N.M.R. STUDIES IN STRONG ACID SOLVENTS

N.M.R. STUDIES OF PROTONATION AND HYDROGEN BONDING IN STRONG ACID SOLVENTS

by

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SCOPE AND CONTENTS:

The protonation for several classes of weak bases has been studied by n.m.r. techniques and the structure of the conjugate acids determined. The rates of proton transfer and the activation energies for some of the processes have been calculated and in the cases of the methylbenzene-HSO_3F systems the mechanism of the proton transfer process has been elucidated.

The acidity function (H_0) for the HSO_3F/SbF_5 system has been redetermined and extended to higher concentrations of SbF_5. The application of some n.m.r. methods to the measurement of H_0 is discussed.

The behaviour of the n.m.r. spectra of sulphuric and fluorosulphuric acids upon the addition of electrolytes has been studied and the results interpreted.

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CHAPTER I

INTRODUCTION

(1) HISTORICAL

(a) General

This thesis describes an investigation of the behaviour of acids and bases in solution by means of nuclear magnetic resonance spectroscopy. This technique can be used particularly to study the rates of proton exchange between acids and bases, and the nature and relative amounts of the species present in acid-base equilibria.

In nuclear magnetic resonance spectroscopy, a nucleus is used as a magnetic probe to investigate local magnetic effects inside a molecular system. The local magnetic field near a particular nucleus depends on its chemical environment and is determined by a number of factors including the polarisation of remote parts of the sample, magnetic moments of neighbouring nuclei, and intramolecular effects due to other nuclei and electrons in the same molecule. This form of spectroscopy is therefore of great value in the investigation of molecular structure and environmental effects and its application to many chemical problems has followed rapidly upon the development and refinement of experimental techniques.[1]

(b) The Nuclear Magnetic Resonance Experiment.

If a nucleus with a magnetic moment is placed in a uniform magnetic field H_0' in the z direction, its energy is $-\mu_z H_0'$, where μ_z is the component of the nuclear moment in the z direction. For a nucleus of

spin I there are 2I + 1 allowed orientations of the magnetic moment with energies

$$-\mu H_o', \ -\frac{I-1}{I}\mu H_o', \ldots\ldots, \ \frac{I-1}{I}\mu H_o', \mu H_o' \qquad (1.1)$$

These energy levels are equally spaced and separated by $\frac{\mu H_o'}{I}$. The basis of the n.m.r. experiment is to induce transitions between these levels. This is done by irradiating the nuclear magnet situated in a magnetic field, with electromagnetic radiation of the appropriate frequency. Only transitions between neighbouring levels are allowed by the selection rules, hence the frequency ν that will cause transitions is given by

$$h\nu = \frac{\mu H_o'}{I} \qquad (1.2)$$

where h is Planck's constant. Equation (1.2) is known as the resonance condition and is often written in the form

$$\nu = \frac{\gamma H_o'}{2\pi} \qquad (1.3)$$

where γ is the gyromagnetic ratio. Thus for a given magnetic field H_o', and provided that all environmental effects are ignored, transitions are observed at a characteristic frequency for each species of nucleus, that is proportional to both H_o' and γ.

(c) The Chemical Shift

The nuclear magnetic resonance frequency of a particular nucleus actually occurs at different values of a given applied magnetic field, according to the nature of the chemical environment of the nucleus. This arises from the fact that when an atom or molecule is placed in a magnetic field, of strength H_o', it acquires a diamagnetic moment by virtue of the induced orbital motions of its electrons. These moving electrons constitute effective currents within the molecule thereby producing a

secondary magnetic field which acts in opposition to the applied field: the magnitude of this secondary field is proportional to the applied field. Thus the magnetic field at the site of the nucleus is given by

$$H = H_o (1 - \sigma) \qquad (1.4)$$

where σ is the screening constant. The value of σ depends on the chemical environment of the nucleus under consideration.

Nuclei of the same kind in chemically non-equivalent positions in a molecule i.e. with different screening constants, resonate at different applied fields, hence they give signals in different parts of the spectrum. The displacement between these signals is referred to as a chemical shift. Such shifts are measured from some reference signal: proton resonances are generally quoted with respect to the single tetramethylsilane resonance. Since the chemical shift, measured in cycles per sec (c.p.s.), is proportional to the applied field, it is convenient to use the nondimensional unit, δ, defined by

$$\delta = \frac{H - H_r}{Hr} \times 10^6 \qquad (1.5)$$

where δ is in parts per million (p.p.m.), and H and Hr are the resonance fields of the sample being measured and that of a reference substance. Since the resonance frequency and applied field are proportional (1.3), an equivalent expression for the chemical shift is

$$\delta = \frac{\nu - \nu_r}{\nu_r} \times 10^6 \qquad (1.6)$$

which can be replaced by

$$\delta = \frac{\nu - \nu_r}{\text{oscillator frequency in Mc.p.s.}} \times 10^6 \qquad (1.7)$$

since ν and νr differ only very slightly from the oscillator frequency.

The spectrum of ethyl alcohol, under conditions of low resolution,

consists of three separate signals corresponding to the three different types of hydrogen atoms present. As a consequence of the fact that the area of a peak depends only upon the number of nuclei from which the signal originates, and since the peaks have relative areas of 1: 2: 3, it is possible to assign the three peaks in ethyl alcohol to the OH, CH_2 and CH_3 groups.

Different functional groups have chemical shifts which are characteristic of the group and which vary only over a limited range for each group. Thus the positions of resonance lines used in conjunction with area measurements can be used to identify the presence of functional groups and the relative numbers of nuclei in each environment in a liquid or gaseous system.

(d) Spin-Spin Interactions

Under high resolution conditions the spectrum of ethyl alcohol, containing a small amount of acid, contains more lines than can be accounted for on the basis of chemical shift considerations. This is because the nuclei in one position can affect the nuclei at another position by electron-coupled spin-spin interaction. The spins of the two protons of the methylene group may be combined in four possible ways as shown in Fig. 1.

	Total spin
↑ ↑	+ 1
↑ ↓	0
↓ ↑	0
↓ ↓	- 1

Fig. 1 SPIN ARRANGEMENTS OF METHYLENE GROUP PROTONS

Each possible value of the total spin produces a different magnetic field at the methyl protons, and consequently the methyl proton resonance is split into a triplet whose components have the relative intensities 1: 2: 1 (there is twice the probability for the total spin to be zero). In a similar manner the spins of the methyl group can combine to give a total spin of $+\frac{3}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, or $-\frac{3}{2}$ with relative probabilities of 1: 3: 3: 1, hence the signal from the methylene group is a quartet with these relative intensities. The separation (in c.p.s.) between the components of a multiplet is a measure of the spin-spin coupling constant J, which is independent of the applied magnetic field.

(e) Exchange Effects

The n.m.r. spectrum may be modified if the nuclei being examined are taking part in a rate process e.g. exchange between different chemical positions. If the exchange is rapid a coalescence of some signals will be observed in accordance with the equation.

$$\tau \Delta \nu \approx \frac{1}{2\pi} \qquad (1.8)$$

where τ is the smallest time for which the two separate states can be distinguished and $\Delta\nu$ is the separation of the corresponding resonance lines. Thus when the exchange is sufficiently rapid, the lifetimes of the states become less than this critical value, and the signals coalesce. The simplest exchange process is that in which a particular type of nucleus is moving from site A to site B: if the exchange rate is slow two signals are observed; if it is rapid, only one signal is observed in an appropriately averaged position. The theory for such an exchange process has been given by Gutowsky et al,[2] and by McConnell[3].

The Bloch equations apply to the macroscopic moment M when all the nuclei are acted upon by the same field Ho. Consider two non-equivalent nuclei A and B with a chemical shift given by $\frac{\omega_A - \omega_B}{2}$ c.p.s. where

$\omega = 2\pi\nu = \gamma$ Ho is the Larmor frequency. Under conditions of no exchange between the positions A and B, there will be two independant macroscopic moments, with complex G components obeying equations

$$\frac{dG_A}{dt} + \alpha_A G_A = -i\gamma H_1 M_{OA} \tag{1.9}$$

$$\frac{dG_B}{dt} + \alpha_B G_B = -i\gamma H_1 M_{OB} \tag{1.10}$$

where H_1 is the rotating field perpendicular to Ho, Mo is equilibrium value of the macroscopic moment, which is given by $Mo = \chi_o Ho$ (χ_o being the volume magnetic susceptibility), and α_A and α_B are complex quantities defined by

$$\alpha_A = \frac{1}{T_{2A}} - i(\omega_A - \omega) \tag{1.11}$$

$$\alpha_B = \frac{1}{T_{2B}} - i(\omega_B - \omega) \tag{1.12}$$

T_{2A} and T_{2B} being the transverse relaxation times of nuclei in the two positions in the absence of exchange.

By allowing for the exchange of nuclei between positions A and B the following expression for the total complex moment is obtained [2,3]

$$G = G_A + G_B = -i\gamma H_1 M_o \frac{\tau_A + \tau_B + \tau_A \tau_B (\alpha_A P_A + \alpha_B P_B)}{(1 + \alpha_A \tau_A)(1 + \alpha_B \tau_B) - 1} \tag{1.13}$$

where τ_A and τ_B are the mean lifetimes for the nucleus on sites A and B, and P_A and P_B are the fractional populations of sites A and B. These are related by the equations

$$P_A = \frac{\tau_A}{\tau_A + \tau_B} \quad ; \quad P_B = \frac{\tau_B}{\tau_A + \tau_B} \tag{1.14}$$

The intensity of absorption at frequency ω is then proportional to the imaginary part of G in equation (1.13). Simplified versions of these equations can be used, to calculate rates of exchange, under certain special conditions, such as those of very slow or very rapid exchange.

Collapse of spin-spin multiplets can also be caused by exchange. The OH resonance of ethyl alcohol, containing a trace of acid, is observed as a single line, instead of the triplet that might be expected as a result of spin-spin coupling with the methylene protons, because the acid catalysed exchange of protons between OH groups causes the triplet to collapse.

The rates of proton exchange can be followed by calculation of theoretical line shapes and comparing these with shapes obtained experimentally. This was first developed by Arnold[4] for exchange between water and alcohols in the presence of small amounts of acid or base. Meiboom and co-workers[5,6] have studied the exchange processes occurring in water at different pH values as well as the processes involved in aqueous alcohol systems. The barrier and rate of rotation about the C-N bond in amides, has been calculated from the collapse of the $N(CH_3)_2$ doublet with increasing temperature, by application of the equation for intermediate exchange rates[7].

(f) Applications of Nuclear Magnetic Resonance to Acid-Base Equilibria and Rates of Proton Exchange

Equilibria between acids and bases in solution can be studied conveniently by n.m.r., particularly with regard to the site from which a proton is removed or to which it becomes attached, and the rate of proton exchange. For example, the rate of proton extraction from

substituted acetylenes in basic solution has been studied by n.m.r. techniques[8]. By observing the changes in the n.m.r. spectrum of aqueous solutions of methylammonium chloride with pH, Grunwald, Loewenstein, and Meiboom[9] were able to obtain quantitative information about the protolysis rate and mechanism. These workers[10] also studied the protolysis of di- and trimethylamine in aqueous solution. Loewenstein and Meiboom[11] have studied di-and trimethylamine solutions and find that the rate of exchange via the solvent increases with increasing methyl substitution. Activation energies of proton transfer reactions in solutions of NH_4^+ and $MeNH_3^+$ have also been obtained[12]. Japanese workers[13,14] have studied the protonation of anilines and pyridine in acetic acid solution. Rapid proton exchange between the base and acid was observed at room temperature. Exchange rates and activation energies for the exchange of N,N-dimethylanilinium ion in trifluoracetic acid solutions have been calculated[15] from the collapse, with increasing temperature, of the methyl doublet due to $H\text{-}\overset{+}{N}\text{-}CH_3$ spin-spin coupling. Protonation of pyridine in trifluoracetic acid has been studied by other workers[16].

A slow proton exchange was postulated to account for the broadness of the β and γ protons in the ring. Danyluk and Schneider[17] found that the n.m.r. spectra of solutions of azulene in CCl_4 and CF_3COOH differed considerably in that the CF_3COOH solution contained an extra peak. This peak, at much higher field than the signal from the aromatic protons of azulene, must be due to a "methylene" group resulting from protonation of the azulene. The site of protonation was deduced from a consideration of the other features of the spectrum.

MacLean and co-workers[18-20] have also observed the appearance of

a "methylene" peak in the spectra of protonated polycyclic aromatic hydrocarbons and polymethyl benzenes. Strongly acidic solvents and in some cases low temperatures were necessary for the observation of the "methylene" peak. These workers[19] corrected the observed chemical shifts obtained for the conjugate acids for the effect of ring currents, and compared the shifts with localised charge densities predicted on the basis of molecular orbital theories. From their work on methylbenzenes in HF/BF_3 solution, MacLean and Mackor[20] have proposed mechanisms for proton exchange. These will be discussed in detail in Chapter IV. These workers[20] have also shown that anisole is protonated on a ring carbon atom rather than the oxygen atom.

The question of O- or N- protonation in amides has been an open one for many years. Jones and Katritzky[21] have recently reviewed the evidence, including the results of n.m.r. studies, that show that protonation occurs predominantly on oxygen. It has been pointed out however[22] that the n.m.r. evidence is rather indirect as no signal from the proton supposedly captured by the oxygen atom on the O- protonated form had been observed in any case. It is shown in this thesis that a separate signal for the OH^+ peak of protonated amides can be obtained by cooling fluorosulphuric acid solutions to low temperatures so that the lifetime of the captured proton becomes long enough for it to give rise to a separate peak in the n.m.r. spectrum[23]. These results are discussed in Chapter III. A low temperature n.m.r. study in HF/BF_3 solution of water, ethyl alcohol, and acetone enabled MacLean and Mackor[24] to obtain the n.m.r. spectra of their protonated forms. Luz and Silver[25] have followed the rate and mechanism of proton exchange for the

$Me_3\overset{+}{P}H$ ion in aqueous solution by observation of the P-H and CH_3-H spin-spin coupling patterns and have calculated a $pK_{B\overset{+}{H}}$ of 8.80 for $Me_3\overset{+}{P}H$.

Edward et al.[26] have attempted to use n.m.r. to measure the extent of protonation of oxygen bases having ethyl groups attached to the site of protonation. MacLean and Mackor[20] were able to observe peaks due to both the protonated and unprotonated forms of some methylbenzenes in solutions of HF/BF_3 under suitable conditions. By measuring the areas of these peaks the extent of protonation was estimated.

(g) The Hammett Acidity Function Ho

The extent of ionisation of acids and bases depends on the solvent. In any protonic solvent the strongest acid and base that can exist in that solvent are the characteristic cation and anion produced in the autoprotolysis of the solvent. In water acids such as HCl, HNO_3, H_2SO_4, and CH_3COOH ionise completely to give $\overset{+}{H_3}O$. Thus it is not possible to detect any differences in the intrinsic strengths of these acids. Indeed the strongest acid that can exist in aqueous solution is the hydronium ion $\overset{+}{H_3}O$. In order to differentiate between the relative strengths of acids such as HCl, HNO_3 and $HClO_4$ it is necessary to use a less basic solvent than water. If sulphuric acid is used as the solvent only $HClO_4$ of the acids mentioned above shows any acid properties. It ionises according to equation (1.15)

$$HClO_4 + H_2SO_4 \rightleftharpoons \overset{+}{H_3}SO_4 + \overset{-}{ClO_4} \qquad (1.15)$$

Sulphuric acid undergoes autoprotolysis according to

$$2H_2SO_4 \rightleftharpoons \overset{+}{H_3}SO_4 + \overset{-}{HSO_4} \qquad (1.16)$$

and an acid may be defined as any compound that produces $\overset{+}{H_3}SO_4$ ions and

a base as one which produces HSO_4^-. HSO_3F and $HB(HSO_4)_4$ are two substances which ionise to produce $H_3SO_4^+$ ions in sulphuric acid solution.

In a similar way HSO_3F undergoes autoprotolysis to give $H_2SO_3F^+$ and SO_3F^- and substances which produce $H_2SO_3F^+$ ions, such as SbF_5[27], are acids, and those which produce SO_3F^- ions are bases e.g. KSO_3F. By measuring the extents of ionisation in a suitable acidic or basic solvent an estimate of the relative strengths of acids and bases can be obtained. However it is difficult to compare the results of an investigation in one solvent system with those in another solvent system. The best method for comparing acid strengths in an absolute manner would be to measure the hydrogen ion activities, a_{H^+}. This is not possible but it was shown by Hammett[28] that a related quantity can be conveniently used.

The Hammett acidity function, Ho, is a measure of the tendancy of a medium to transfer a proton to a base.

From the equation

$$BH^+ \rightleftharpoons B + H^+ \qquad (1.17)$$

the dissociation constant of the conjugate acid BH^+ is given by

$$K_{BH^+} = \frac{C_B \cdot C_{H^+}}{C_{BH^+}} \cdot \frac{f_B \cdot f_{H^+}}{f_{BH^+}}$$

$$= a_{H^+} \cdot \frac{C_B}{C_{BH^+}} \cdot \frac{f_B}{f_{BH^+}} \qquad (1.18)$$

where a is the activity, C is the molar concentration and f is the activity coefficient. The assumption is then made that the ratio $\frac{f_B}{f_{BH^+}}$ is independant of B and its concentration, which is always small.

Hence

$$h_o = K_{BH^+} \cdot \frac{C_{BH^+}}{C_B} = a_{H^+} \cdot \frac{f_B}{f_{BH^+}} \qquad (1.19)$$

is a property of the solution and

$$H_o = -\log h_o = pK_{BH^+} - \log \frac{C_{BH^+}}{C_B} \qquad (1.20)$$

The measurement of Ho then resolves itself into the measurement of the ratio of the concentration of the protonated form to the concentration of the unprotonated form of a base of known pK_{BH^+} dissolved in the solvent being studied. The amounts of BH^+ and B have generally been measured by means of absorption spectra using bases (indicators) that have unprotonated forms. If the extinction coefficients of the fully ionised base ε ion, and of the unionised form ε B are known at a particular wavelength, then for a solution in which the base is incompletely ionised

$$\frac{C_{BH^+}}{C_B} = \frac{\varepsilon \text{ ion} - \varepsilon}{\varepsilon - \varepsilon_B} \qquad (1.21)$$

where ε is the molar extinction coefficient of the base at the same wavelength.

A plot of $\log \frac{C_{BH^+}}{C_B}$ against acid composition of the medium, for each base, gives a series of curves which overlap and are roughly parallel over a limited acid concentration range. By choosing an acid concentration where the overlap between two bases is good, and knowing the pK_{BH^+} of one base, the pK_{BH^+} of the other base can be calculated from (1.22).

$$H_o = pK_{B'H^+} - \log \frac{C_{B'H^+}}{C_{B'}} = pK_{B''H^+} - \log \frac{C_{B''H^+}}{C_{B''}} \qquad (1.22)$$

In this manner it is possible to measure the acidity of solutions of

progressively higher acidity by the use of a series of suitable indicators of decreasing basicity.

