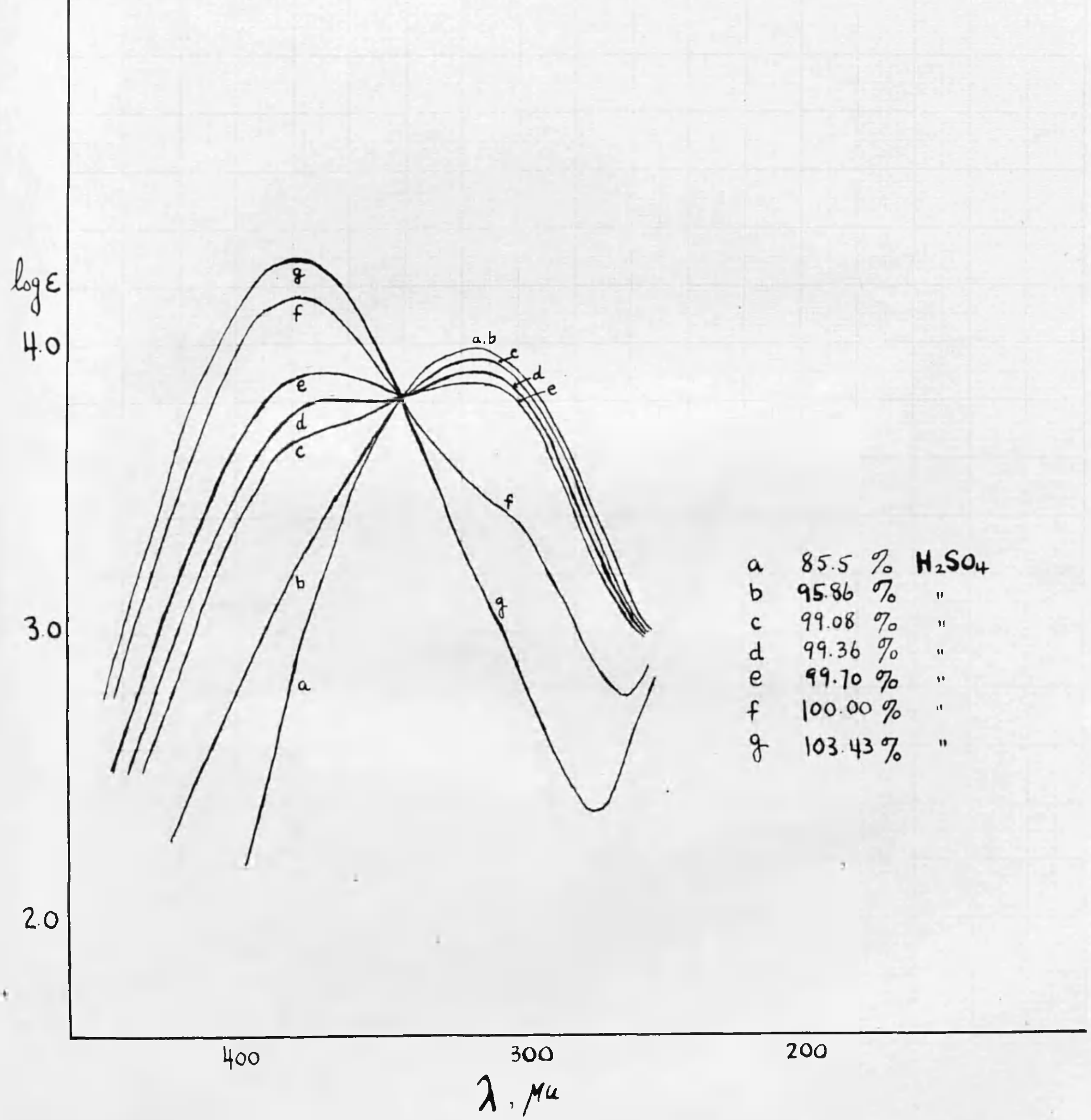


FIGURE 2. ABSORPTION SPECTRA of p-NITROTOLUENE in SULPHURIC ACID



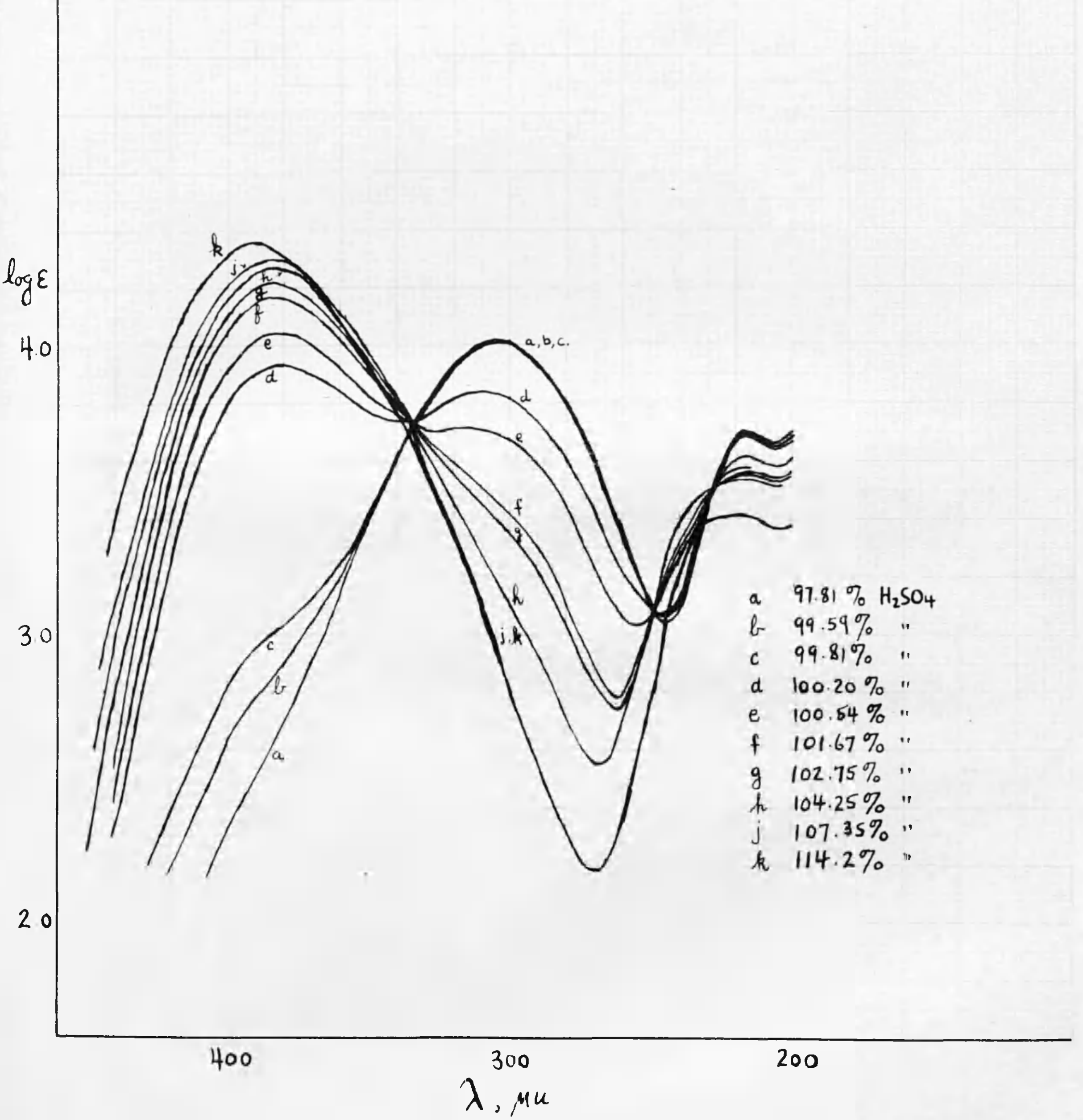


FIGURE 3. ABSORPTION SPECTRA of p-NITROCHLOROBENZENE in SULPHURIC ACID