(h) Acidity Functions and Nuclear Magnetic Resonance

Values of pK_{BH^+} for weak bases have generally been determined by Hammett's spectrophotometric method[29]. Edward et al.[26] have used the chemical shift difference between the CH_3 and CH_2 protons in ethyl compounds to estimate the relative amounts of BH^+ and B (section (e)). A plot of this chemical shift difference against the acidity function Ho, of the solvent, gave a sigmoid type curve. The steepest portion of this curve was assumed to give the solvent composition at which $C_{BH^+} = C_B$. Equation (1.20) then reduces to

$$Ho = pK_{BH^+} \qquad (1.23)$$

and hence the pK_{BH^+} of the base was obtained. Taft and Levins[30] have used the relatively large chemical shift between the resonances of the protonated and unprotonated forms of fluorobenzene derivatives in the F^{19} n.m.r. spectrum as a means of quantitative pK_{BH^+} determination. By plotting F^{19} chemical shifts vs. the acidity function (Ho) they obtained sigmoid curves and from the point of inflection they obtained pK_{BH^+} as described above. These workers have stated that they intend to use this method to determine acidity functions. Utyanskaya et al.[31] have estimated the acidity function of HF solutions from F^{19} n.m.r. data; the results agree with Ho values obtained by the more usual spectrophotometric method but doubt has been cast[32] on their interpretation of the chemical shifts.

(i) Acid Dissociation, Solvation, and Hydrogen Bonding

Because the rate of proton exchange is rapid in aqueous solutions

of electrolytes the chemical shift of an exchanging proton appears as a weighted average of the chemical shifts of all the species present. This fact has been used to calculate dissociation constants for strong acids. Gutowsky and Saika[33], Masuda and Kanda[34], Hood et al.[35], Gillespie and White[36], and others[37,38] have all examined the dissociation of acids by n.m.r. techniques. Agreement with other physical methods is not always good[1,34]. In studying the dissociation of water in sulphuric acid attempts have been made[35,36] to obtain absolute chemical shifts for H_3O^+ and HSO_4^-, but different values have been obtained for $H_3\overset{+}{O}$ and HSO_4^- in two independent investigations as a consequence of different assumptions made in the interpretation of the results. Hood and Reilly assumed that the chemical shifts of the various species are independent of the composition of the solution over the whole range from water to sulphuric acid, whereas Gillespie and White assume constancy of the chemical shifts over a limited composition range only. In view of the large body of experimental data on the effect of electrolytes upon the chemical shift of ions in solution the assumption of the constancy of chemical shifts is probably not justified and these results probably need some reinterpretation.

It is well recognised that in protonic solvents such as water, ammonia and sulphuric acid intermolecular hydrogen bonding occurs to a greater or lesser extent. It is also known that when ions are present in solution they are generally solvated i.e. associated with a number of solvent molecules. When ions that have a tendancy to solvate are present in a hydrogen-bonded solvent it is clear that they will in general have an effect on the structure of the solvent. Such changes in the solvent

structure will affect the environment around any magnetic nuclei present and hence affect the chemical shifts in their n.m.r. spectra. A comprehensive review of the study of the hydration of ions in aqueous solution by n.m.r. techniques has appeared [39] recently which critically discusses the literature up to 1961. Chemical shifts produced by addition of electrolytes are interpreted in terms of solvation, polarisation and structure breaking effects. Attempts have been made to separate effects such as polarisation and solvation for individual ions. Hindman [40] in a recent paper has analysed the chemical shifts produced by salts in water in terms of bond breaking, structural, polarisation, and nonelectrostatic effects. Gillespie and White [36] have studied the effect of added metal hydrogen sulphates to the proton resonance of sulphuric acid: they obtained an order for the extent of solvation of cations which is in agreement with other measurements.

(2) OBJECTS OF THE PRESENT WORK

One of the objects of the present work was to study the protonation of very weak bases in strong acid solvents. In view of its high acidity and low freezing point, and because a general study of the fluorosulphuric acid solvent system was being carried out in our laboratories, fluorosulphuric acid was chosen as a solvent that appeared to be very suitable for the elucidation of the structures of the protonated forms of weak bases. It was also hoped that by comparison of the extent of protonation of a variety of weak bases in several acid solvents such as HF, HSO_3F and H_2SO_4 it would be possible to obtain information on the relative acidity of these solvents, their mixtures with each other and with water. In particular it was hoped to devise an n.m.r. method for measuring the acidity function for these systems.

In order to provide some background information that might prove useful in the interpretation of chemical shifts in the n.m.r. spectra of bases in acid solvents, it was also decided to extend the work of Gillespie and White[36], on the effect of metal hydrogen sulphates on the proton magnetic resonance spectra of sulphuric acid, to include the effect of metal fluorosulphates and other bases on the HSO_3F proton and fluorine resonances.

CHAPTER II

EXPERIMENTAL

(1) PREPARATION AND PURIFICATION OF MATERIALS

Sulphuric Acid

100% sulphuric acid was prepared by mixing C.P. Reagent grade sulphuric acid and Reagent grade fuming sulphuric acid (30% free SO_3) until a product having a maximum freezing point of 10.37° was obtained [41].

Oleums

Oleums of known composition were obtained by distilling sulphur trioxide from stabilised liquid sulphur trioxide ("Sulphan B"), into a weighed amount of 100% sulphuric acid.

Fluorosulphuric Acid

Technical grade fluorosulphuric acid was distilled twice at atmospheric pressure in the apparatus shown in Fig. 1. Before use the still was dried out by passing dry air through it and at the same time warming with a Bunsen flame. The pure acid had a boiling point of 163 - 164°.

Tetrahydrogensulphato boric acid

The stoichiometric amount of boric acid, twice recrystallised from water and dried at 120°, was dissolved in oleum of known sulphur trioxide concentration to give the required composition of tetrahydrogensulphato boric acid in sulphuric acid [42].

Trifluoracetic acid

Reagent grade trifluoracetic acid was distilled using a 20" fractionating column packed with glass helices. The fraction boiling at 72° (lit. b.p. 72.4°) was collected.

Sulphates

Except for those listed below all the sulphates were "Analar" salts dried at 120° and stored over phosphoric oxide until required.

Lithium sulphate

The "Analar" monohydrate was heated at 190° to constant weight, then stored over phosphoric oxide.

Rubidium sulphate

"Analar" rubidium carbonate was dissolved in water and titrated with 0.2N sulphuric acid to neutrality. The neutral aqueous solution was evaporated until the rubidium sulphate began to crystallise, then cooled, filtered, washed with acetone, then ether; finally dried at 120° and stored over phosphoric oxide.

Calcium sulphate

Calcium sulphate dihydrate was dissolved in 100% sulphuric acid, the solution filtered through a sintered glass filter and the dihydrate precipitated by pouring the solution into distilled water. The precipitate was filtered, washed free of SO_4^{--}, dried and ignited at red heat in a platinum crucible to constant weight. The calcium sulphate was stored over phosphoric oxide.

Tetraethylammonium sulphate

To a solution of tetraethylammonium bromide in water was added an excess of freshly prepared silver oxide and the mixture shaken to ensure thorough mixing. The excess silver oxide and the precipitated

silver bromide were filtered off. A portion of the filtrate was tested for the presence of bromide ion with silver nitrate; all of the bromide ion had been removed. The filtrate was titrated to pH7 with 0.2 N H_2SO_4, evaporated until crystallisation occurred, cooled, filtered in a dry atmosphere and washed with dry ether. The pale yellow crystals obtained were redissolved in distilled water, the solution treated with active charcoal and filtered after standing for a few minutes; the filtrate was clear and colourless. Evaporation to dryness was effected by heating at 110° on an oil bath while a current of dry, filtered air was blown over the surface. This stream of dry air over the heated crystals was continued for several hours with frequent stirring to ensure that all the moisture was removed. Finally the salt was allowed to cool, under vacuum over phosphoric oxide. The crystals were very **hygroscopic**

Analysis

% SO_4 = 26.11 (Calculated 26.95)

Tetraphenylarsonium sulphate

30 gms. of anhydrous aluminium chloride, 30 gms. of triphenyl arsine and 15.6 gms. of bromobenzene were heated at 200° under reflux (air condenser) for one hour. A vigorous reaction occurred which later subsided. The temperature was then raised to 280° over a period of half an hour and maintained at this temperature for a further half hour. The mixture was poured into 1200 mls. water, boiled with active charcoal, filtered and when cold, the filtrate was treated with 30 gms. KI dissolved in a few mls. of water. Crude Ph_4AsI_3 was obtained as yellow crystals which were filtered off and recrystallised from hot water containing KI and 10 gms. Na_2SO_3 to yield pure Ph_4AsI_3.

This iodide was dissolved in ethyl alcohol water mixture and the solution treated with freshly precipitated silver oxide. After shaking, the mixture was filtered to remove the precipitated AgI and excess Ag_2O, then neutralised with 0.2N H_2SO_4. The solution was evaporated to dryness and purified in the same way as described for tetraethylammonium sulphate. The white solid was stored over phosphoric oxide.

Analysis

% SO_4 = 10.86, 10.91 (Calculated 11.14)

Fluorosulphates

Metal fluorosulphates were prepared by distillation of excess fluorosulphuric acid on to the anhydrous metal chlorides, then removing the hydrogen chloride formed and the excess fluorosulphuric acid by heating on a water bath under high vacuum [44]. The fluorosulphates were used within a few days of their preparation.

Antimony Pentafluoride

Commercial antimony pentafluoride was distilled twice in a dry atmosphere, a low boiling fraction being rejected both times. The fraction boiling between 142 - 144° was collected for use.

Organic Solvents

Carbon tetrachloride and chloroform of "Spectrochemical" grade were used without further purification.

Dioxan

Purification was effected by refluxing over sodium, followed by fractional distillation through a 20" column packed with glass helices. The fraction boiling between 101 - 102° (lit. b.p. 101-5°) was collected for use.

Acetone

Commercial acetone was refluxed with successive small quantities of potassium permanganate until the violet colour persisted. It was then dried with anhydrous calcium sulphate, filtered from the desiccant, and fractionally distilled: care was taken to exclude moisture. The fraction boiling between 56 - 56.5° (lit. b.p. 56°) was collected.

Nitromethane

Commercial nitromethane was dried over calcium chloride then distilled using a 20" column packed with glass helices. The fraction boiling between 100 - 101° (lit. b.p. 101°) was collected for use.

Organic Bases

The organic bases used were generally obtained commercially; solids were recrystallised from suitable solvents and stored over phosphoric oxide, liquids were used without further purification except those listed below. In all cases the n.m.r. spectra, run at high gain, showed no peaks which could be attributed to impurities.

Acetophenone

Acetophenone was distilled from a flask fitted with an air condenser and take off. The fraction boiling between 201 - 202° was collected (lit. b.p. 202°).

N-Methyl-2,4-dinitroaniline

To a solution of 1-chloro-2,4-dinitrobenzene in n-butanol was added the stoichiometric amount of methylamine. On standing yellow crystals of N-methyl-2,4-dinitroaniline were formed which were filtered, washed with butanol, recrystallised from butanol, dried and stored over phosphoric oxide. m.p. 85° (lit. m.p. 85 - 86°).

N,N-Dimethyl-2,4-dinitroaniline

Dimethylamine was added, in stoichiometric quantity, to a solution of 1-chloro-2,4-dinitrobenzene in n-butanol when a yellow solution resulted. This solution was treated with NaOH, until excess base was present, then shaken vigorously until yellow crystals formed. These were filtered, recrystallised from aqueous ethanol, dried and stored over phosphoric oxide m.p. 79° (lit. m.p. 80°).

N-Methyl-2-chloro-4-nitroaniline[45]

8.2 gms. of 2-chloro-4-nitroaniline were mixed with 4.5 mls. of Me_2SO_4 and the mixture heated on a waterbath for one hour. Aqueous NaOH solution was added, the mixture cooled, the solid filtered off, washed well with water and finally recrystallised from aqueous ethanol. The yellow crystals were dried and stored over phosphoric oxide. m.p. 116° (lit. m.p. 116 - 117°).

N-Methyl-4-chloro-2-nitroaniline

This was prepared from 4-chloro-2-nitroaniline by the same procedure as above. The orange crystalline product had a m.p. of 105° (lit. m.p. 106 - 106.5°).

N,N-Dimethyl-2,4,6-trinitroaniline[46]

Dimethylamine was added to a hot solution of 1-chloro-2,4,6-trinitrobenzene in 95% ethanol when crystals were rapidly precipitated. These were filtered off, recrystallised from benzene, dried and the melting point determined. m.p. 138-139° (lit. m.p. 138°).

N-Methyl-p-toluenesulphonamide

To 1 gm. of methylamine was added 20 mls. of a 10% sodium hydroxide solution and 1 gm. of p-toluenesulphonyl chloride. The mixture

was shaken vigorously then filtered. The filtrate was acidified with concentrated HCl and cooled: the solid produced was filtered off, washed well with water, recrystallised from 95% ethyl alcohol, dried and stored over phosphoric oxide. m.p. 78° (lit. m.p. 78 - 79°).

N,N-Dimethyl-p-toluenesulphonamide

This was prepared from dimethylamine by the same procedure as above. In this case acidification was not necessary since the product is insoluble in NaOH solution. The product was recrystallised from 95% ethyl alcohol, dried and stored over phosphoric oxide. m.p. 86 - 87° (lit. m.p. 86 - 87°).

Urea

The gift of a sample of N^{15} urea from Dr. K. Yates is gratefully acknowledged.

Dry Air

Air was dried by passing it successively through tubes containing anhydrous calcium chloride and anhydrous magnesium perchlorate. Dust from the drying agents was removed from the gas stream by plugs of glass wool.

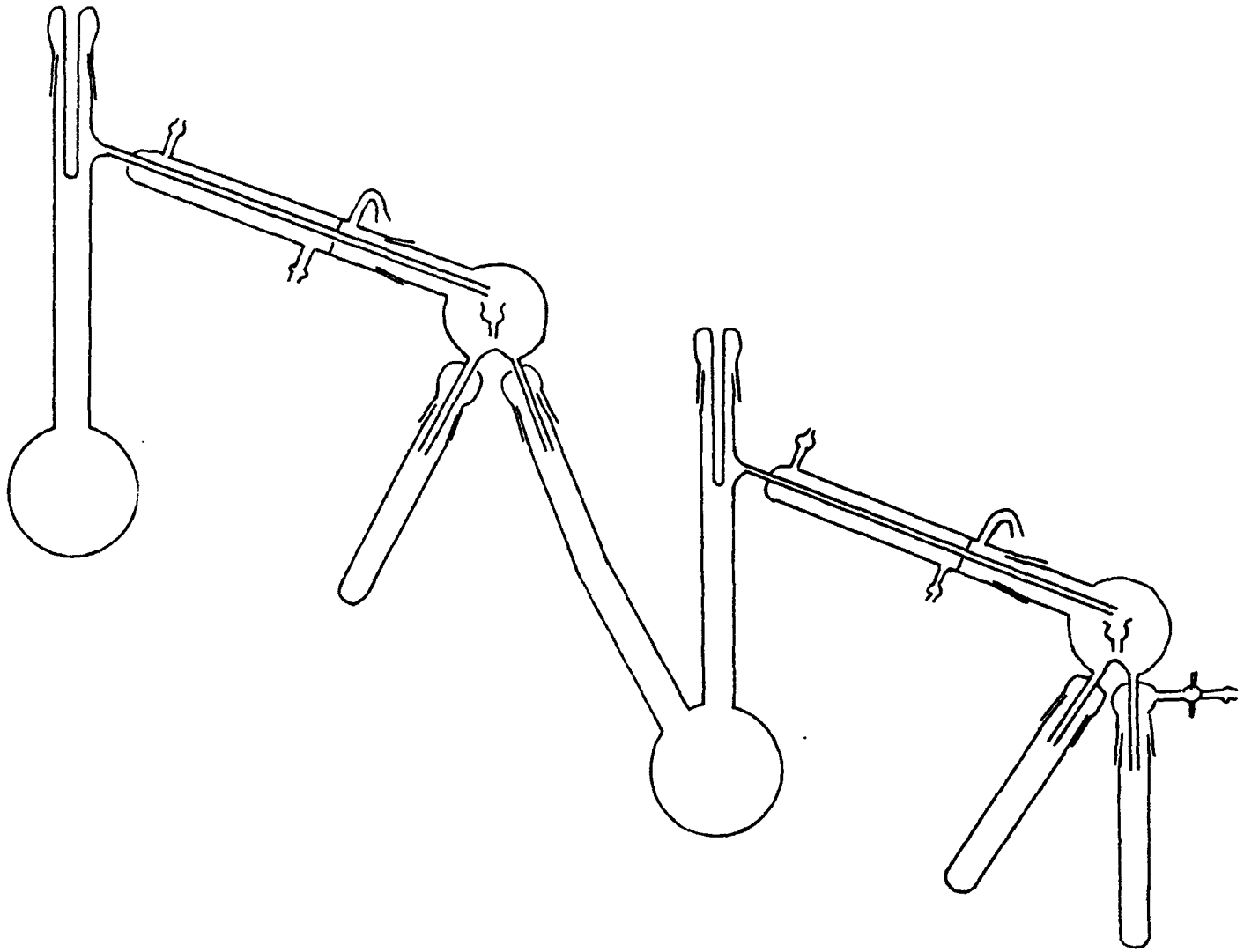


Fig. 2 FLUOROSULPHURIC ACID DISTILLATION APPARATUS

(2) NUCLEAR MAGNETIC RESONANCE SPECTRA

The n.m.r. Spectra were recorded with a Varian H.R-60 N.M.R. spectrometer equipped with a field homogeneity control unit, an integrator, and a variable temperature probe. Proton spectra were recorded at 60 Mc.p.s., except where stated, and Fluorine^{19} spectra at 56.4 Mc.p.s.

Samples were contained in 5 m.m. O.D. "Pyrex" tubes made from carefully selected tubing. Except where the solvent was an organic one external references were used throughout. The reference liquid was contained in a thin walled capillary tube held central in the sample tube by a tightly fitting teflon cap. Signal separations were measured by the side-band technique due to Arnold and Packard[47]. The magnetic field is modulated with a low-amplitude audio-frequency signal which produces side bands on either side of the resonance signals in the spectrum. The separation of these side bands from the resonance signal is equal to the modulation frequency. By judicious choice of one, or more, modulation frequencies, the separation of all the peaks in the spectrum, from the reference signal, are accurately determined.

The separations of the peaks in a spectrum found by the above method is a measure of the chemical shift between the species present. These separations may be expressed in frequency or magnetic field units, and the two units may be interconverted by the equation for the resonance condition (1.2). However it is more usual to express chemical shifts in a nondimensional unit defined by (1.7).

Diamagnetic susceptibility corrections

Due to the difference between the bulk diamagnetic susceptibilities

of the sample and the reference compound contained in a thin walled capillary, a correction must be applied to the observed chemical shift. For a cylinder of length large compared with the radius the field is given by (2.1).

$$H = H_{obs}\left(1 - \frac{2\pi}{3}\chi_V\right) \tag{2.1}$$

where χ_V is the volume susceptibility of the liquid. Hence

$$\delta = \frac{H - Hr}{Hr} + \frac{2\pi}{3}(\chi_{V\,ref} - \chi_V)$$

$$= \delta_{obs} + \frac{2}{3}(\chi_{V\,ref} - \chi_V) \tag{2.2}$$

The volume susceptibility χ_V is related to the molar magnetic susceptibility χ_M by (2.3)

$$\chi_M = \frac{M\chi_V}{d} \tag{2.3}$$

where M is the molecular weight and d the density. For a mixture of diamagnetic substances the molar susceptibility of the mixture is given by Wiedemann's additivity law.

$$\chi_{M\ mixt} = x_1\chi_{M1} + x_2\chi_{M2} \tag{2.4}$$

where x_1 and x_2 are the mole fractions and χ_{M1} and χ_{M2} the molar susceptibilities of the pure components.

Where bulk diamagnetic susceptibility corrections were applied, χ_M was calculated from Pascal constants for the constitutive elements[48].

(3) ULTRA-VIOLET AND VISIBLE SPECTRA

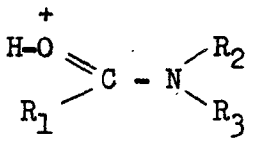
Ultra-violet and visible spectra were recorded on a Bausch and Lomb "Spectronic 505" spectrometer; quartz 1 cm. cells were used throughout. The pure, dry base was weighed directly into a 25 mls. volumetric flask and the solvent added to the graduation mark. After thorough mixing 1 ml. of this solution was pipetted into a 50 mls. volumetric flask and diluted to the mark. The spectrum of this solution was recorded.

CHAPTER III

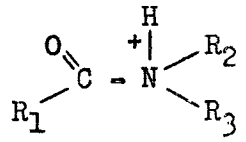
PROTONATION OF AMIDES, THIOAMIDES, UREAS AND SULPHONAMIDES.[23]

(1) INTRODUCTION

The basic nature of amides has long been recognised, but the structure of the ion formed when they are protonated has been the subject of discussion since Hantzsch[49] first presented evidence for O-protonation of benzamide in concentrated sulphuric acid from ultra-violet absorption spectra studies. A variety of other evidence has since been put forward by other workers in support of O-protonation I, but much evidence has also been adduced in favour of N-protonation II.



I

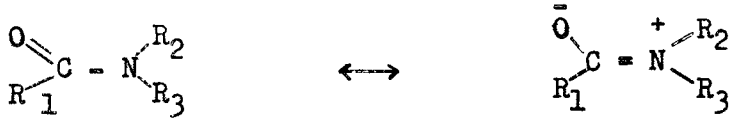


II

Support for N-protonation has been obtained from vibrational spectra. It has been suggested that the frequency of the CO stretching vibration should be lower for the O-protonated cation than the value for the parent amide. Strong bands, assumed to be carbonyl bands, have been found for several amide cations[50-54] at frequencies higher than those in the parent amide and hence it was argued that there is N-protonation. Urea nitrate[53], and the hydrochlorides of urea, thiourea and acetamide[54] give bands in their infra-red spectra which have been considered diagnostic of $-NH_3^+$ and hence of N-protonation. Edward and coworkers[55] have used ultra-violet absorption spectra to study the basicities of substituted benzamides and concluded

that their results were best explained on the basis of N-protonation although O-protonation was not completely excluded. N-protonation has also been reported[56] for the protonation of thioacetamide on the basis of an ultra-violet absorption spectra study.

One might expect that O-protonation would be favoured from a consideration of the resonance forms possible for the amide III, and indeed Pauling[57] has calculated on this basis that O-protonation is much favoured.



III

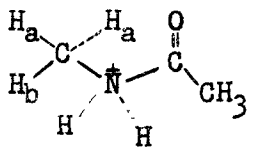
However he assumed, without justification, that the resonance energy of an amide and its O-protonated form are the same. Some infra-red and ultra-violet absorption spectra studies[58-63] indicate O- or S- protonation for amides, thioamides and urea's. However in these investigations the assignment of the bands is not always unambiguous. Stewart and Muenster[59] have prepared O^{18} labelled dicyclohexyl urea and its p-toluenesulphonate and found that the carbonyl band in the labelled urea shows the expected shift to lower frequency but the band at 1669cm^{-1} in the salt is unaffected by isotopic substitution and is therefore not a carbonyl stretching frequency as other workers have assumed. The crystal structures of acetamide hemihydrochloride[64] and N-methylurea nitrate[65] have been determined by X-ray diffraction. In both cases the distances between the anions and the carbonyl oxygen is short strongly suggesting that this is a hydrogen bond with the proton located on oxygen.

By far the strongest evidence for O-protonation has come from proton magnetic resonance studies. For example, the spectrum of pure

liquid dimethylformamide shows two peaks of equal area for the N-methyl groups[5,66]. It was concluded that the two methyl groups have different environments because of restricted rotation about the $OC-NMe_2$ bond, due to its partial double bond character (III above). Fraenkel and Niemann[67] have shown that these two peaks remain unchanged in solution in aqueous strong acids and in 100% H_2SO_4 and D_2SO_4. They concluded that in the O-protonated form (I) rotation around the $OC-NMe_2$ bond would still be restricted while in the N-protonated form (II) the $\overset{+}{N}HMe_2$ group would be free to rotate; and therefore that the O-protonated form predominates in these strong acid solutions. For N-methyl formamide the signal from the N-methyl protons is a doublet attributed to spin-spin coupling with the single hydrogen attached directly to nitrogen. This doublet collapses to a single peak in basic or weakly acidic solutions but reappears again as a doublet, and not a triplet, in strongly acidic media which rules out the possibility of an $\overset{+}{N}H_2Me$ group. Similar results have been obtained for N-methylacetamide[68], and for N,N-dimethylthiobenzamide[62]. Fraenkel and Franconi[69] have shown that there is an increase in the activation energy for the barrier to rotation about the OC-N bond when amides are protonated. This can only be explained by protonation on oxygen. If protonation had occurred on nitrogen, as in I, then the nitrogen lone pair could not be used to give double bond character to the C-N bond as in IIIb and rotation about the C-N bond would be increased i.e. the barrier to rotation decreased. Protonation on oxygen on the other hand would be a favoured by structure IIIb and the barrier to rotation thereby increased. Fraenkel and Franconi conclude that there is O-protonation. They also found that a solution of acetamide in 100% sulphuric acid gives a spectrum consisting

of two signals of relative areas 3:2 which they interpreted as being due to the CH_3 and NH_2 peaks of an O-protonated cation.[70] Bunton and coworkers measured the areas of peaks due to protons on nitrogen for formamide, acetamide, benzamide and their N-methyl and N,N-di-methyl derivatives and found that there is no increase in area on going from neutral solution to a solution in 98% sulphuric acid. The results of a wideline n.m.r. study[65] of crystalline salts of urea, thiourea and their derivatives are consistent with protonation on O or S.

Spinner, who obtained infra-red evidence[54] for N-protonation has suggested, however, that the n.m.r. results can also be explained on this basis.[22] For example, he attributes the doublet N-methyl group signal observed in the spectrum of protonated N-methyl acetamide to the non-equivalent hydrogen atoms H_a and H_b resulting from restricted rotation about the C-N bond in the N-protonated form IV. However this would give



IV

components of the methyl group signal of relative areas 1:2 and not 1:1 as observed. It must also be assumed that the expected spin-spin coupling between the N-methyl group and the two hydrogens directly attached to nitrogen is too weak to be observed.

All of the work up to 1961 was critically reviewed by Jones and Katritzky[21] who concluded that amides are predominantly protonated on oxygen, or sulphur in the case of thioamides. However, Spinner[22] points out that all the n.m.r. evidence is rather indirect as in no case has a signal been observed in the spectrum from the proton supposedly captured

by the oxygen atom in the O-protonated form. This has been attributed by other workers to rapid exchange of this proton with the solvent.

It was evident that the site of protonation could be determined unambiguously if the rate of exchange of the captured proton with the solvent could be slowed down sufficiently so that a separate signal for this proton could be observed in the spectrum. Fluorosulphuric acid is a stronger acid and a weaker base than 100% sulphuric acid [71] and has the added advantage of a low freezing point of -89.0° [72]. By recording the spectra of fluorosulphuric acid solutions of amides at sufficiently low temperatures it has been possible to observe for the first time the signal from the captured proton and thus to determine unambiguously the site of protonation. The solutions which were approximately 6 mole % with respect to the amide, were prepared at the temperature of an acetone - solid carbon dioxide mixture (c.a. - 85°) and stored at this temperature until their n.m.r. spectra were recorded. Spectra were recorded at the lowest temperature first and then at successively higher temperatures. This procedure ensured that reactions between the amides and the solvent were minimised.

(2) AMIDES

Table I summarizes the chemical shifts and spin-spin coupling constants for the protonated forms of acetamide, formamide, benzamide, and their N-methyl and N,N-dimethyl derivatives.

Acetamide

The proton magnetic resonance spectrum of a 6 mole % solution of acetamide in fluorosulphuric acid at 25° consists of two peaks, B and C, of relative areas 2.04:3.00 in addition to a signal due to the solvent (Fig. 3). Essentially the same spectrum has been obtained previously for an aqueous solution of pH7 and for a solution in 100% sulphuric acid[69], and the peaks have been assigned to the NH_2 and CH_3 groups. The NH_2 peak B is approximately 70-80 c.p.s. wide due to N^{14}-H coupling and quadrupole relaxation of the N^{14} nucleus. As the temperature is lowered the NH_2 peak becomes sharper and eventually splits into a doublet. At -80° another peak, A, becomes visible on the high field side of the solvent peak (Fig.4) which shifts to higher field as the temperature is further decreased until at -92° it was recorded as a separate well resolved peak (Fig. 5). This new peak can only be assigned to a proton on the carbonyl oxygen, and in agreement with this conclusion the relative areas of the three peaks were found to be A:B:C:: 1.07: 2.10: 3.00, confirming their assignment to the OH, NH_2 and CH_3 groups respectively. Protonation on nitrogen with no exchange would give a spectrum consisting of two peaks of equal area.

The splitting of the NH_2 resonance may be attributed to non-equivalence of the two hydrogens as a consequence of restricted rotation about the C-N bond due to its partial double-bond character. The loss of resolution in the NH_2 doublet at -92° can probably be attributed to

the increased viscosity of the solution, which is very close to the freezing point or possibly slightly supercooled. Even at -92° the OH peak has a width of 23.2 c.p.s. and although some of this broadening is perhaps due to the increased viscosity of the solutions much of it can probably be attributed to slow OH -solvent proton exchange.

N-Methylacetamide

The proton magnetic resonance spectrum of a solution of N-methylacetamide in fluorosulphuric acid at 25° consists of three peaks of relative areas 0.83: 3.05: 3.00, in addition to that of the solvent, which can be attributed to the NH, $N-CH_3$ and $C-CH_3$ groups respectively. The NH_2 peak is 52-65 c.p.s. wide due to N^{14}-H coupling and quadrupole relaxation of the N^{14} nucleus. Spin-spin coupling ($J = 5.03$ c.p.s.) is also observed between the NH and the $N-CH_3$ protons resulting in the latter peak having a doublet structure. At -85° an additional peak appears, with a chemical shift of approximately -10 p.p.m, which is assigned to the protonated carbonyl oxygen atom. In agreement with this assignment the relative areas of the four peaks were found to be 1.17: 1.05: 3.11: 3.0. The width of the OH peak is 12.5 c.p.s. suggesting that exchange is still occurring with the solvent. Addition of antimony pentafluoride to the solution has the effect of reducing the basicity of the solvent and the $C=\overset{+}{O}-H$ line width decreases indicating a further reduction in the rate of proton exchange.

N,N-Dimethylacetamide

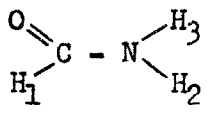
The spectrum of a solution of N,N-dimethylacetamide in fluorosulphuric acid at 25° contains only two signals, due to the $N(CH_3)_2$ and $C.CH_3$ groups respectively. On decreasing the temperature a new peak, A,

appears with a chemical shift of approximately -10 p.p.m. which is at first broad and then gradually narrows until it has a width of only 2.8 c.p.s. at -79° (Fig. 6). This peak may be assigned to the protonated oxygen atom by comparison with the similar peak which occurs in the spectrum of acetamide at low temperatures. No further change occurs below -79°, indicating that exchange of the captured proton with the solvent has become very slow. The relative areas of the three peaks at -79° were found to be A:B:C:: 0.96: 5.91: 3.00 and they are assigned to the OH, $N(CH_3)_2$, and $C.CH_3$ groups respectively. If N-protonation occurred three peaks of relative area 1: 6: 3 would be expected as for O-protonation. However the new peak due to the captured proton has a chemical shift of -9.80 p.p.m., which is close to the chemical shifts of -10.40 p.p.m. and -10.15 p.p.m. for the analogous peaks in the acetamide and N-methylacetamide spectra which can be unambiguously assigned to the $=\overset{+}{O}H$ group. Moreover, A is a single sharp line showing no evidence of fine structure, although if N-protonation occurred spin-spin coupling between the NH and $N(CH_3)_2$ protons would be expected, since in a solution of N-methylacetamide in fluorosulphuric acid J $H.N.CH_3$ = 5.03 c.p.s. At all temperatures the $N(CH_3)_2$ signal is essentially a single peak, although its width (2.4 c.p.s. at 25° and 5.6 c.p.s. at -79°), its unsymmetrical shape, and the presence of several ill-defined shoulders strongly indicate that it has an unresolved fine structure. This can presumably be attributed to a very small chemical shift between the two methyl groups, their non-equivalence being due to restricted rotation about the central C-N bond, and mutual spin-spin coupling. There is possibly also some coupling with the OH and $C.CH_3$ protons. The greater width of the $N(CH_3)_2$ signal at $-79^{\circ}C$ can perhaps

be attributed to a small increase in the chemical shift between the two methyl groups with decreasing temperature. In the pure liquid, and in solution in various organic solvents, the signals from the two N-methyl groups are clearly separated at room temperature[73]. However, in 100% sulphuric acid Fraenkel and Franconi[69] were unable to resolve the two separate methyl groups. They attributed this to the broadening of the peaks caused by the high viscosity of sulphuric acid. However, as the viscosity of fluorosulphuric is only 1/10 that of sulphuric acid[72], this cannot be the only factor involved. Presumably the chemical shift between the N-methyl groups is smaller in the protonated than in the neutral amide. It is interesting to note that a recent study of the spectra of solutions of dimethylacetamide in a variety of organic solvents has shown that the chemical shift between the two methyl groups is solvent and concentration dependent and can become zero or even change sign in suitable solvents[73].

Formamide

The spectrum of pure liquid formamide at room temperature is shown in Fig. 7a. The broad peak C can be attributed to the NH_2 protons and the peak B to the formyl proton H_1 split by coupling with the H_3 proton (v)[74]. The chemical shifts between the three protons are relatively small and they will not therefore give rise to a simple first-order



V

spectrum, which is the reason for the unsymmetrical nature of the formyl proton doublet. In solution in fluorosulphuric acid the spectrum changes

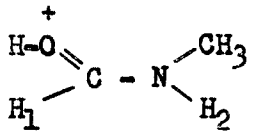
to that shown in Fig. 7b. It seems clear that the broad NH_2 peak has now split into the triplet expected as a result of N^{14}-H coupling and that the middle peak of this triplet lies beneath the sharper doublet that can be attributed to H_1. Unresolved splitting due to coupling with H_2, in addition to H_3, is evident in the form of shoulders on the centre peak. The observed separation of the outer components of the NH_2 triplet gives $J_{NH} = 62 \pm 5$ c.p.s., which is in good agreement with the value of 60 ± 4 c.p.s. obtained by Roberts[75] for pure liquid formamide at temperatures above 50°. An integrated spectrum gave relative areas for the three peaks of 0.74: 1.55: 0.71, which is in reasonable agreement with the expected values of 0.67: 1.66: 0.67 in view of the extensive overlap of the broad peaks.

With decreasing temperature the NH_2 signal collapses to a single peak that is coincident with the peak due to the formyl proton (Fig. 7c). At -80° a new peak, A, appears at low field which may be attributed to the $C = \overset{+}{O}H$ group. At -98° the A peak has a chemical shift of -10.69 p.p.m. and integration of the spectrum gave relative peak areas A: B + C:: 1.00: 3.03, in agreement with their assignment to the $C = \overset{+}{O}H$ and NH_2 plus CH groups respectively. The width of the $C = \overset{+}{O}H$ peak (14.9 c.p.s.) presumably indicates that exchange of this proton with the solvent is still occurring at -98°, although some of the broadening could be due to the increased viscosity of the solvent at this temperature.

N-Methylformamide

The n.m.r. spectrum of N-methylformamide in fluorosulphuric acid solution at 25° consists of two well defined peaks due to the formyl proton and the $N-CH_3$ proton: in addition there is a broad peak with the same

chemical shift as the formyl proton. This peak is attributed to the proton attached to nitrogen. In agreement with this assignment the relative areas of the combined formyl +NH protons to the N-CH_3 peak is 2.18: 3.00. The N-CH_3 peak has a doublet structure due to spin-spin coupling with the N-H proton ($J_{H_2,\ CH_3}$ = 4.4 c.p.s.) VI.



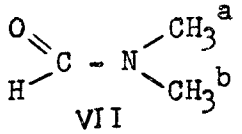
VI

In addition the formyl proton further splits each peak of the CH_3 doublet into a smaller doublet ($J_{H_1,\ CH_3}$ = 1 c.p.s.) and it is also coupled to H_2 ($J_{H_1,\ H_2}$ = 4.5 c.p.s.). These results are consistent with protonation on oxygen with rapid exchange. Upon lowering the temperature a new peak appears at -10.48 p.p.m. which can be attributed to the captured proton attached to the carbonyl oxygen. Area measurements confirm this conclusion ($H\text{-}\overset{+}{O}\text{=}C$: $H_1 + H_2$: NCH_3 :: 1.04: 1.90: 3.0). However the $H\text{-}\overset{+}{O}\text{=}C$ peak is quite broad at -85° indicating that exchange is still occurring. In a solution containing ~ 3 mole % SbF_5 the rate of proton exchange can be slowed down sufficiently so that a doublet structure for the $HO\text{=}\overset{+}{C}$ peak can be observed: this is attributed to spin-spin coupling with H_1.