FIGURE 4. ABSORPTION SPECTRA of m-NITROANILINE in SULPHURIC ACID

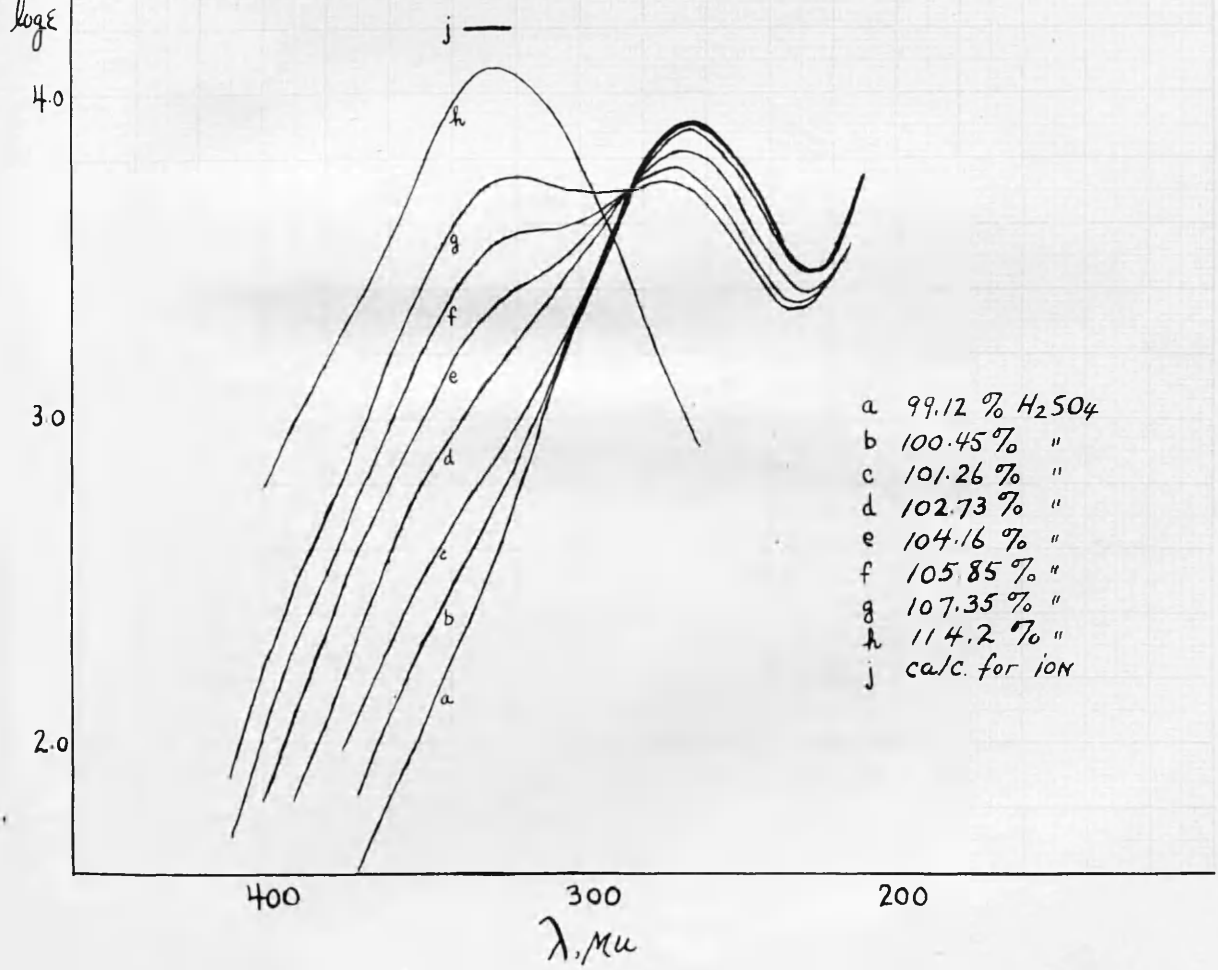


FIGURE 5. ABSORPTION SPECTRA of 2,4-DINITROTOLUENE in SULPHURIC ACID

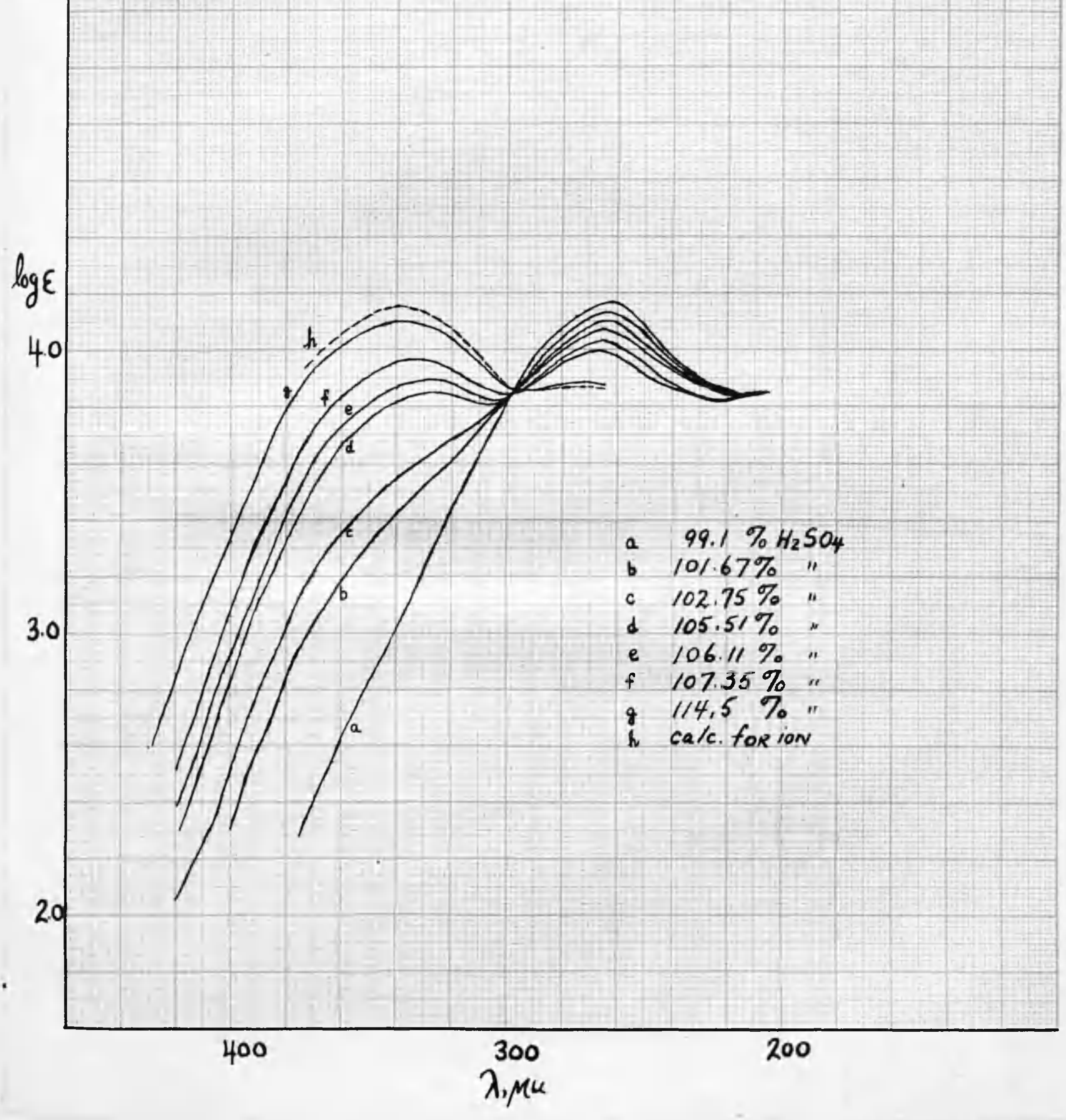