N,N-Dimethylformamide

The spectrum of a solution of dimethylformamide in fluorosulphuric acid at 25° consists of the peak B, due to the formyl proton, and the doublet C, due to the two N-methyl groups (Fig. 8). For the pure liquid dimethylformamide and for solutions in a large number of organic solvents, it has been found that two peaks are obtained for the N-methyl groups,

and it has been shown that this is because they are non-equivalent as a consequence of hindered rotation about the OC-N bond [5,66,73]. The peak at higher field is split into a doublet of separation 1.1 c.p.s. and the peak at lower field is split into a doublet of 0.7 c.p.s. These splittings are almost exactly twice as large as those found by Hatton and Richards [73] for the pure liquid (0.65 and 0.3 c.p.s. respectively). The splitting is attributed to coupling of the N-methyl groups with the formyl proton, and the high-field peak is assigned to the CH_3^a group trans to the formyl hydrogen and the low-field peak CH_3^b group cis to the formyl proton (VII).



VII

The greater coupling between the formyl proton and the N-methyl groups in the protonated form than in the neutral amide may reasonably be associated with a greater double-bond character of the central C-N bond in the protonated form. In solutions of dimethylformamide in 100% sulphuric acid Fraenkel and Franconi [69] found rather larger splittings of the N-methyl resonances of 1.2 and 1.7 c.p.s. respectively. The reason for the difference between their results and those reported here is not clear. The resonance of the formyl proton is somewhat broad (2.9 c.p.s.) and a number of shoulders on the line strongly indicate unresolved fine structure. This must arise from spin-spin coupling between the formyl proton and the N-methyl groups. At low temperatures a new peak, A, appears in the spectrum at low field (-9.98 p.p.m.), which can evidently be attributed to the OH group of the O-protonated form. At -80° (Fig.9) the relative areas of the peaks were found to be A:B:C:: 1.04: 0.96: 6.00

in agreement with the suggested assignment. The OH and CH peaks are both doublets due to mutual spin-spin coupling, $J_{CH,OH} = 4.7$ c.p.s. That the resolution of the CH doublet is poorer than that of the OH doublet is presumably due to weak spin-spin coupling of the CH proton with the two N-methyl groups. The reason for the loss of the fine structure in the doublet C due to the N-methyl groups is, however, not clear.

Benzamide, N-methyl benzamide, and N,N-dimethylbenzamide

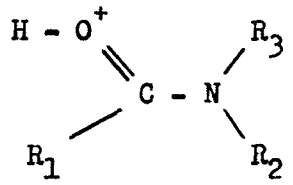
In fluorosulphuric acid solution these bases give n.m.r. spectra at 25°C which are very similar to those observed in a neutral medium. Thus benzamide gives a spectrum which consists of two peaks due to NH_2 and phenyl protons; N-methylbenzamide gives three peaks of relative area 1.01: 5.22: 3.00 corresponding to the NH, C_6H_5, and $N\text{-}CH_3$ protons. The $N\text{-}CH_3$ peak is observed as a doublet ($J = 5.37$ c.p.s.) due to spin-spin coupling with the N-H proton indicating that the N-H proton is not exchanging. Only two peaks are observed for N,N-dimethylbenzamide of relative area 5.09: 6.00 which are assigned to the C_6H_5 and $N(CH_3)_2$ protons. Restricted rotation about the C-N bond results in the methyl groups having different chemical shifts and a separation of 9.48 c.p.s. is observed.

Upon lowering the temperature a new peak appears at $\sim$ -10 p.p.m. which by comparison with the other amides studied is assigned to a proton attached to the carbonyl oxygen. Area measurements confirm this assignment; for benzamide at -85° the relative areas of $\overset{+}{O}H$: $NH_2 + C_6H_5$ were found to be 0.83: 7.00; for N-methylbenzamide at -86°, $\overset{+}{O}H$: NH: C_6H_5: $N.CH_3$ :: 1.01: 1.07: 5.18: 3.00; and for N,N-dimethylbenzamide at -72°, $\overset{+}{O}H$: C_6H_5: $N(CH_3)_2$ :: 0.89: 4.98: 6.00. In each case (except

N,N-dimethylbenzamide) the $\overset{+}{O}H$ peak is somewhat broad at -85°, indicating that even at this low temperature there is slow proton exchange between the solvent and the conjugate acid of the amide. It is found that the doublet separation of the N-methyl peak of N,N-dimethylbenzamide in fluorosulphuric acid solution changes from 9.46 c.p.s. at 25° to 6.74 c.p.s. at -85°. Hatton and Richards[73] have attributed the changes in chemical shifts of the methyl groups of N,N-dimethylamides, in aromatic solvents, to the association of the amide with a solvent molecule: this association producing an effect which is different for each methyl group hence the change in separation of the doublet. If in a similar way lowering the temperature of a solution of N,N-dimethylbenzamide in HSO_3F, in addition to slowing down the proton exchange, also increases the extent of hydrogen bonding between the carbonyl oxygen and solvent molecules then this may in turn effect the chemical shift of one methyl group more than the other: the result being a decrease in the chemical shift between these groups.

TABLE I

CHEMICAL SHIFTS OF AMIDES IN FLUOROSULPHURIC ACID



Amide	Temp. (°C)	$-\delta$ (p.p.m.) from Ext. T.M.S. O-H	C-R_1	N-R_2	N-R_3	J (c.p.s.)
Acetamide	+25	-	2.76	8.28	8.28	
	-80	10.72	2.67	8.24	8.36	
	-92	10.40	2.67	8.26	8.36	
N-Methylacetamide	25	-	2.69	8.31	3.36	J_{R_2, R_3} 5.0
	-85	10.15	2.58	8.27	3.25	
N,N-Dimethylacetamide	+25	-	2.73	3.55	3.55	
	-79	9.80	2.64	3.45	3.45	
Formamide	+25	-	8.55	8.68	8.68	$J_{N,R_{2,3}}$ 62 ± 5 J_{R_1,R_3} 8.5
	-84.5	10.81	8.60	8.60	8.60	
	-98	10.69	8.60	8.60	8.60	
N-Methylformamide	25	-	8.50	~8.58	3.44	J_{R_2,R_3} 4.4 J_{R_1,R_3} 1.0 J_{R_1,R_2} 4.5
	-85	10.49	8.48	8.66	3.33	
	-69*	10.39	8.57	8.76	3.46	$J_{R_1,OH}$ 3.5

* Solution in 10 mole % SbF_5 in fluorosulphuric acid.

TABLE I (Contd.)

Amide	Temp. (°C)	$-\delta$ (p.p.m.) from Ext. T.M.S. O-H	C-R_1	N-R_2	N-R_3	J (c.p.s.)	
N,N-Dimethylformamide	+25	-	8.38	3.49	3.59	J_{R_1,R_3}	1.1
						J_{R_1,R_2}	0.7
	-80	9.98	8.38	3.43	3.53	$J_{R_1,OH}$	4.7
Benzamide	25	-	8.08	8.59	8.59		
	-85	10.20	8.03	8.72	8.72		
N-Methylbenzamide	25	-	7.93	8.61	3.54	J_{R_2,R_3}	5.4
	-71	10.37	7.97	8.72	3.50		
	-86	10.34	7.93	8.73	3.47		
N,N-Dimethylbenzamide	25	-	7.85	3.72	3.56		
	-72	9.91	7.84	3.61	3.49		
	-85	9.95	7.85	3.63	3.51		

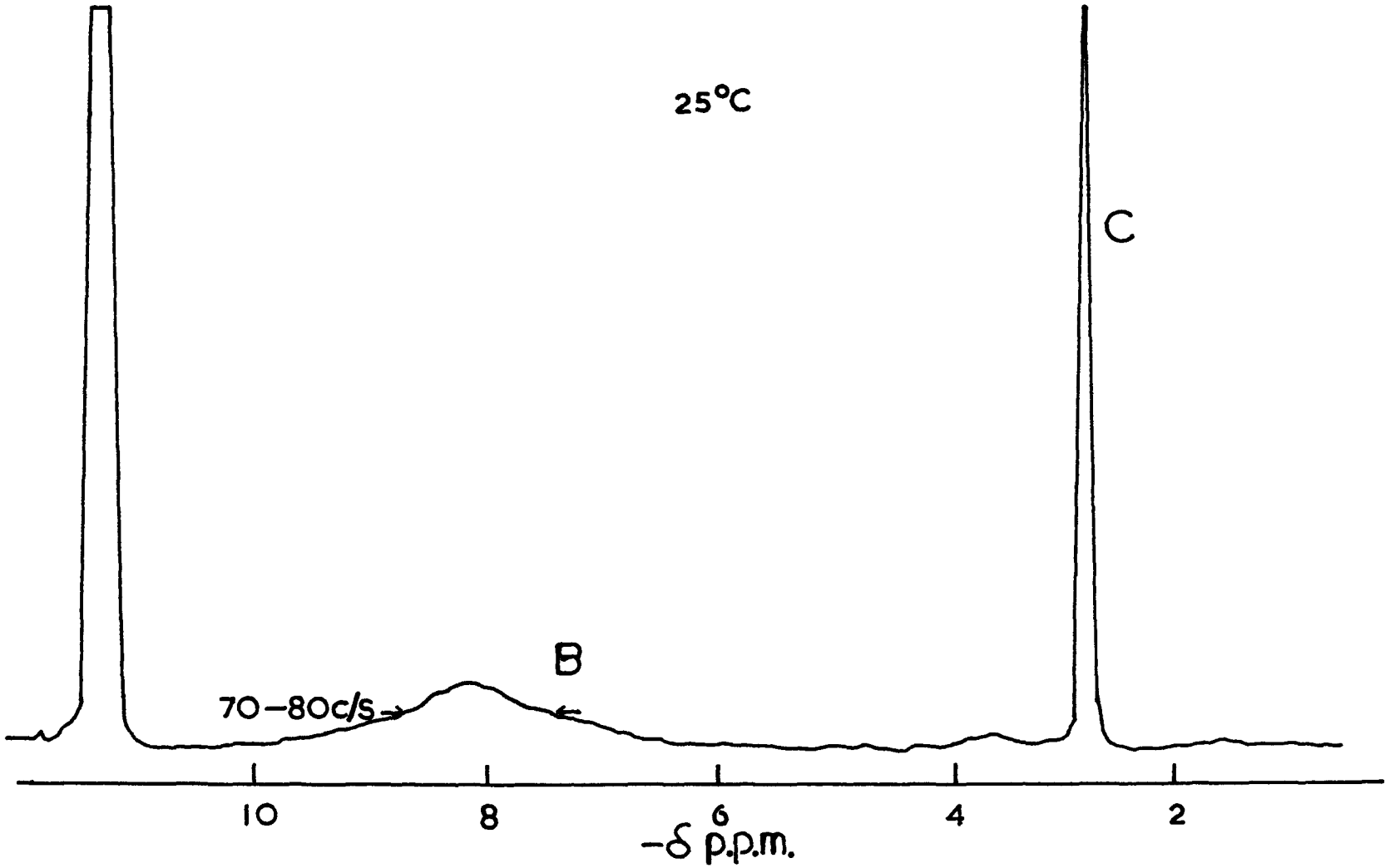


Fig. 3 N.m.r. SPECTRUM OF A SOLUTION OF ACETAMIDE IN FLUOROSULPHURIC ACID AT 25°.

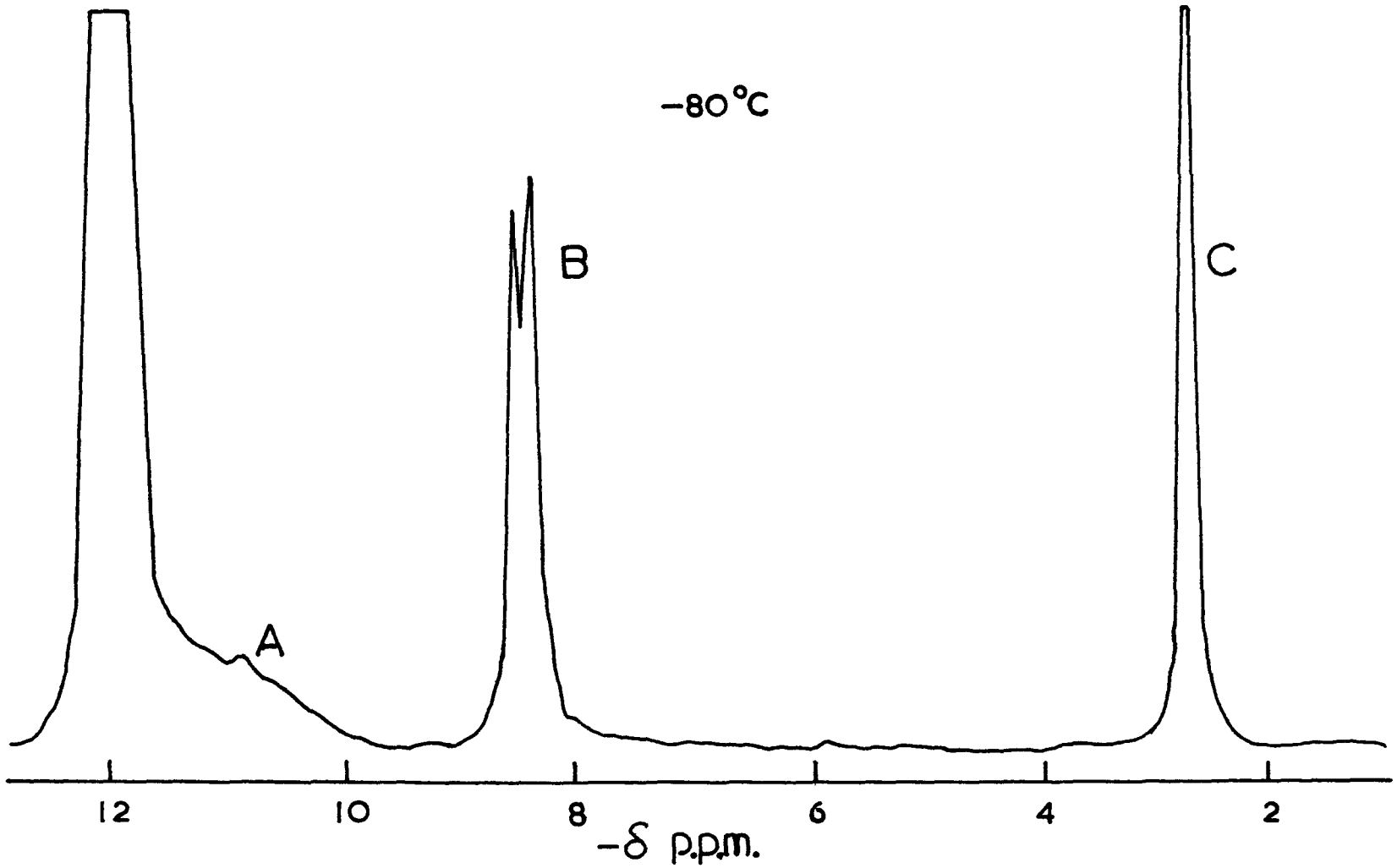


Fig. 4 N.m.r. SPECTRUM OF A SOLUTION OF ACETAMIDE IN FLUOROSULPHURIC ACID AT -80°.

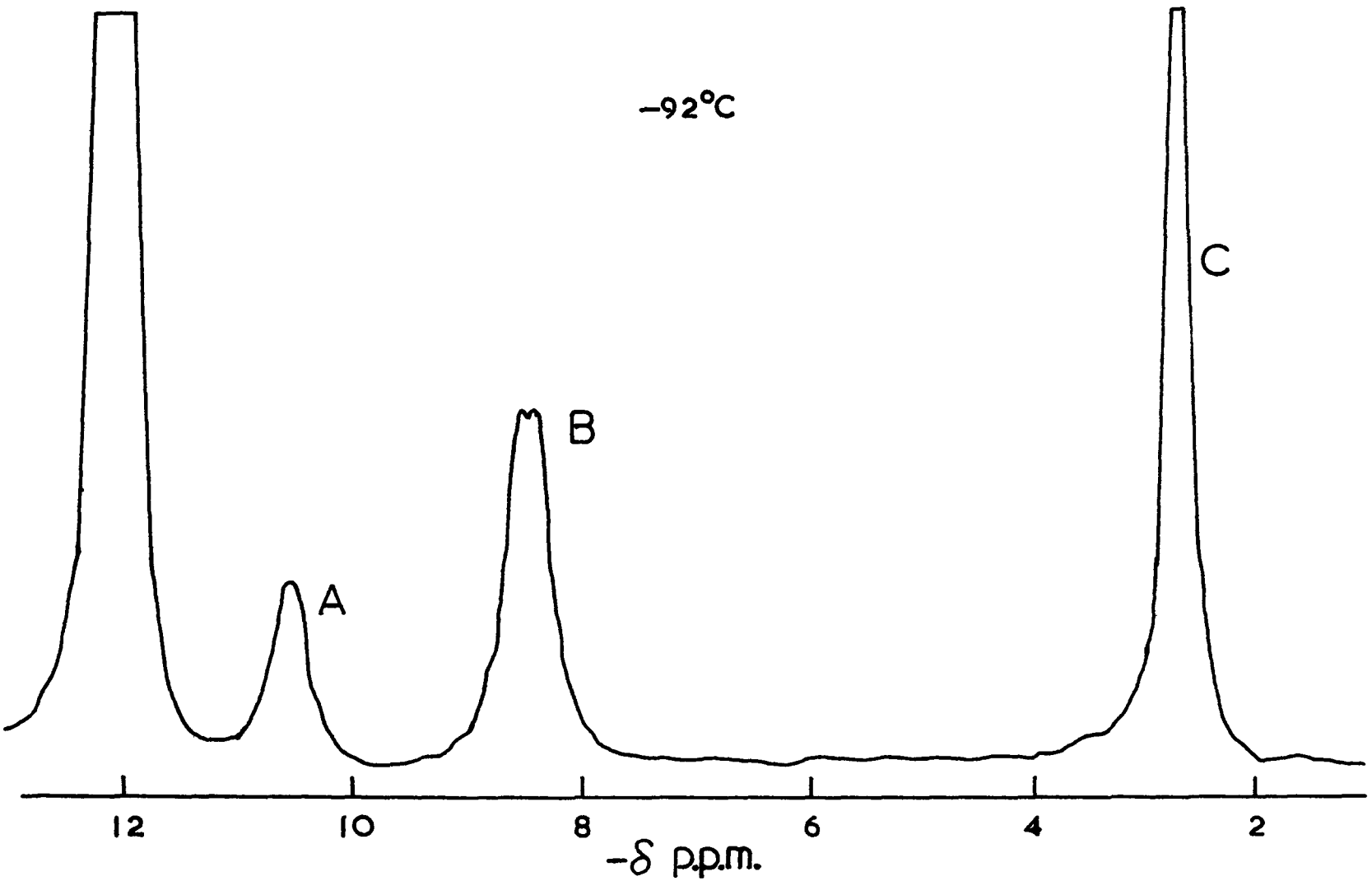


Fig. 5 N.m.r. SPECTRUM OF A SOLUTION OF ACETAMIDE IN FLUOROSULPHURIC ACID AT -92°.

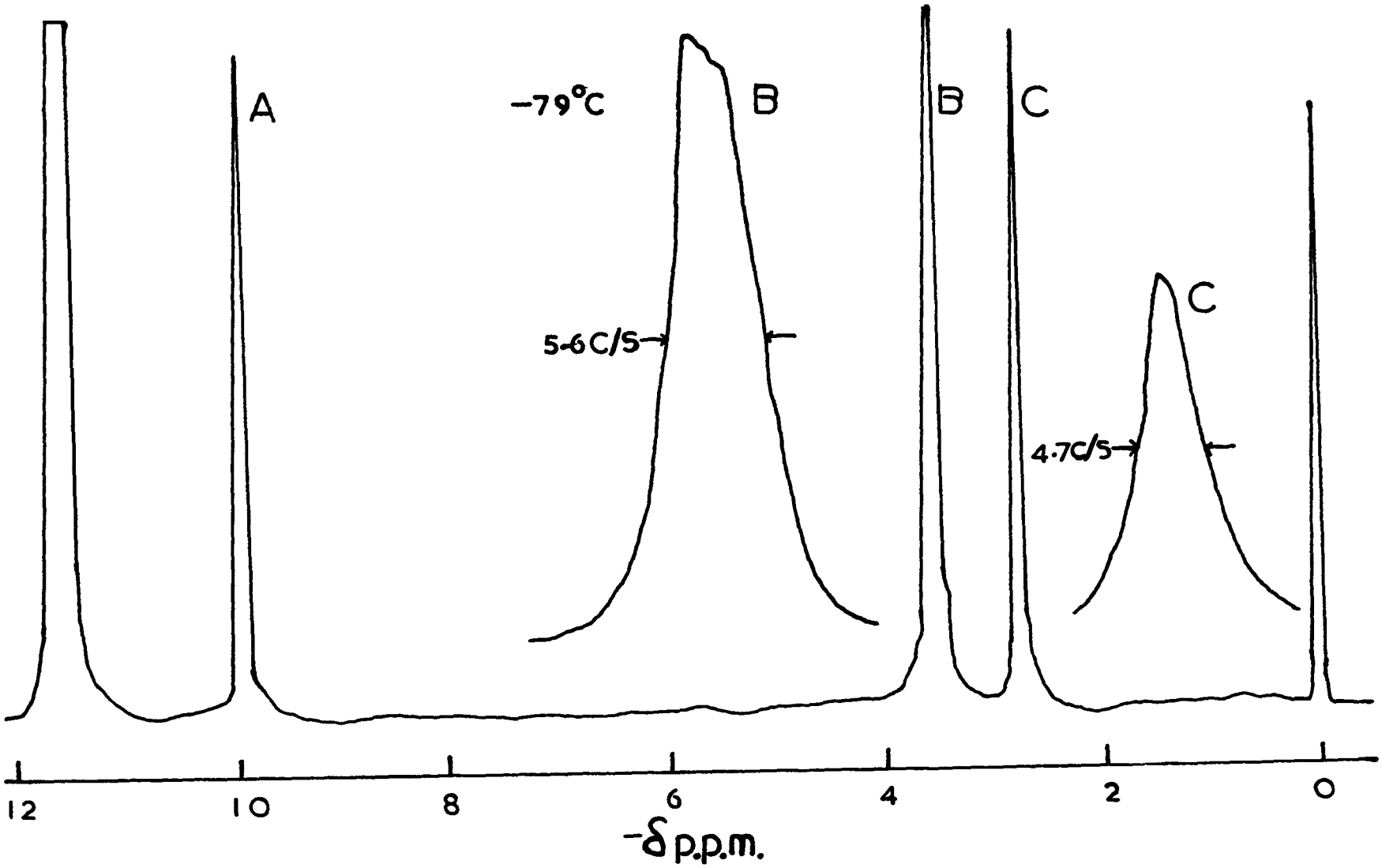


Fig. 6 N.m.r. SPECTRUM OF A SOLUTION OF N,N-DIMETHYLACETAMIDE IN FLUOROSULPHURIC ACID.

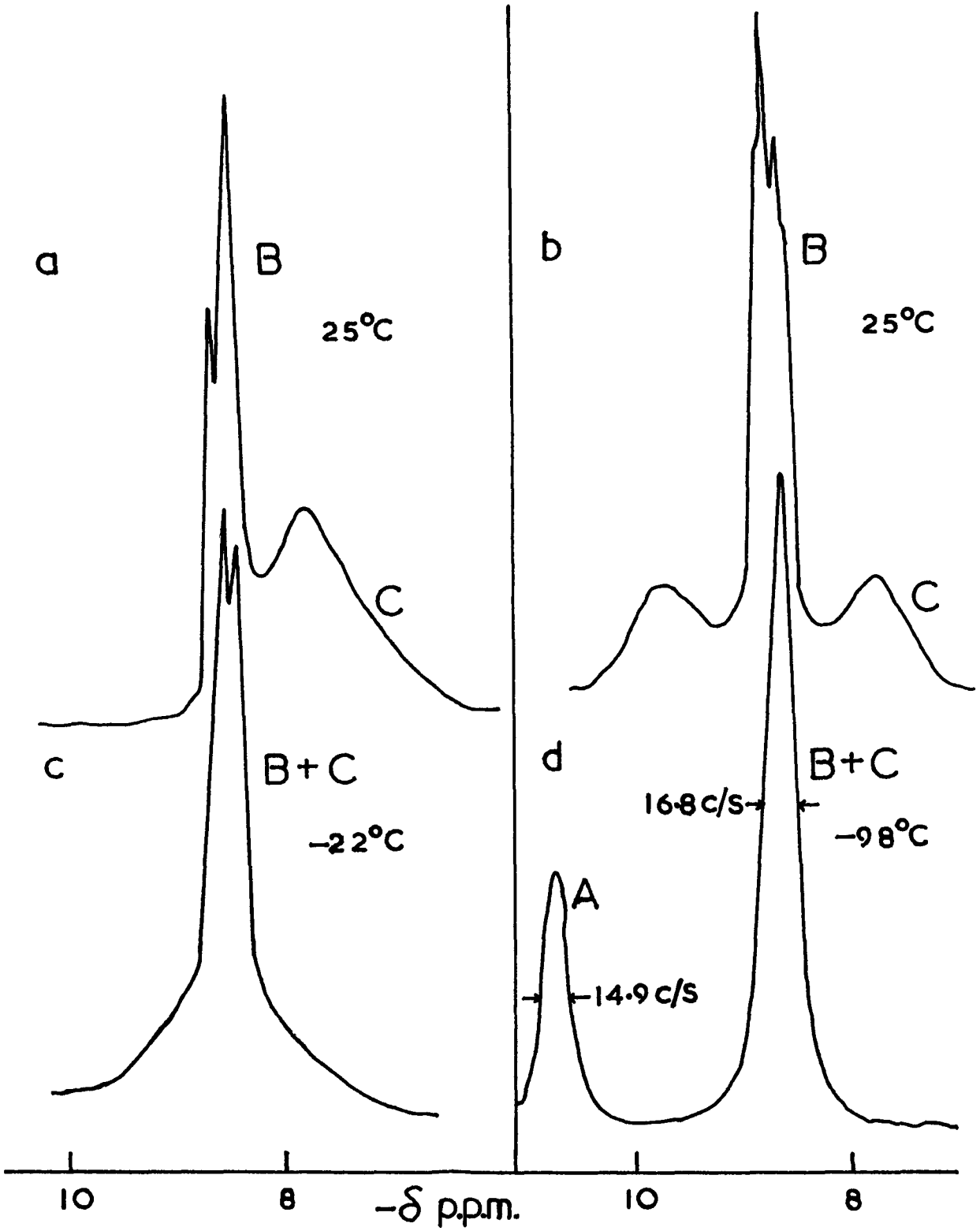


Fig. 7 N.m.r. SPECTRA OF (a) LIQUID FORMAMIDE AND (b,c,d) A SOLUTION OF FORMAMIDE IN FLUOROSULPHURIC ACID.

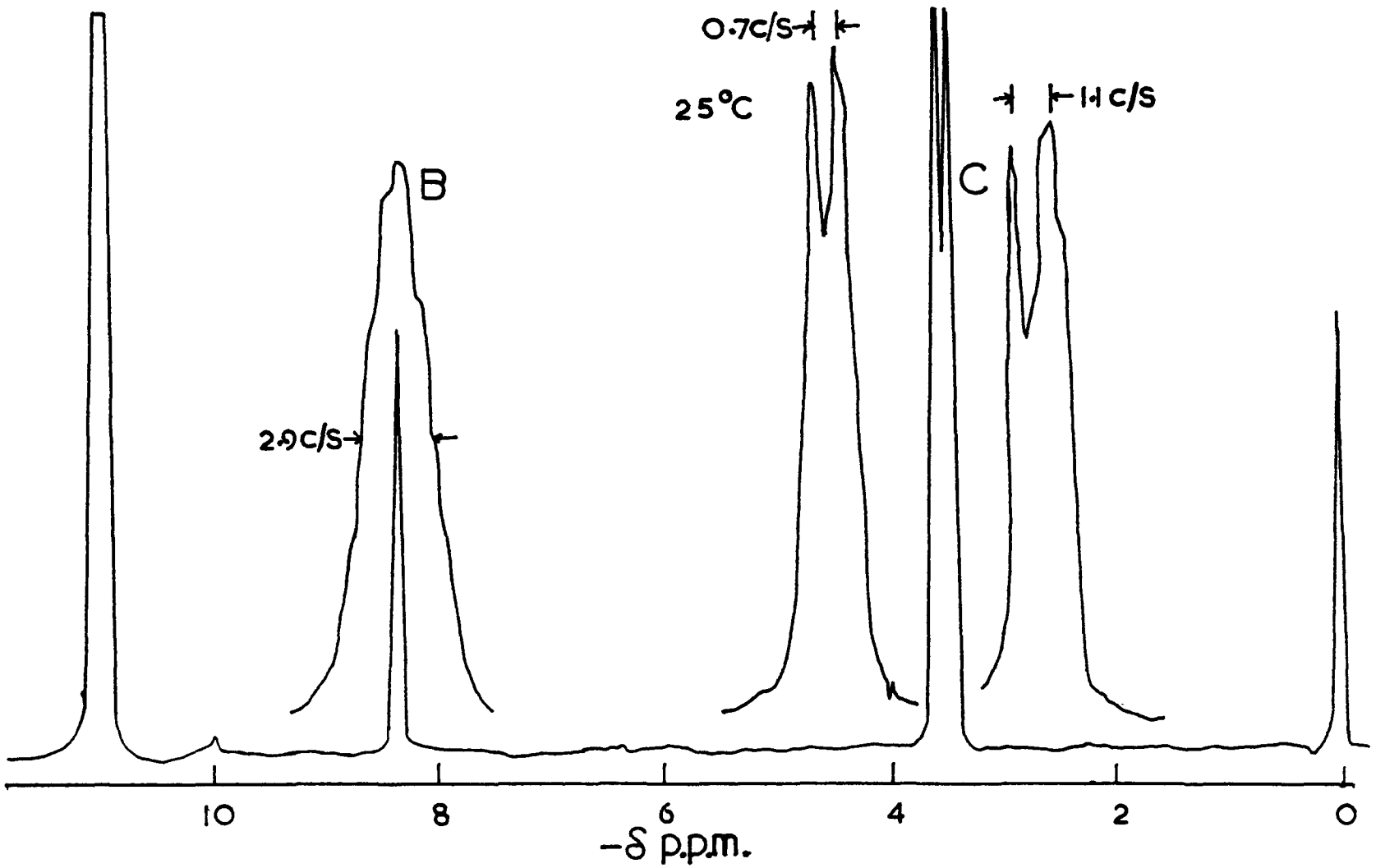


Fig. 8 N.m.r. SPECTRUM OF A SOLUTION OF N,N-DIMETHYLFORMAMIDE IN FLUOROSULPHURIC ACID AT 25°.

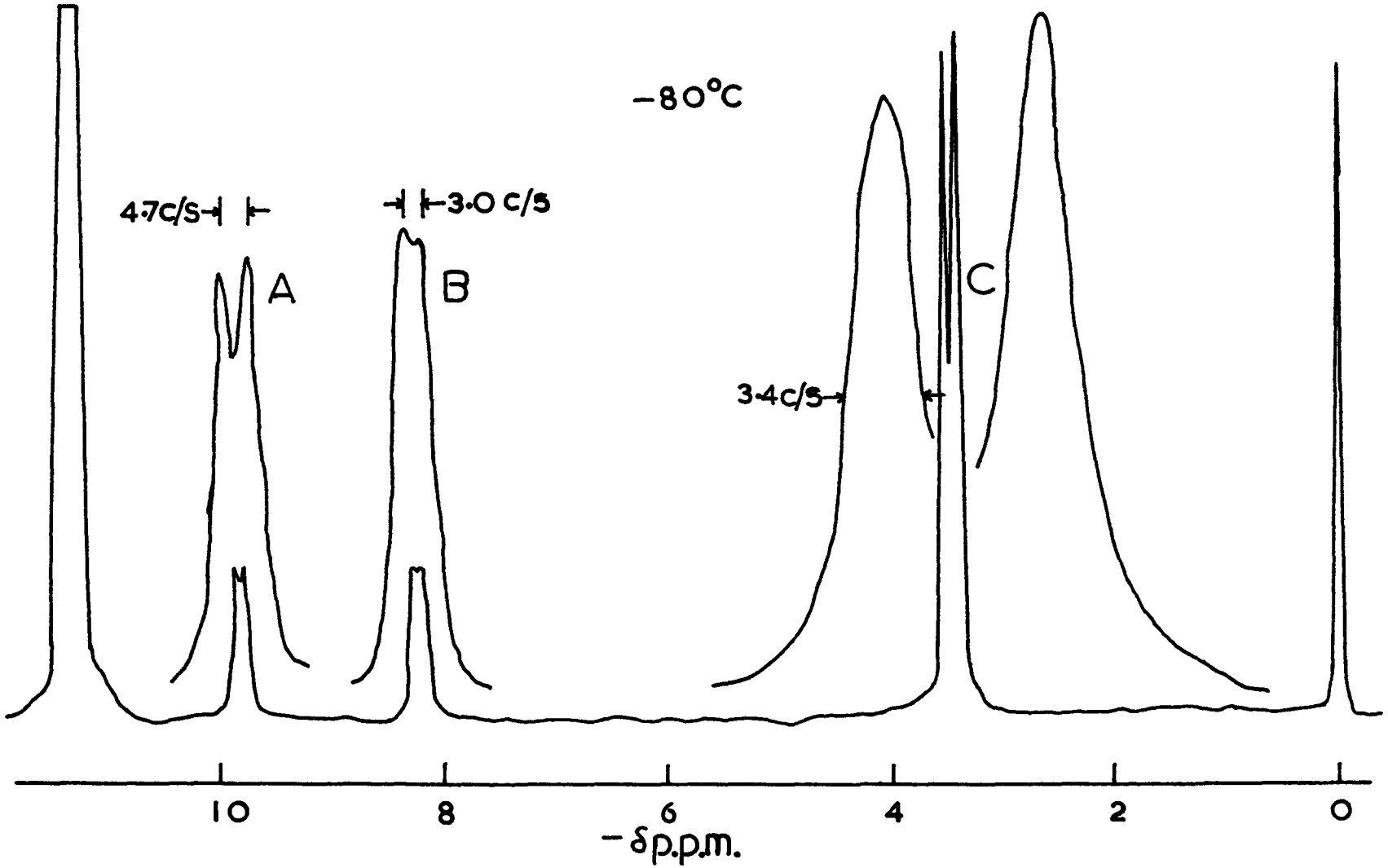


Fig. 9 N.m.r. SPECTRUM OF A SOLUTION OF N,N-DIMETHYLFORMAMIDE IN FLUOROSULPHURIC ACID AT -80°.

(3) THIOAMIDES

As with O-amides some workers have presented evidence for protonation on the sulphur atom of thioamides [58,60,62,63] while others have concluded that protonation occurs on nitrogen [54,56]. The results for thioacetamide and thioacetanilide presented in Table II clearly establish that protonation occurs on sulphur.

Thioacetamide

The spectrum of a solution of thioacetamide in fluorosulphuric acid at 25° contained in addition to the solvent and tetramethylsilane peaks, three peaks A, B and C of relative areas 1.98: 0.90: 3.00 which may be assigned to the NH_2, $C{=}\overset{+}{S}H$ and $\overset{+}{C}H_3$ groups respectively (Fig.10). It is interesting to note that the C=SH peak (B) is quite sharp indicating that proton exchange with the solvent is slow even at 25°. The NH_2 peak (A) is a broad triplet due to N^{14}-H coupling. Reducing the temperature causes this triplet to collapse to a single line as has also been found to occur in the case of acetamide and formamide.

Thioacetanilide

A solution of thioacetanilide in acetone gives a spectrum with three peaks, in addition to the solvent and reference peaks, that may be attributed to the NH, C_6H_5 and CH_3 protons. In fluorosulphuric acid at 25° an additional peak appears that may be assigned to the $C{=}\overset{+}{S}H$ group. The spectrum at -40° (Fig. 11) is essentially the same except that the NH peak is sharper and is more clearly resolved from the solvent peak: the four peaks A, B, C and D may be attributed to the NH, C_6H_5, $C{=}\overset{+}{S}H$ and CH_3 groups respectively. The $C{=}\overset{+}{S}H$ resonance occurs at approximately -5.5 p.p.m. from tetramethylsilane which is at considerably higher field

than the $C{=}O\overset{+}{H}$ resonance ($\sim$ -10 p.p.m.). The chemical shifts for the S-H group in thiophenol and thiolacetic acid are -3.2 and -4.73 p.p.m. respectively[76,77], whereas the chemical shifts for the OH group in phenol and acetic acid are $\sim$ -7.5[1] and -11.37[77] p.p.m. respectively. The sharpness of the $C{=}S\overset{+}{H}$ resonance at 25° indicates that proton exchange is very much slower than for the $C{=}O\overset{+}{H}$ group under the same conditions.