FIGURE 6. ABSORPTION SPECTRA of 2,4-DINITROCHLOROBENZENE in SULPHURIC ACID

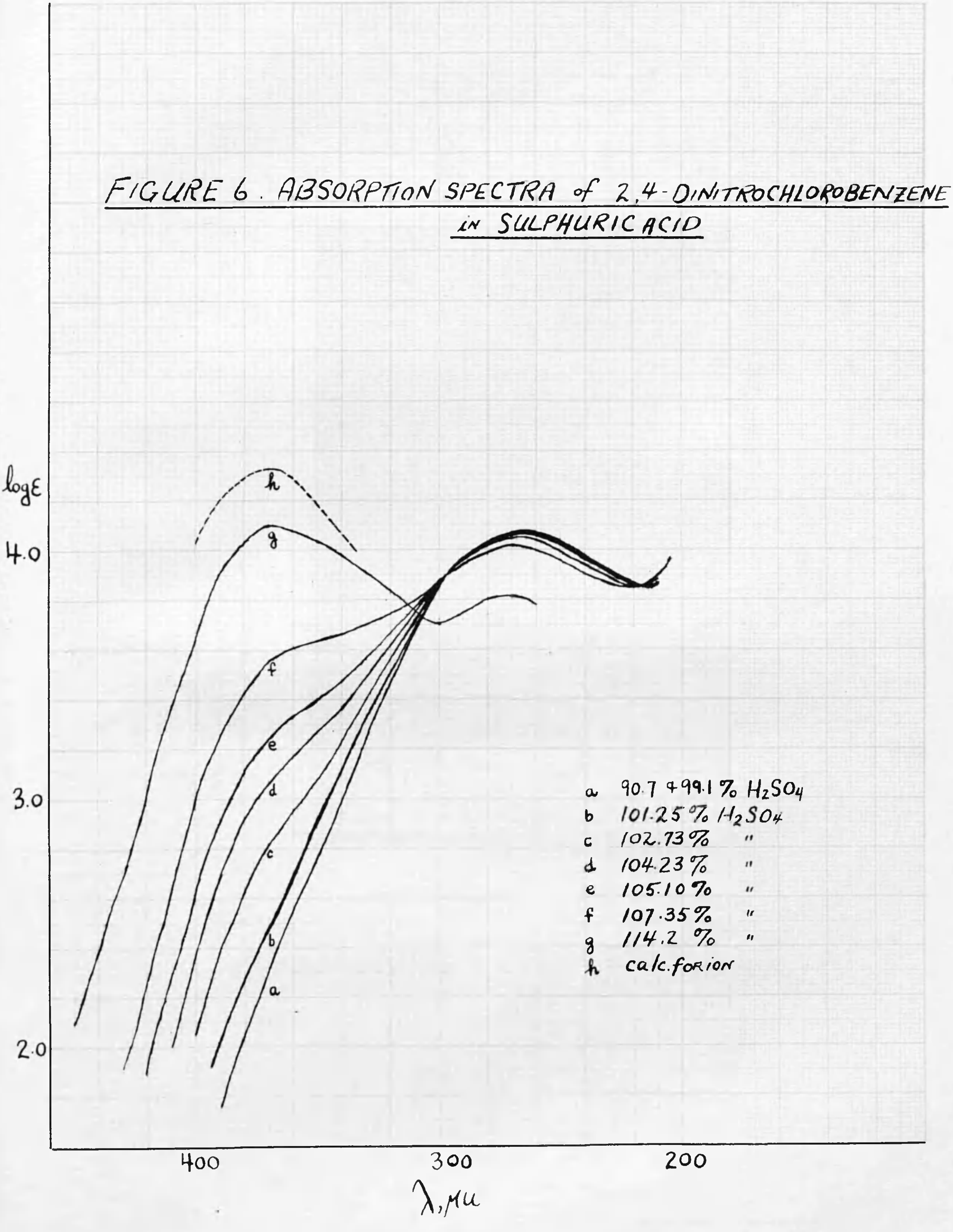
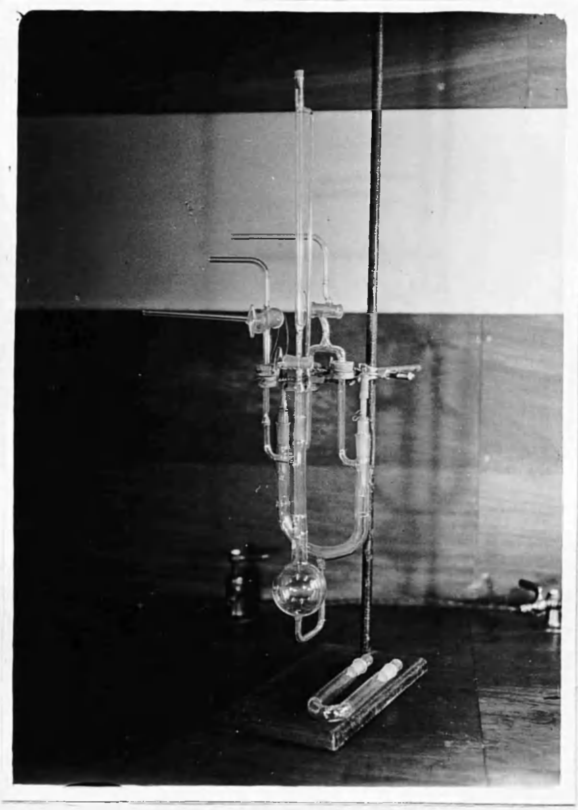
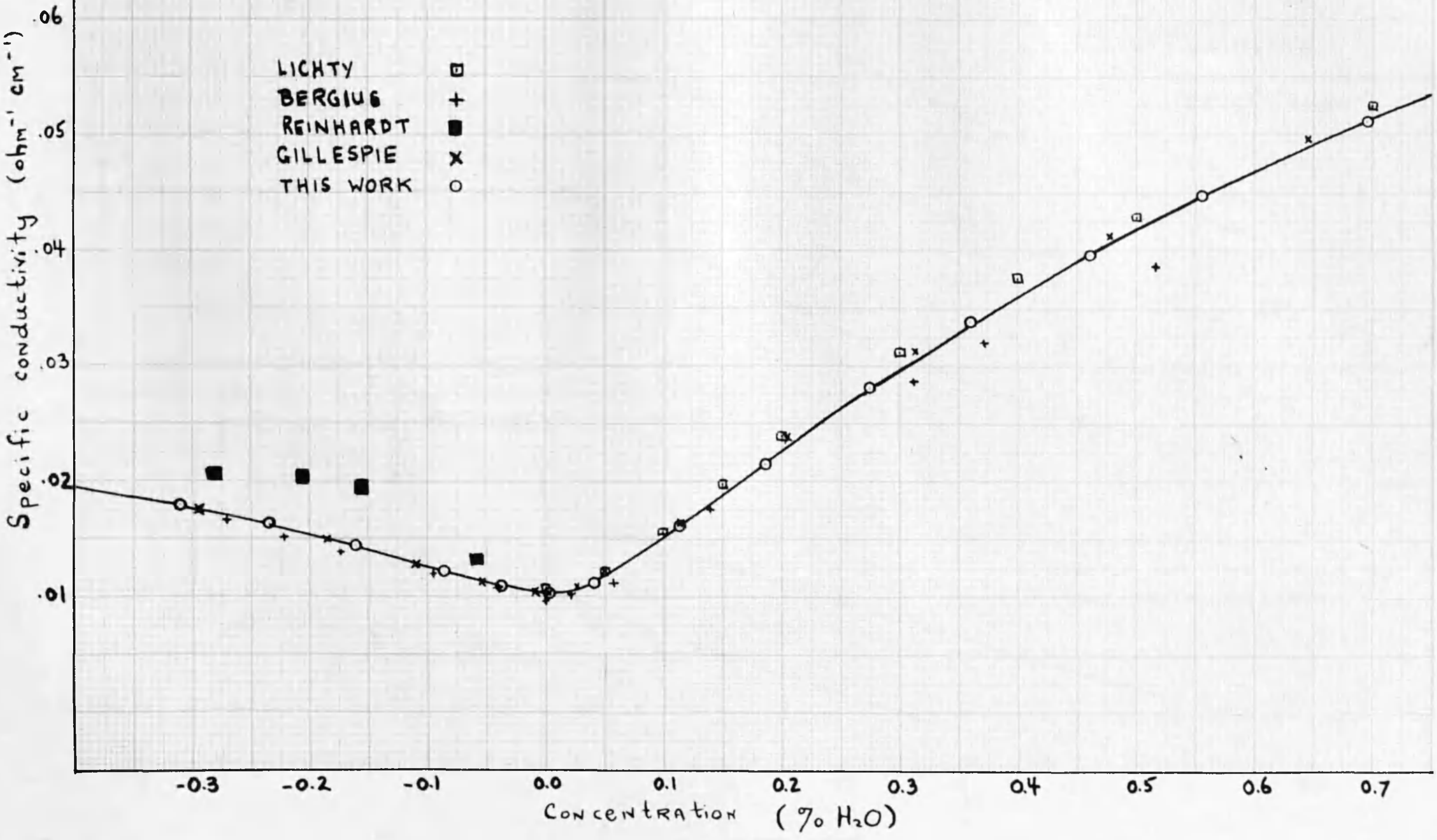


FIGURE 7



CONDUCTIVITY APPARATUS

FIGURE 8. CONDUCTIVITY of SULPHURIC ACID



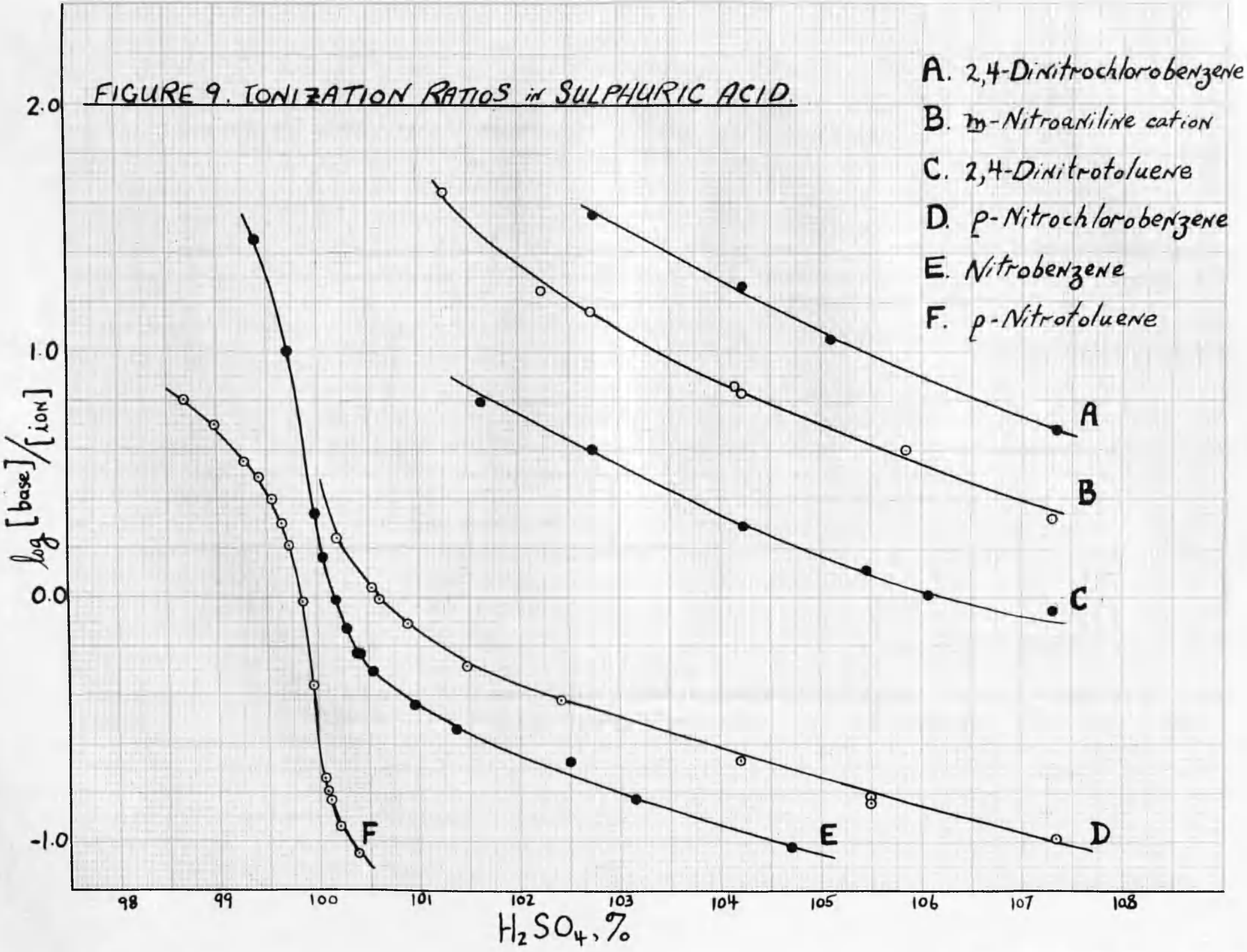


FIGURE 9. IONIZATION RATIOS in SULPHURIC ACID.

FIGURE 10. ACIDITY FUNCTION, J-FUNCTION and VAPOUR PRESSURE of FUMING SULPHURIC ACID

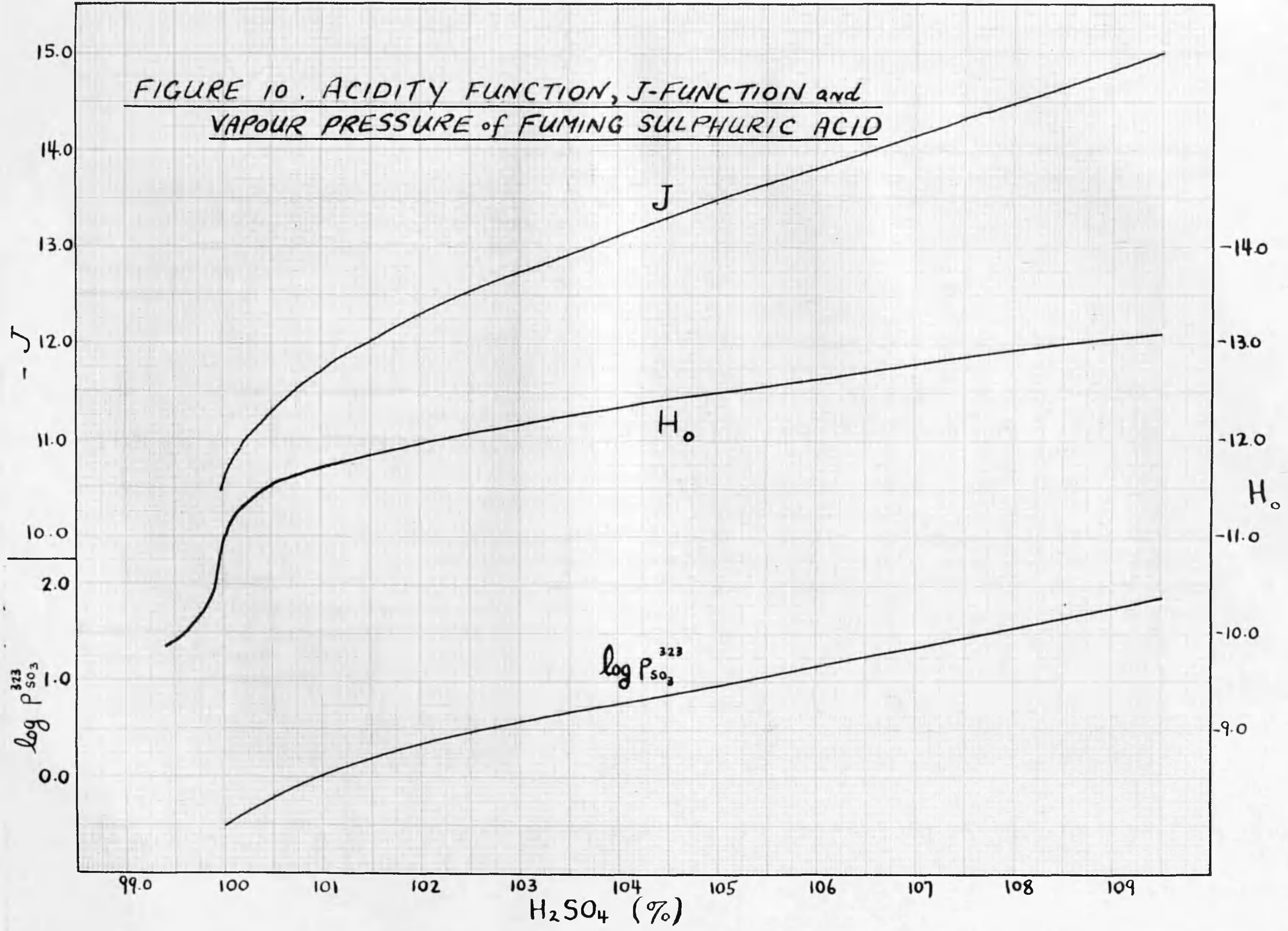
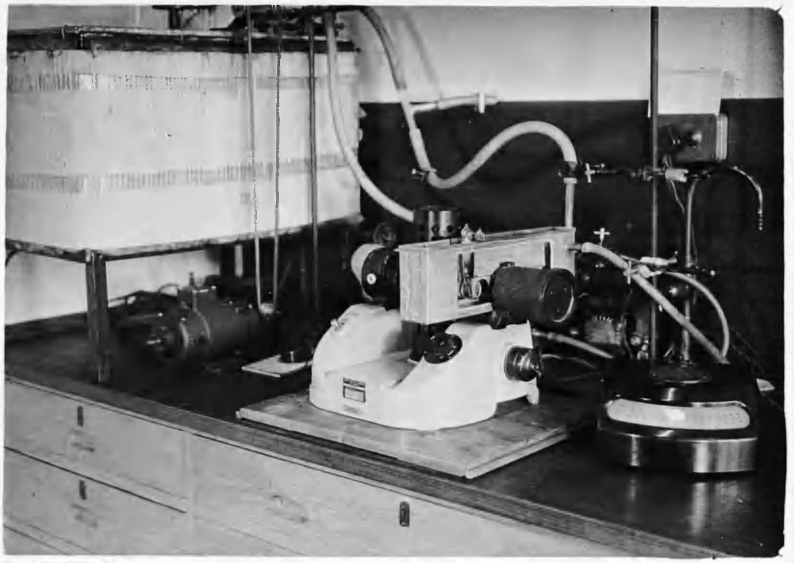
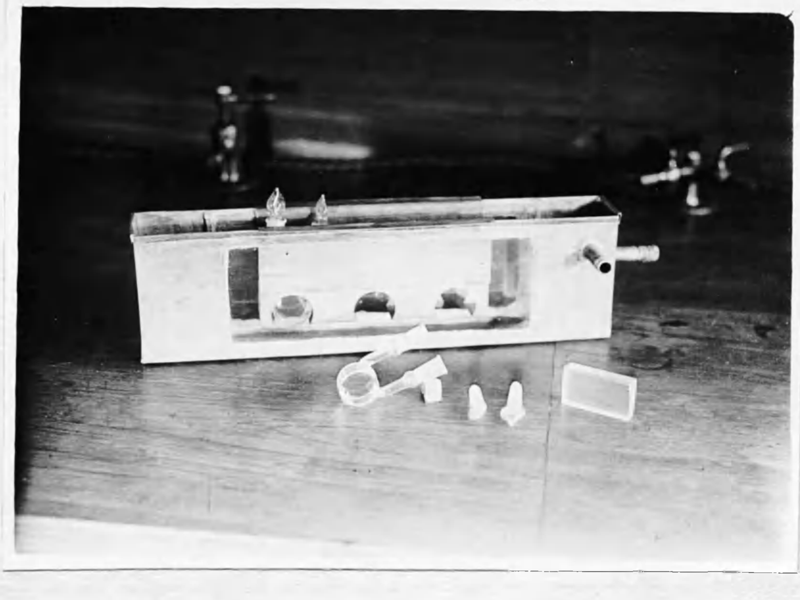