A rough comparison of the lifetimes of the conjugate acids of acetamide and thioacetamide was made as follows.

The width of the $O\overset{+}{H}$ peak of protonated acetamide is still somewhat broad at -92° indicating that exchange is still occurring. Since there are distinct signals for the solvent and $O^{+}H$ the conditions for slow exchange may be applied to equation (1.13) which reduces to

$$G \simeq G_A \approx -i\,\gamma\, H_1 M_0 \frac{P_A \tau_A}{1 + \alpha_A \tau_A} \qquad (3.1)$$

The imaginary part is

$$v = -\gamma H_1 M_0 \frac{P_A T'_{2A}}{1 + (T'_{2A})^2(\omega_A - \omega)^2} \qquad (3.2)$$

i.e. there will be a broadened signal centred at ω_A with width given by the parameter

$$T'^{-1}_{2A} = T^{-1}_{2A} + \tau^{-1}_A \qquad (3.3)$$

Thus if T_{2A} is known τ_A can be found from the width of the broadened signal T'^{-1}_{2A}. If T^{-1}_{2A} is taken as π . 6.0 sec^{-1} (estimated from linewidths of $O^{+}H$ of protonated ketones at c.a. -90° Chapter V) then τ^{-1} will have a value of (π .23.2 - π .6.0) sec^{-1} = π 17.2 sec^{-1} and this is equal to k, the rate constant for proton loss by the conjugate acid. The dependence of the rate of proton exchange on the

temperature can be expressed by the Arrhenius equation

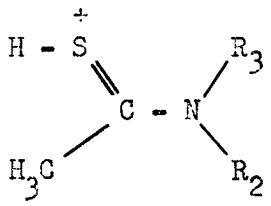
$$k = k_o e^{-E/RT} \qquad (3.4)$$

From this equation an estimate of the rate of proton exchange for the conjugate acid of acetamide at 25° can be calculated. This was found to be 1.5×10^7 sec^{-1} (appropriate value for E of 11.5 K cals was estimated from data on the conjugate acids of ketones Chapter V). Since the S^+H peak of protonated thioacetamide is quite sharp and has a chemical shift from the solvent of approximately 5.8 p.p.m. the lifetime of the captured proton on the sulphur atom at 25° must be greater than $\frac{1}{2\pi \times 350}$ sec. or $k = 2.2 \times 10^3$ sec^{-1}.

Thus the lifetime of the conjugate acid of thioacetamide is considerably greater than that of the conjugate acid of acetamide. This might appear to suggest that thioacetamide is a stronger base than acetamide. However the value of pK_{BH^+} for thioacetamide[78] of -1.76 indicates that it is a weaker base than acetamide pK_{BH^+} +0.37[79] and -0.51[80]. In agreement with this it has also been found that thiolactams[81] are weaker bases than lactams[82]. If thioacetamide is indeed a weaker base than acetamide then one must conclude that the rate of proton exchange of amides and thioamides is influenced by several other factors in addition to their basic strengths.

TABLE II

CHEMICAL SHIFTS FOR SOLUTIONS OF THIOAMIDES



Amide	Temp. (°C)	Solvent	-δ(p.p.m.) from Ext. T.M.S. S-H	C-CH_3	N-R_2	N-R_3	$J_{N^{14},R}$ (c.p.s.)
Thioacetamide	25	acetone	-	2.35	8.47	8.47	
	"	water	-	2.94	9.48	9.48	50±8
	"	fluorosulphuric acid	5.75	3.00	9.25	9.25	
	-50	"	5.69	2.89	9.21	9.21	
	-81	"	5.72	2.92	9.29	9.29	
Thioacetanilide	25	acetone	-	2.47	10.55	7.19	
	"	fluorosulphuric acid	5.45	3.17	~10.5*	7.72	
	-40		5.39	3.09	10.64	7.68	

* N-H peak broad and very close to solvent.

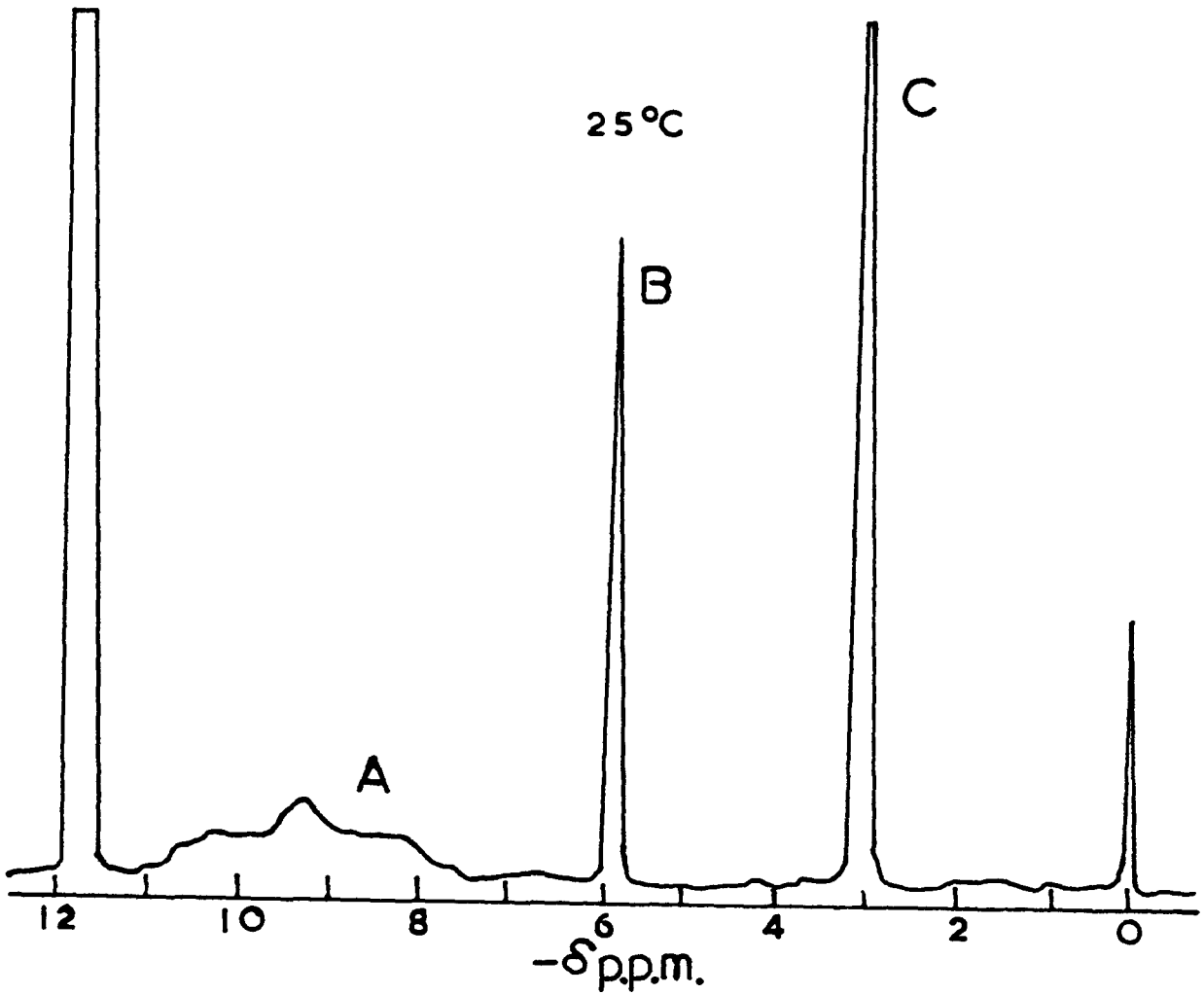


Fig. 10 N.m.r. SPECTRUM OF THIOACETAMIDE IN FLUOROSULPHURIC ACID.

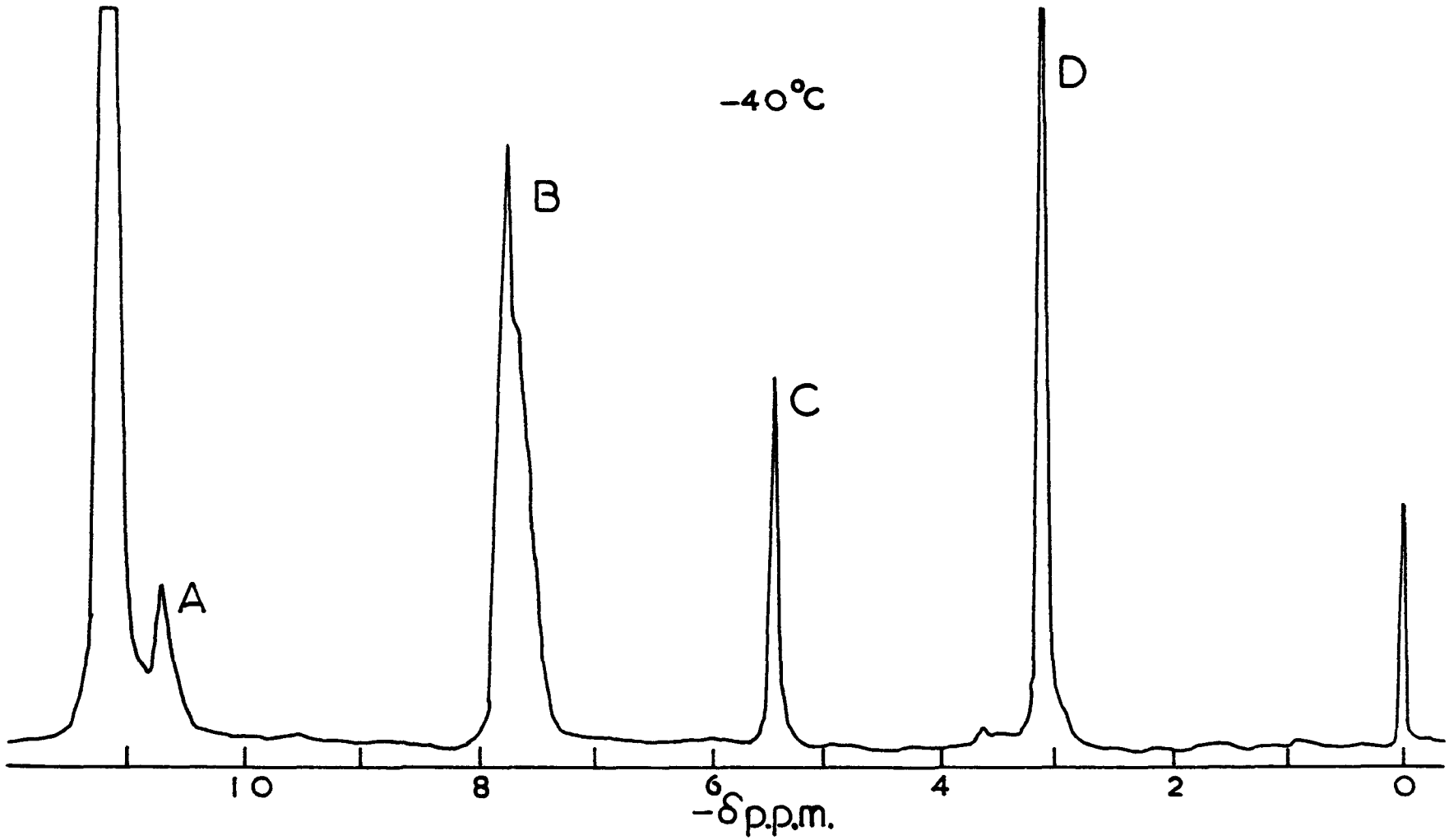


Fig. 11 N.m.r. SPECTRUM OF THIOACETANILIDE IN FLUOROSULPHURIC ACID

(4) UREAS

The results for thiourea, N-methylthiourea, urea and N,N-dimethylurea are given in Table III.

Thiourea and N-methylthiourea

The spectrum of thiourea in water or trifluoracetic acid contains only one line due to the NH_2 group in addition to the solvent peak. The fact that the trifluoracetic acid peak is quite broad suggests that although protonation occurs in this medium proton exchange is rapid at 25°. In the more acidic (and less basic) medium sulphuric acid, a new peak appears in the spectrum at approximately -5 p.p.m. that can be attributed to the $C{=}\overset{+}{S}H$ group and the NH_2 peak disappears. In fluorosulphuric acid the spectrum is essentially the same except that the $C{=}\overset{+}{S}H$ peak is somewhat narrower indicating that proton exchange with the solvent is slower than in sulphuric acid. Decreasing the temperature causes a further narrowing of this line, as expected. At the same time the solvent peak increases in width with decreasing temperature. This observation and the disappearance of the NH_2 peak can only be reasonably interpreted as being due to diprotonation, the first proton being attached to sulphur and exchanging only very slowly with the solvent and the second proton being attached to nitrogen and exchanging rather rapidly with the solvent.

The behaviour of N-methylthiourea is similar. In water and trifluoracetic acid the spectrum consists of three peaks A, B and C, due to the NH, NH_2 and $N{-}CH_3$ groups respectively (Fig. 12). The latter peak is a doublet due to spin-spin coupling with the NH proton ($J = 4$ c.p.s.) Area measurements gave a ratio A + B: C = 2.8: 3.0. Fig. 13a shows the spectrum of a fluorosulphuric acid solution at -47.5° . A $C{=}\overset{+}{S}H$ peak (B)

has appeared, the NH peak has disappeared and the $N\text{-}CH_3$ peak (C) has collapsed to a single line. The relative areas were found to be A:B:C = 1.81: 0.95: 3.00. It must be concluded that a second protonation occurs on the nitrogen of the $NH.CH_3$ group but proton exchange between the $\overset{+}{N}H_2.CH_3$ group and the solvent is quite rapid even at -80°. By using a less basic SbF_5/HSO_3F mixture as solvent it was found possible to reduce the rate of this exchange sufficiently, so that at -67°, a new peak D is observed in the spectrum at -8.19 p.p.m. (Fig. 13b) which can presumably be attributed to the two protons on the methylated nitrogen atom. The $N\text{-}CH_3$ peak was found to have a width of 15 c.p.s. which must be at least partly due to slow proton exchange: in the absence of exchange this peak would be expected to be a triplet due to coupling with the $\overset{+}{N}H_2$ protons. At low temperatures these solutions become very viscous and this is also partly responsible for the broadness of the signals.

The conclusion that protonation of thiourea and its N-methyl derivatives occurs first on sulphur is in agreement with ultra-violet and infra-red spectroscopic studies[58,60] and wide line n.m.r.[63] studies on thiourea salts. It appears that a second protonation occurs on the nitrogen atom in very strong acid solution.

Urea and N,N^1-dimethylurea

In dilute aqueous solution the spectrum of urea consists of an NH_2 peak. In sulphuric and fluorosulphuric acids this peak disappears and no peak was observed for urea even at -86° or in fluorosulphuric acid containing 10% SbF_5 at -88°. However in both these latter cases the solvent peak is quite broad indicating that, contrary to the behaviour of other amides, proton exchange is fairly slow but not slow enough for a

separate peak from the conjugate acid of urea to be observed. That the disappearance of the N-H resonance is not due to quadrupole relaxation was demonstrated by the use of N^{15} urea (N^{15} has spin $\frac{1}{2}$ and hence no quadrupole moment): as before no peaks were observed.

Only a single peak was observed due to NCH_3 group in the spectrum of a 6 mole % solution of N,N'-dimethylurea in water. Thus it appears that in this case the NH protons exchange with the solvent even in dilute aqueous solution. Redpath and Smith[63] however observed both an NH peak (width = 23 c.p.s.) and an unsymetrical methyl doublet (J = 4.3 c.p.s.) in a solution containing 0.6 weight fraction of N,N'-dimethylurea in water. This doublet collapses in sulphuric acid solution. Although, as in the case of urea, the solvent peak became very broad at low temperatures it was not possible to slow down exchange sufficiently, even at -88° in HSO_3F containing 10% SbF_5, to observe peaks due to $\overset{+}{N}H_2$ or $C{=}\overset{+}{O}H$. Unfortunately these results do not enable any definite conclusions to be drawn concerning the site of protonation in urea and N,N'-dimethylurea. In the case of simple amides, by decreasing the basicity of the solvent, the rate of proton exchange with the solvent can be decreased sufficiently so that a separate n.m.r. signal from the conjugate acid can be observed. However in the case of urea and its derivatives decreasing the basicity (and therefore increasing the acidity) of the solvent probably leads to a second protonation of the amide and the diprotonated species exchanges more rapidly with the solvent than the conjugate acids of simple amides. Evidence for the diprotonation of tetraethylurea has been obtained from freezing-point measurements in 100% sulphuric acid[83]. Evidence that the site of the first protonation is on the oxygen atom is given by the

results of an X-ray diffraction study[65] of the crystal structure of N-methylurea nitrate in which a short hydrogen bond was found between the carbonyl oxygen and an oxygen of the nitrate ion. Redpath and Smith[63] have also obtained evidence from the line-widths in the n.m.r. spectra of various crystalline urea salts that the conjugate acid of urea has a proton on the carbonyl oxygen. The infra-red and ultra-violet spectra of urea hydrochloride have also been interpreted[58] on the basis of protonation on the carbonyl oxygen.

TABLE III

CHEMICAL SHIFTS FOR SOLUTIONS OF UREAS AND THIOUREAS

Urea	Temp (°C)	Solvent	$-\delta$ (p.p.m.) from Ext. T.M.S. Solvent	X-H	N-H	$N-CH_3$	J (c.p.s.)
Thiourea	25	water	5.12	-	7.66	-	
	"	trifluoracetic acid	11.95(22)+	-	7.83	-	
	"	sulphuric acid	10.89(29)	5.25(44)	-	-	
	"	fluorosulphuric acid	10.30(15)	4.87(21)	-	-	
	-50	"	10.63(46)	4.81(~5)	-	-	
	-73	"	11.05(69)	4.84(~5)	-	-	
N-Methylthiourea	25	water	-	-	8.07,7.59	3.33	J_{H,CH_3} 3.8
	"	trifluoracetic acid	11.45(21)	-	8.02,7.55	3.16	J_{H,CH_3} 4.2
	"	sulphuric acid	11.21(29)	5.21(broad)	7.84	3.56)	No coupling
	-47.5	fluorosulphuric acid	11.11(33)	4.79(sharp)	7.29	3.24)	observed
	-67.5	fluorosulphuric acid*	10.81(29)	4.86	8.19,7.32	3.35	

+ Values in brackets denote line width

* Fluorosulphuric acid solution contains 4.47 mole % SbF_5

TABLE III (Contd.)