FIGURE 11



SPECTROPHOTOMETRIC APPARATUS



OPTICAL CELLS and SMALL THERMOSTAT

FIGURE 12. ABSORPTION SPECTRA of NITRATION and SULPHONATION PRODUCTS of $p\text{-}F \cdot C_6H_4 \cdot NMe_3^+$ in SULPHURIC ACID

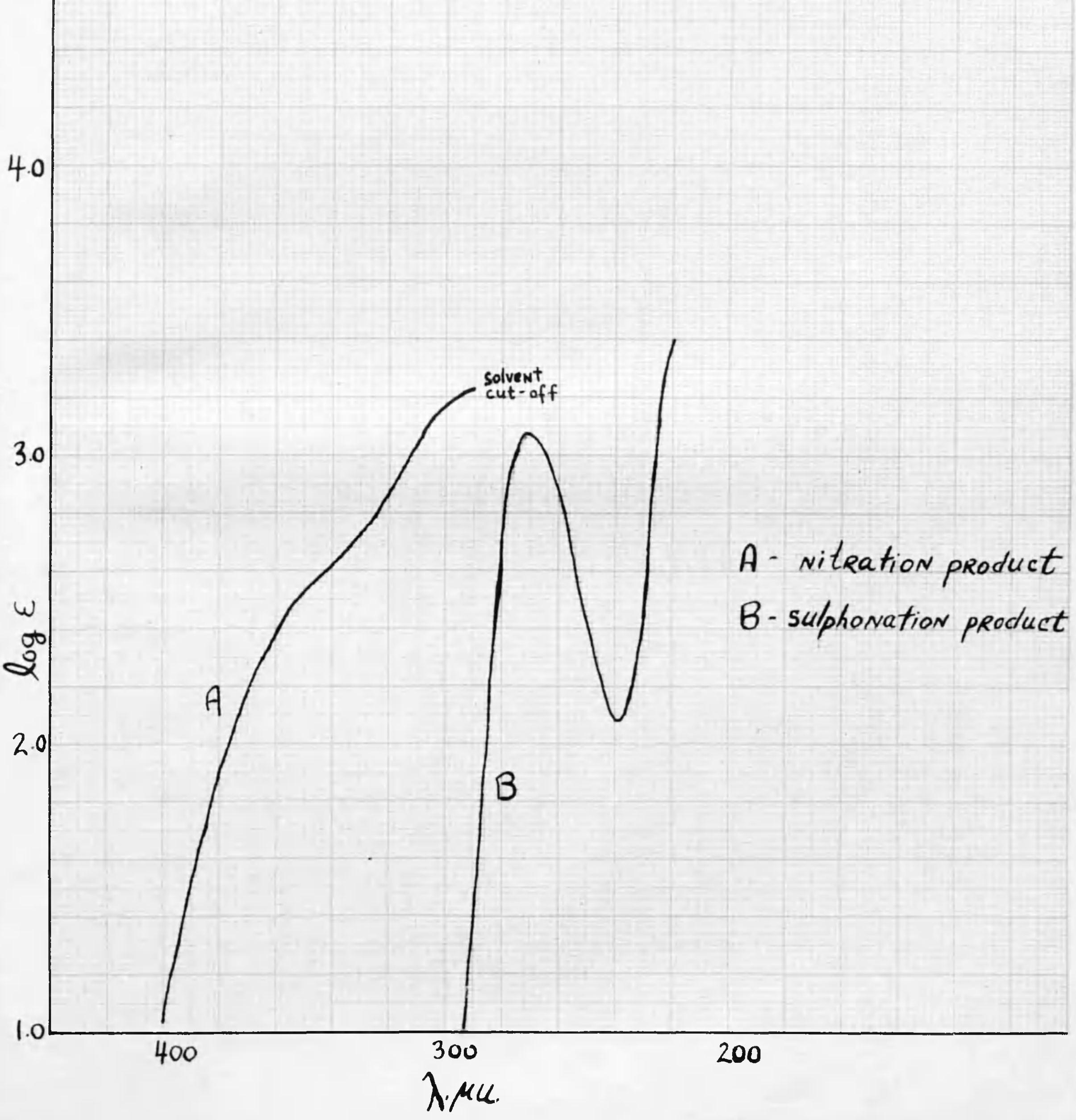
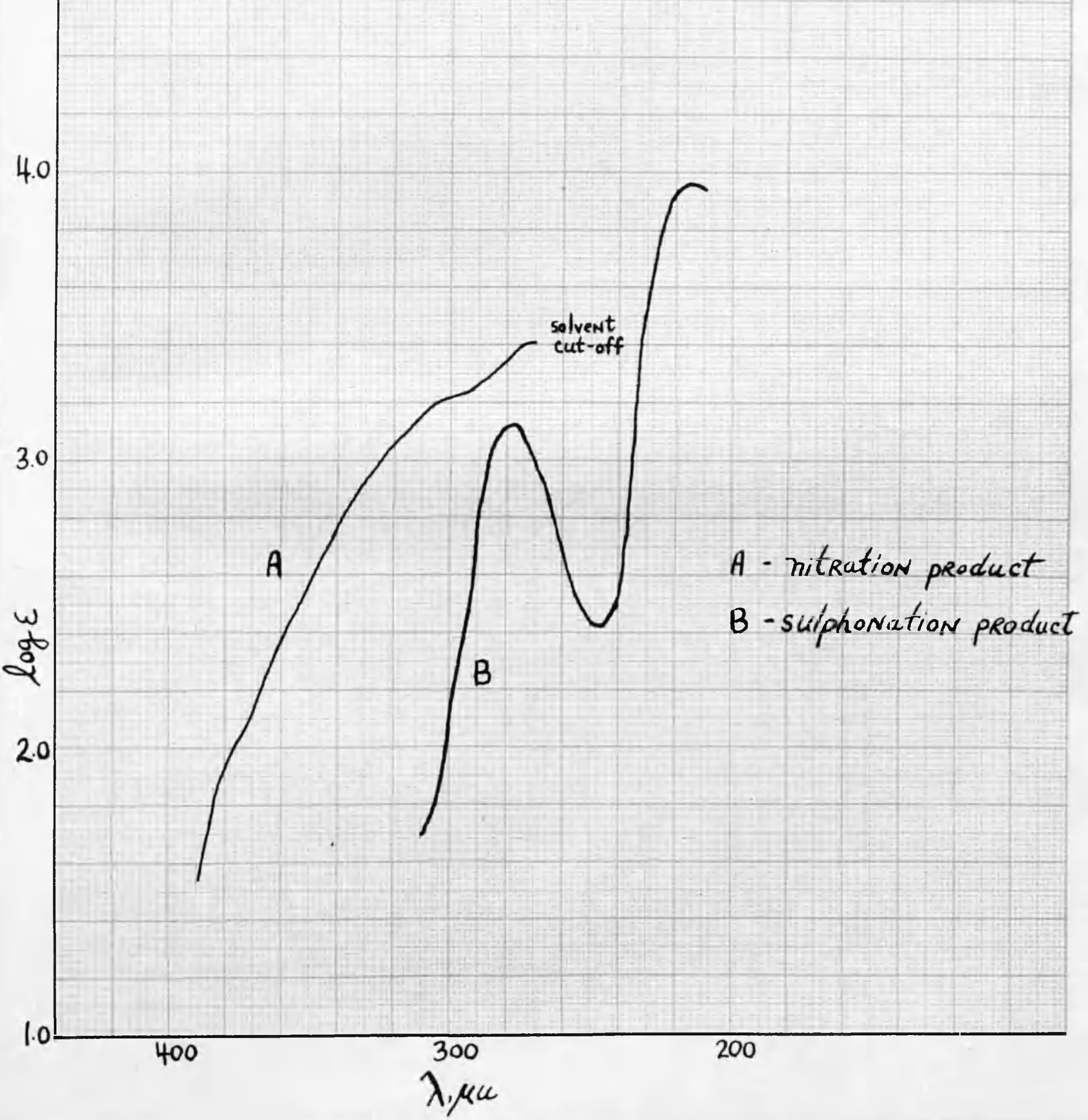


FIGURE 13. ABSORPTION SPECTRA of NITRATION and SULPHONATION PRODUCTS of $p\text{-Cl}\cdot C_6H_4\cdot NMe_3^+$ in SULPHURIC ACID



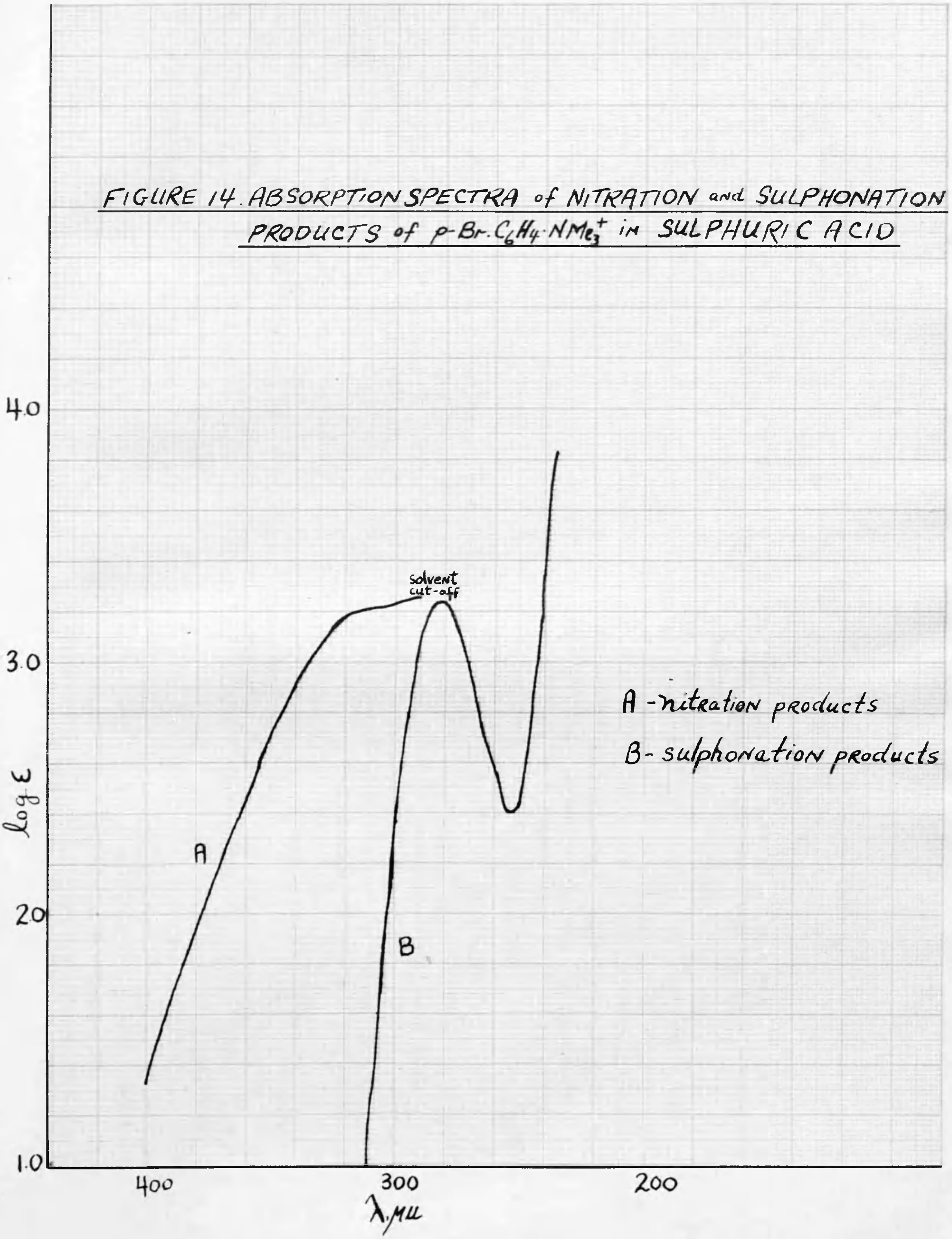


FIGURE 14. ABSORPTION SPECTRA of NITRATION and SULPHONATION