Urea	Temp (°C)	Solvent	- δ (p.p.m.) from Ext. T.M.S. Solvent	X-H	N-H	N-CH_3	J (c.p.s.)
Urea	25	water	5.13	-	6.08	-	
	"	trifluoracetic	10.11(13)	-	-	-	
	"	sulphuric acid	10.81(~ 4)	-	-	-	
	"	fluorosulphuric acid*	9.10(~ 5)	-	-	-	
	-60	"	9.38(16)	-	-	-	
	-80	"	9.52(34)	-	-	-	
N,N'-dimethyl urea	25	water	5.32	-	-	3.08	
	"	trifluoracetic acid	11.09(8)	-	-	2.97	
	"	sulphuric acid	10.94	-	-	3.43	
	-86	fluorosulphuric acid	11.67(64)	-	-	3.33(31)	
	25	fluorosulphuric acid*	9.97	-	-	3.34	
	-88	"	11.94(93)	-	-	3.59(~120)	

+ Values in brackets denote line width

* Fluorosulphuric acid solution contains 4.47 mole % SbF_5

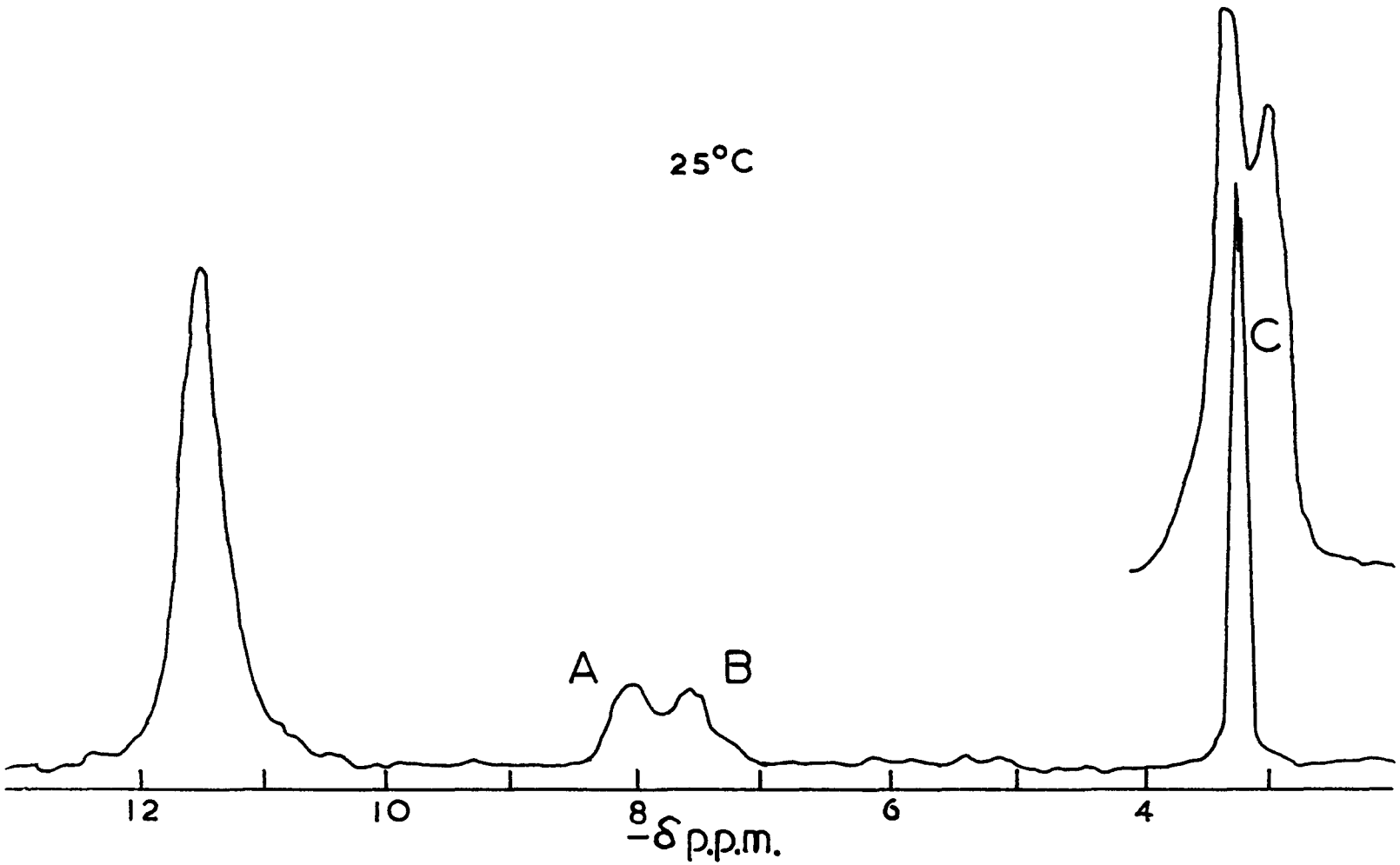


Fig. 12 N.m.r. SPECTRUM OF N-METHYLTHIOUREA IN TRIFLUORACETIC ACID.

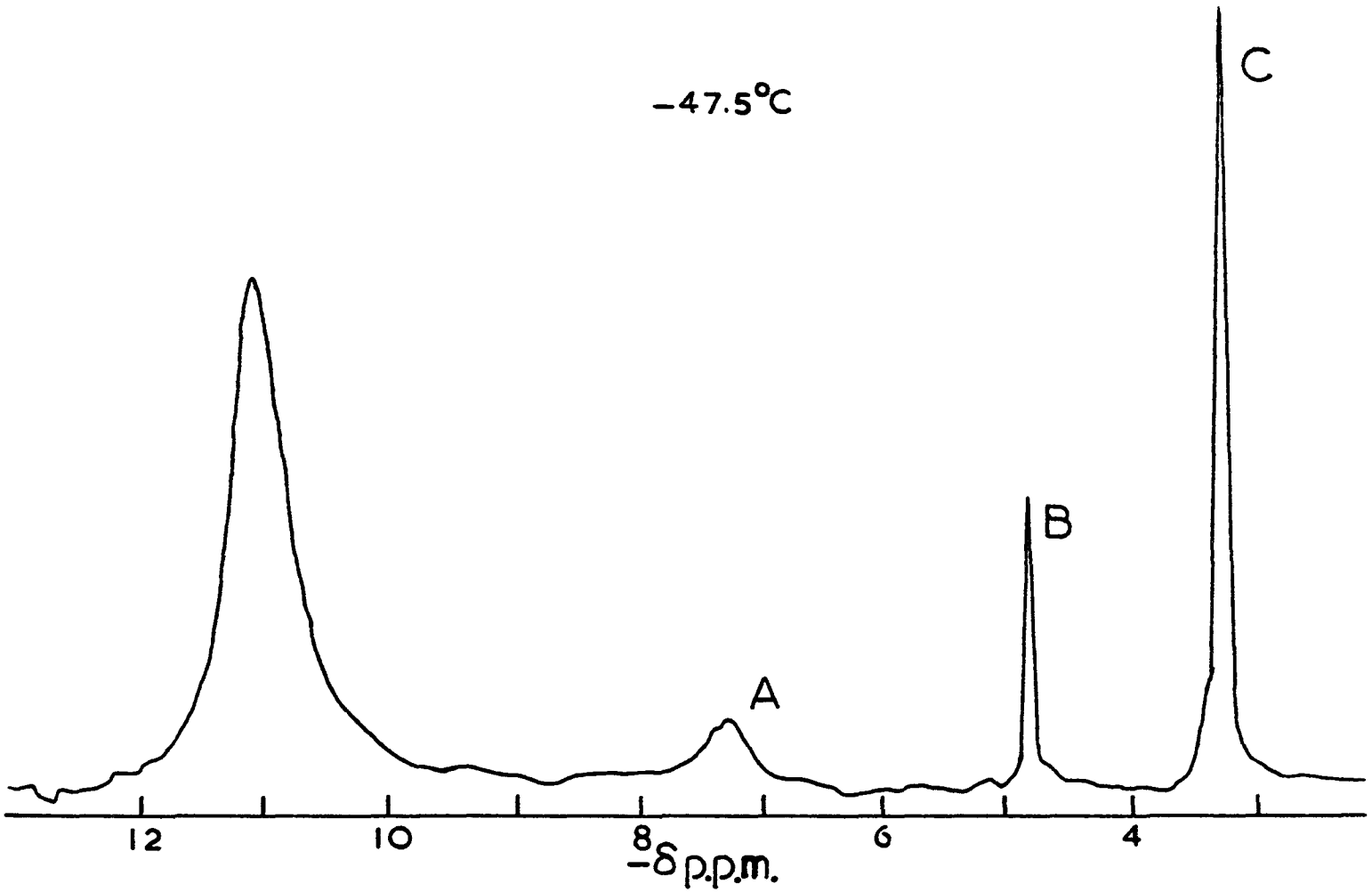


Fig. 13a N.m.r. SPECTRUM OF N-METHYLTHIOUREA IN FLUOROSULPHURIC ACID.

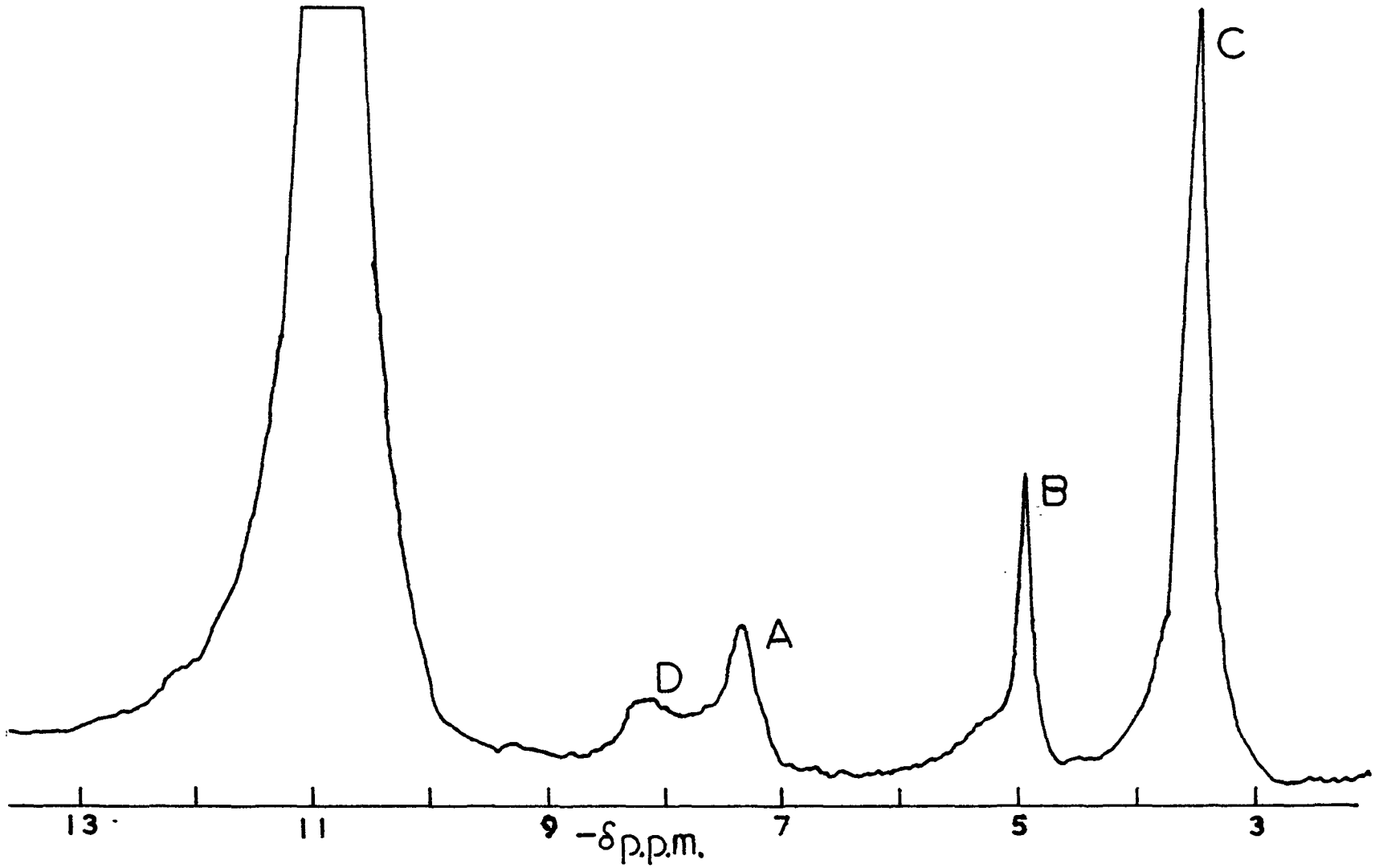


Fig. 13 b N.m.r. SPECTRUM OF A SOLUTION OF N-METHYLTHIOUREA IN FLUOROSULPHURIC ACID CONTAINING 4.47 MOLE % ANTIMONY PENTAFLUORIDE.

(5) SULPHONAMIDES

The results are summarised in Table IV. The conjugate acids of these bases undergo extremely slow proton exchange with the solvent even at room temperature. Fig. 14 shows the spectrum of N-methyl-p-toluenesulphonamide at -5°: A is assigned to the C_6H_4 and $\overset{+}{N}H_2$ protons, B to the N-CH_3 group and C to the p-CH_3 group. This assignment is confirmed by the relative areas of the peaks which were found to be A: B: C = 6.13: 3.05: 3.00 and the fact that B is a poorly resolved triplet due to spin-spin coupling with the NH_2 protons. Fig. 15 shows the spectrum of N,N-dimethyl-p-toluenesulphonamide at 25°. A is assigned to the C_6H_4 and $\overset{+}{N}H$ protons, B to the N-CH_3 group and C to the p-CH_3 group. This assignment is confirmed by the relative areas of the peaks which were found to be A: B: C = 4.87: 6.30: 3.00 and the fact that B is a doublet due to spin-spin coupling with the $\overset{+}{N}H$ proton. It is clear that in both these cases protonation is on nitrogen.

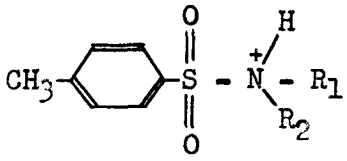
Sulphamide

A solution of sulphamide in fluorosulphuric acid at 25° gave the spectrum in Fig. 16, consisting of a moderately broad peak superimposed on a very broad peak. The former is assigned to the $\overset{+}{N}H_3$ group and the latter to the NH_2 group in the conjugate acid of sulphamide $O{=}S(NH_2)(\overset{+}{N}H_3)$. No peaks other than the solvent peak were visible in the spectrum of a sulphuric acid solution at room temperature presumably because of relatively rapid proton exchange between the conjugate acid of sulphamide and the solvent.

TABLE IV

CHEMICAL SHIFTS OF SULPHAMIDE AND SOME SULPHONAMIDES

IN FLUOROSULPHURIC ACID



Sulphonamide	Temp. (°C)	$-\delta$ (p.p.m.) from Ext. T.M.S. Phenyl	N-H	$N-CH_3$	$C-CH_3$	J c.p.s.
N-Methyl-p-toluenesulphonamide	25	8.06	~7.79	3.30	2.77	
	-5	8.06	~7.79	3.29	2.74	J_{H,CH_3} 5.4
	-70	8.06	~7.79	3.26	2.68	
N,N-Dimethyl-p-toluenesulphonamide	25	8.06	~7.56	3.32	2.76	J_{H,CH_3} 5.2
	-50	8.04	~7.56 $+NH_3$	3.29 NH_2	2.74	
Sulphamide	25		8.21	7.68		

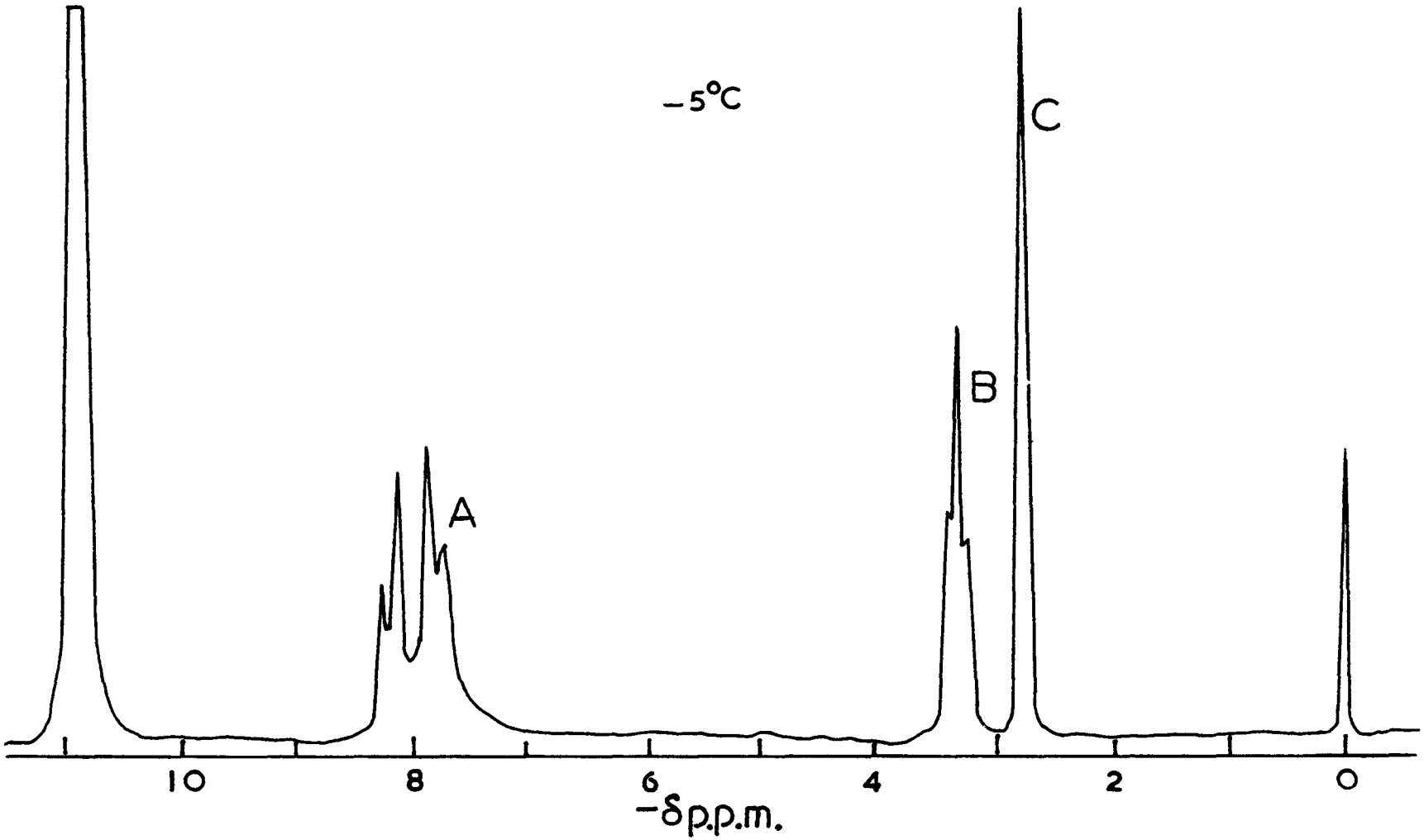


Fig. 14 N.m.r. SPECTRUM OF N-METHYL-P-TOLUENE-SULPHONAMIDE IN FLUOROSULPHURIC ACID.