PRODUCTS of p-Br.C_6H_4.NMe_3^+ in SULPHURIC ACID

FIGURE 15 . SPECTROPHOTOMETRIC VELOCITY COEFFICIENTS for SULPHONATION in FUMING SULPHURIC ACID

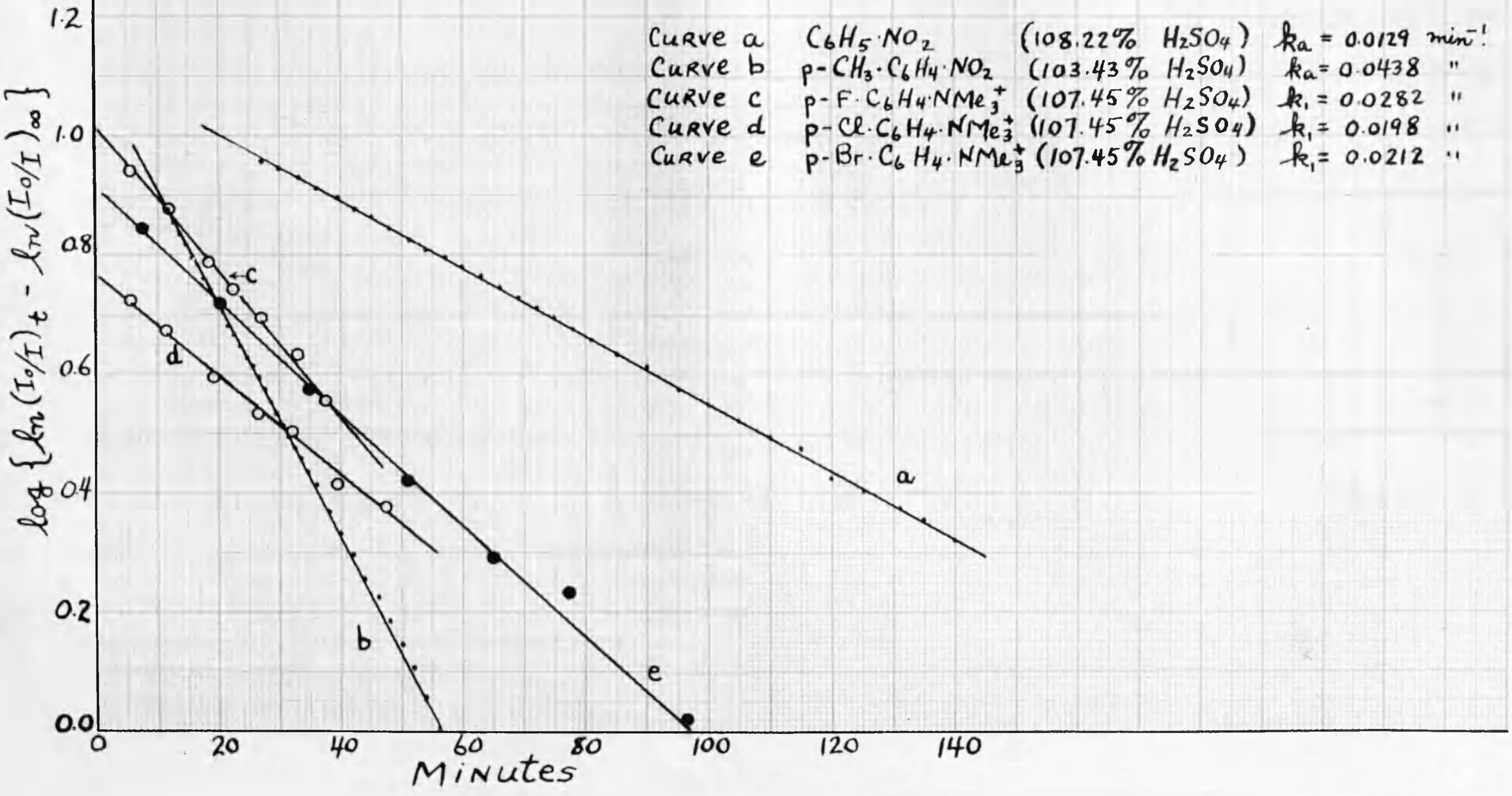
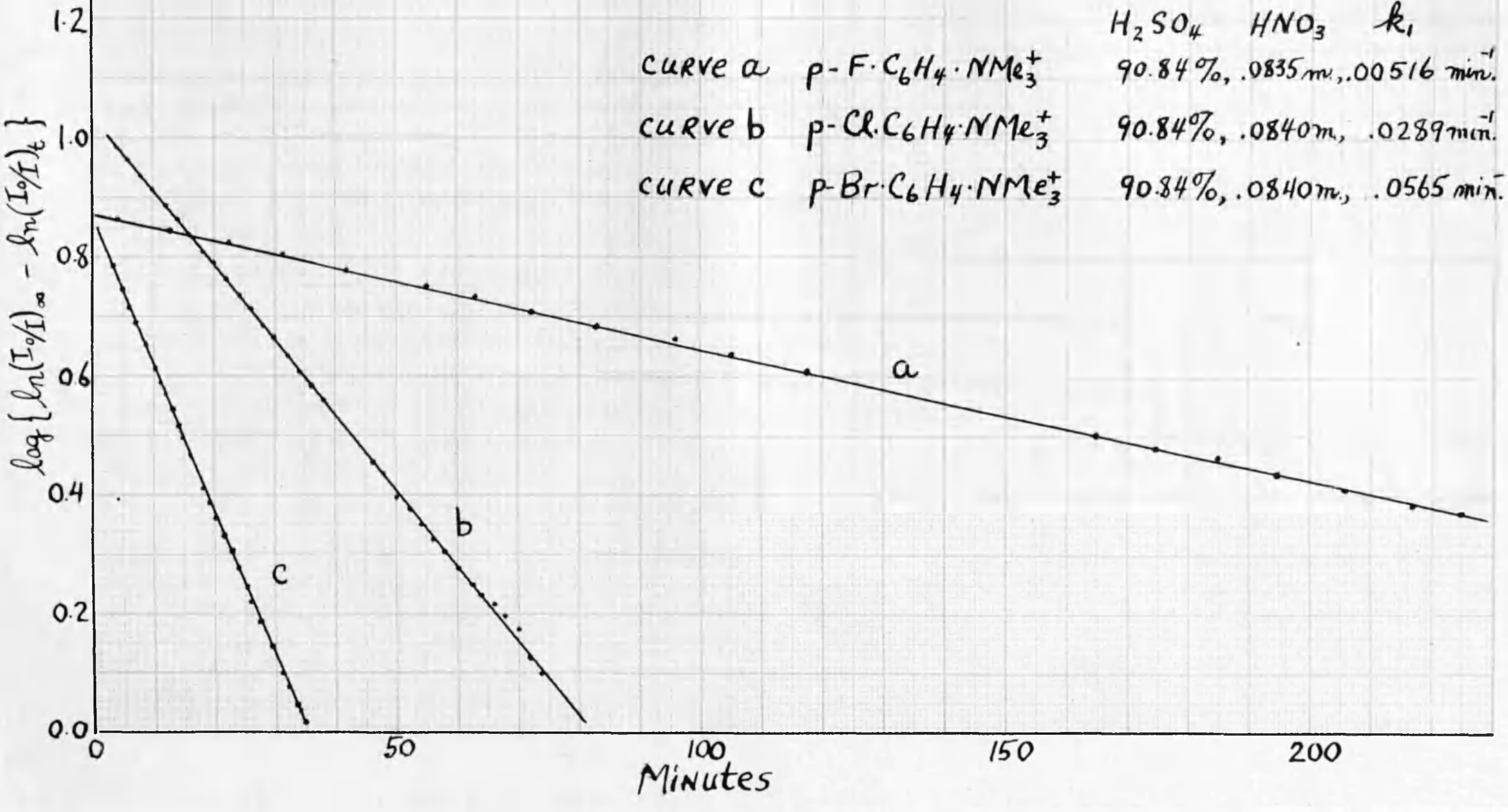


FIGURE 16. SPECTROPHOTOMETRIC VELOCITY COEFFICIENTS for NITRATION in SULPHURIC ACID



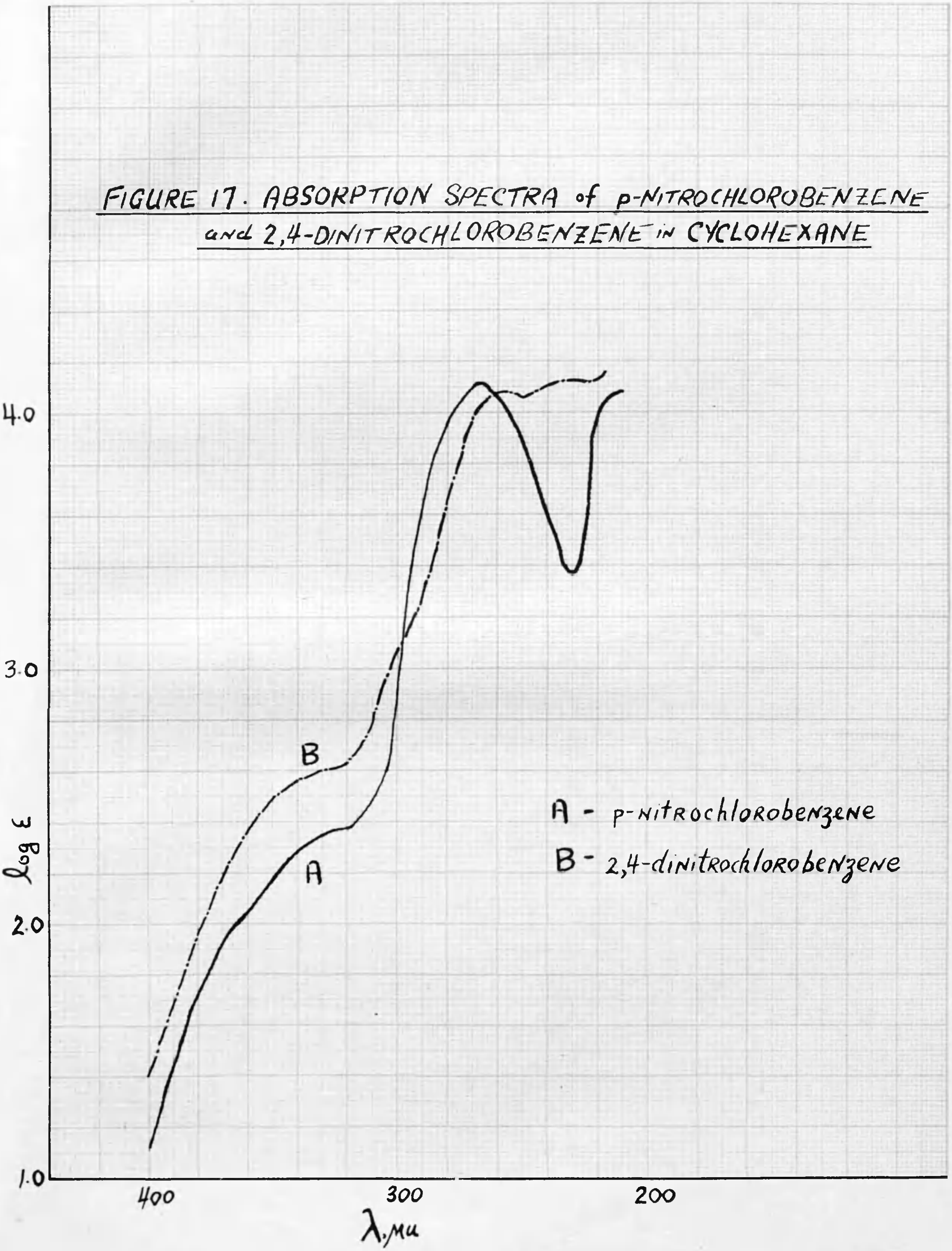


FIGURE 17. ABSORPTION SPECTRA of p-NITROCHLOROBENZENE and 2,4-DINITROCHLOROBENZENE in CYCLOHEXANE

FIGURE 18. ACTIVITY COEFFICIENTS IN SULPHURIC ACID

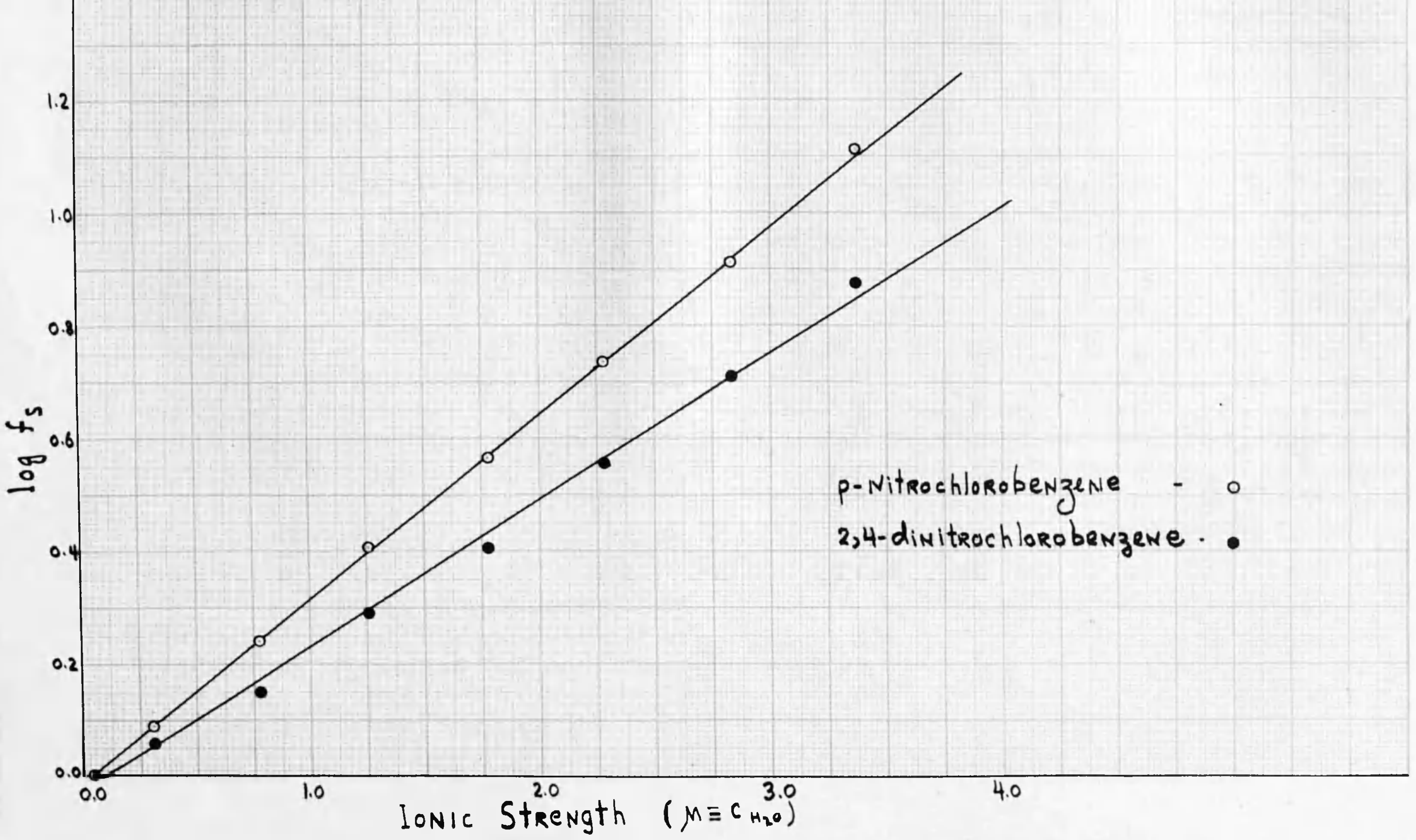


FIGURE 19. VELOCITY of SULPHONATION as a FUNCTION of J

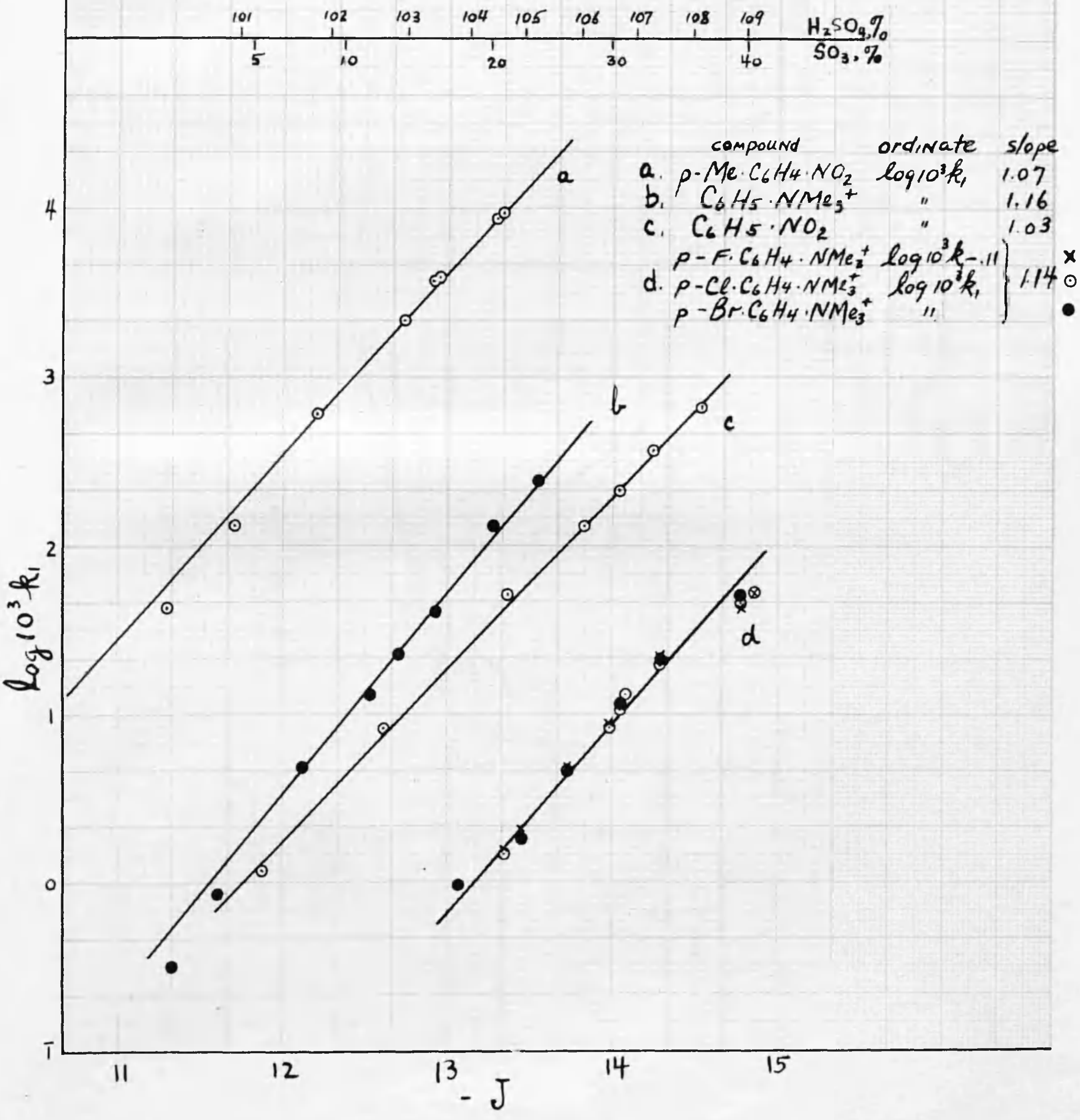


FIGURE 20. RELATIVE VELOCITIES of SUBSTITUTION of $p\text{-Hal}\cdot C_6H_4\cdot NMe_3^+$