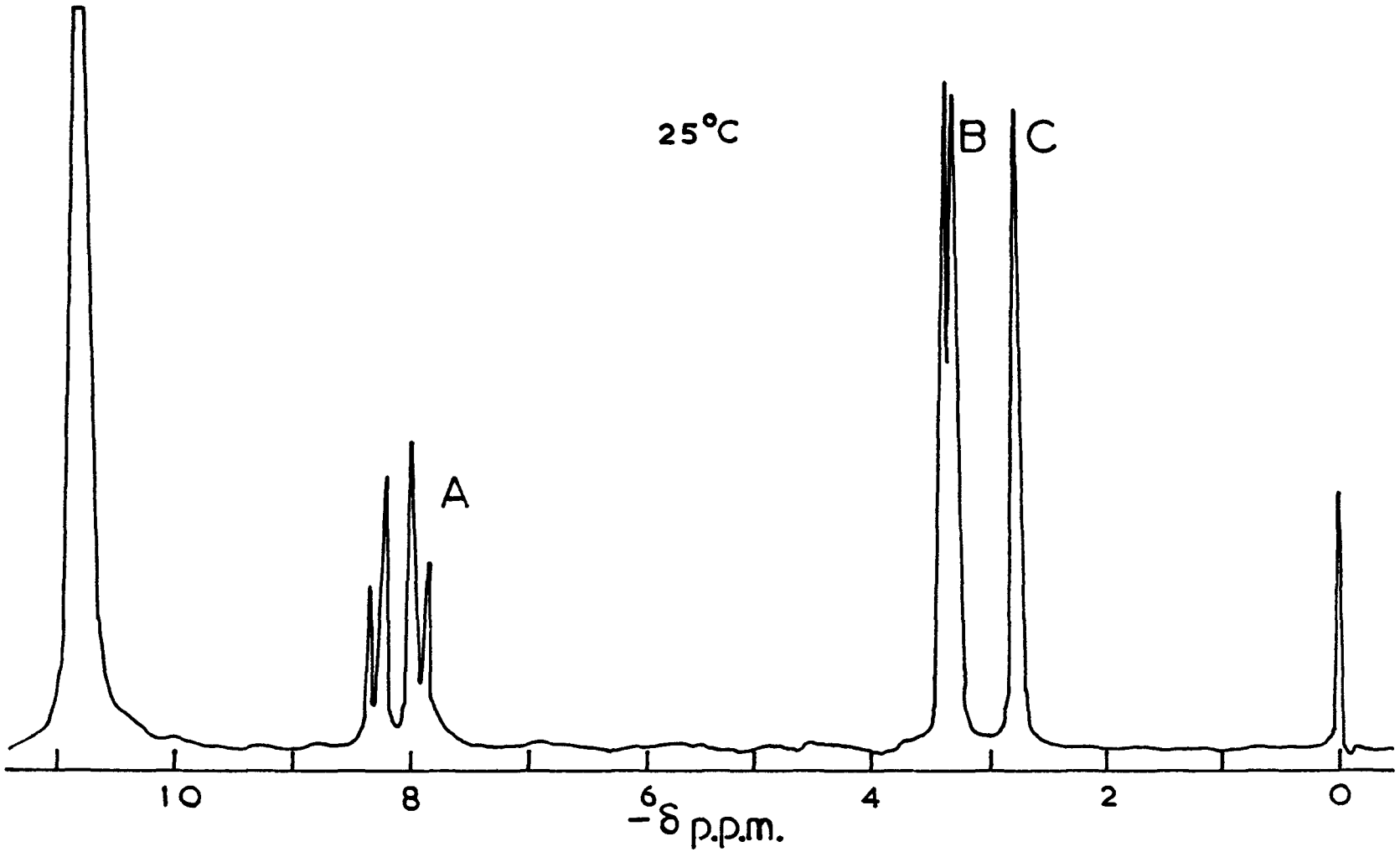


Fig. 15 N.m.r. SPECTRUM OF N,N-DIMETHYL-P-TOLUENE-SULPHONAMIDE IN FLUOROSULPHURIC ACID.

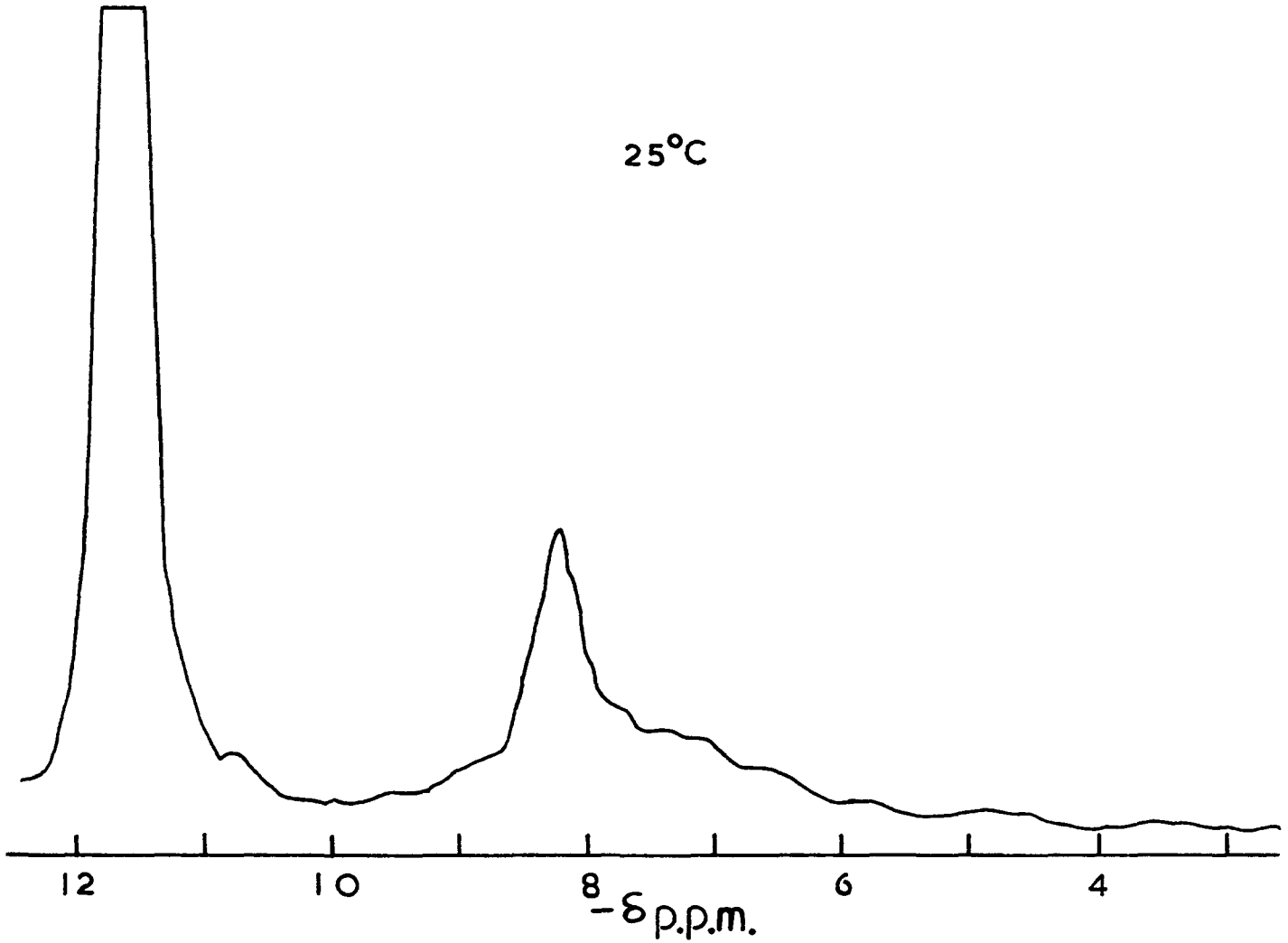


Fig. 16 N.m.r. SPECTRUM OF SULPHAMIDE IN FLUOROSULPHURIC ACID.

CHAPTER IV

PROTONATION OF METHYL BENZENES AND ANISOLE IN FLUOROSULPHURIC ACID

(1) INTRODUCTION

The protonation and relative basicities of the various methylbenzenes has been discussed in a number of papers[84-88]. Mackor et al.[88] have measured the basicity constants for a large number of aromatic hydrocarbons in HF solution. The electronic absorption spectra of aromatic carbonium ions of type AH have been studied[87] and π-electron resonance energies calculated. It has been assumed that the proton adds to one carbon atom thereby forming an "aliphatic" CH_2 group as first suggested by Gold and Tye[85] in the case of anthracene. Definite evidence in support of this assumption has been obtained from the n.m.r. spectra of the conjugate acids of a number of aromatic hydrocarbons obtained by dissolving the hydrocarbon in astrongly acid medium such as $BF_3.H_2O/CF_3COOH$ or BF_3/HF[19]. Although for pentamethylbenzene in BF_3/HF a rather broad line due to the CH_2 group was observed at room temperature, in the case of hexamethylbenzene, mesitylene and other weaker bases it was necessary to make measurements at low temperatures in order to observe the resonance of the CH_2 protons. This has been attributed to the exchange of the CH_2 protons by one or more of three processes.

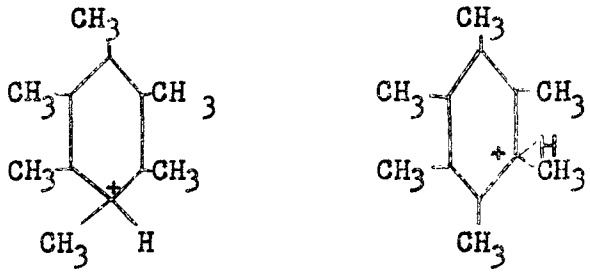
(i) Exchange with the solvent HS

$$AH^+ + S^- = A + HS \qquad (4.1)$$

(ii) Intermolecular exchange between the aromatic hydrocarbon and its conjugate acid

$$A + AH^+ = AH^+ + A \qquad (4.2)$$

(iii) Intramolecular exchange of the proton between positions of equal proton affinity on the same carbonium ion, e.g.



(4.3)

From the results of their studies of the protonation of aromatic hydrocarbons in HF/BF_3 MacLean and Mackor[20] have concluded that for hexamethylbenzene, durene and prehnitene exchange proceeds by (4.3) for mesitylene by (4.2) and (4.1) and for m-xylene by process (4.2) while for pentamethylbenzene they observed no exchange.

Fluorosulphuric acid has a somewhat greater acid strength than HF and a similar low freezing point, but unlike HF can be handled in conventional glass apparatus. It was hoped that useful information on the exchange of protons between aromatic hydrocarbon and acid solvents would be obtained by a parallel study to that carried out by MacLean and coworkers using HSO_3F rather than HF as a solvent. One particular aim was to ascertain if the novel mechanism (4.3) also operates in HSO_3F solutions.

(2) SPECTRA OF HYDROCARBON CONJUGATE ACIDS

For each of the hydrocarbons studied it was found that at sufficiently low temperatures and under sufficiently acid conditions the lifetime of the hydrocarbon conjugate acid is long enough for its n.m.r. spectrum to be observed. Table V contains chemical shift data for these bases.

Mesitylene

The spectrum of a 6.16 mole % (1.2 molar) solution of mesitylene in fluorosulphuric acid at -79° is shown in Fig. 17. It consists of three peaks A, B and C of relative areas 2.02: 1.96: 9.08. These three peaks must arise from the two aromatic protons A, the two "methylene" protons B, and the three methyl groups C respectively, indicating that protonation has occurred on one of the ring carbon atoms. Since the three methyl groups are no longer equivalent the methyl resonance actually consists of two overlapping peaks of relative area 1:2. The spectra of other solutions with concentrations in the range 2-6 mole % are all quite similar. No signals were observed for any of the solutions that could be attributed to the unprotonated mesitylene indicating that, under the experimental conditions, the protonation of mesitylene is essentially complete. This is of some interest since MacLean and Mackor's[20] n.m.r. spectrum of a 3.5 molar solution in anhydrous hydrogen fluoride saturated with boron trifluoride indicated that only 60% of the mesitylene was present in the protonated form, the remainder being present as the free base.

No fine structure due to spin-spin coupling was observed, although in HF solution MacLean and Mackor found that the paramethyl

group was a triplet. They attributed this to spin-spin coupling with the "methylene" group although the expected quartet splitting of the methylene signal was not observed.

Durene

Four peaks, A, B, C, and D are observed in the spectrum of durene in fluorosulphuric acid at low temperature (Fig. 18). These may be attributed to the CH, and CH_2 groups and two nonequivalent methyl groups respectively. The relative areas were found to be A: B: C: D = 0.87: 1.79: 6.0 in agreement with the proposed assignment.

Pentamethylbenzene

Protonation of pentamethylbenzene occurs at the only unsubstituted ring position. The spectrum of a fluorosulphuric acid solution at -49° is shown in Fig. 19: it consists of four peaks A, B, C, and D of relative areas A: B: C: D = 1.77: 3.14: 6.09: 6.00 which may be attributed to the CH_2, p-CH_3, o-CH_3, and m-CH_3 groups respectively.

Hexamethylbenzene

A solution of hexamethylbenzene (2.7 mole %) in fluorosulphuric acid was found to give at -85°, a spectrum consisting of five peaks of relative areas A: B: C: D: E = 0.99: 3.06: 6.13: 6.35: 3.00 (Fig. 20a). Under favourable conditions E was observed as a poorly resolved doublet due to coupling with the single proton A (J=5.8 c.p.s.) but no corresponding splitting of peak A was observed. In HF/BF_3 solution MacLean and Mackor found J_{AE} = 6.7 c.p.s. and also J_{AB} = 3.5 c.p.s. and J_{AC} = 1 c.p.s.[19,20]. No fine structure, other than the doublet E, was observed in this investigation.

m-Xylene

Fig. 21 shows the spectrum of a solution of m-xylene in 1.2 mole % SbF_5/HSO_3F at -50°. The relative areas of the peaks were found to be A:B:C = 2.91: 1.80: 6.00. The spectrum is best explained by assuming protonation ortho to one methyl and para to the other methyl group. The "doublet" C is due to the nonequivalent methyl groups and B arises from the "methylene" protons. The phenyl part of the spectrum A consists of a peak B due to the proton ortho to both methyl groups superimposed on an AB quartet arising from the other two ring protons. The unequal heights of the methyl peaks may be attributed to unresolved spin-spin coupling causing a greater broadening of one peak than the other.

p-Xylene

The much weaker base p-xylene was examined in a 13 mole % SbF_5/HSO_3F solution. At -63°, which was the lowest temperature at which a reasonable spectrum could be recorded due to the high viscosity of the solution, only two very broad lines were visible in the spectrum; one due to the ring protons and the other to the methyl groups. From an integrated spectrum the relative areas of the two peaks were found to be 4.77: 6.00 indicating that ring protonation had taken place.

Anisole

The spectrum of a solution of anisole in fluorosulphuric acid shown in Fig. 22a closely resembles that obtained in an organic solvent except that the spectrum is shifted 0.6 p.p.m. to lower field. Figs. 22b and 22c show the effect of temperature. At low temperatures a new peak appears at 4.4 p.p.m. below the tetramethylsilane referance; this

can be attributed to a "methylene" group formed by ring protonation. At 0° the lack of resolution in the phenyl spectrum indicates that exchange of the CH_2 protons with the solvent is still occurring, but at -64° fine structure can be observed in the phenyl spectrum and as this does not change further at lower temperatures it is reasonable to suppose that exchange has become very slow. The spectrum is best explained by postulating protonation at the ring position para to the methoxy group as MacLean and Mackor have previously done in order to explain the results of their studies of HF solutions[20], and not on the oxygen as has been assumed to explain the results of ultra-violet spectroscopic measurements[89]. Evidence for ring protonation has also been obtained recently in the cases of dimethoxybenzene from n.m.r. studies[20] and for trimethoxybenzene from reaction rate studies[90].

TABLE V

CHEMICAL SHIFTS OF METHYLBENZENES AND ANISOLE IN FLUOROSULPHURIC ACID

Base	Temp. (°C)	Chemical Shifts δ (p.p.m.) from Ext. T.M.S. Solvent	CH	CH_2	CH_3			
Mesitylene	-77	10.99	7.67	4.56	2.93	2.77		
(concn.1.93 mole %)	-35	10.84	7.68	4.57		2.83		
	-25	10.61	7.72	4.59		2.85		
Durene	-88	11.19	8.75	5.02	2.85	2.58		
(concn.1.49 mole % + (9.04 mole % SbF_5)	-69.5	11.09	8.69	4.99		2.69		
	-60	11.06	8.65	5.02		2.68		
Hexamethyl	-85	11.60	4.19		2.85	2.71	2.41	1.71
-benzene	-73	11.59	4.23		2.68	2.53	1.61	
(concn.8.21)	-62	11.56	4.20		2.58	1.89		
	-46	11.49	4.21			2.51		
Pentamethyl	-49	0.0		6.52	8.43	8.59	8.88	
-benzene * (concn.2.82 mole % + 3.39 mole % KSO_3F)								

* The chemical shifts of these bases were referenced with respect to the solvent.

TABLE V (Contd.)

Base	Temp. (°C)	Chemical shifts δ (p.p.m.) from Ext. T.M.S. Solvent	Phenyl				CH_2	CH_3	
m-Xylene*	-80	0.0	1.91	2.04	2.77	2.89	5.97	7.70	7.81
(concn.7.82 mole % + 11.35 mole% SbF_5)	-50	0.0	1.74	1.88	2.62	2.77	5.85	7.55	7.67
	-31.5	0.0	1.72	1.85	2.57	2.74	5.78		7.58
								OCH_3	
Anisole	-64	11.14	8.92	8.76	8.59	8.42	4.34	4.65	
(concn.4.12 mole %)			7.76	7.60	7.47	7.28			
	0	10.95	8.81	8.46	8.26	7.69	4.40	4.77	
						7.57			
	25	10.79	8.66	8.31	8.15	7.58	-	4.34	
						7.44			

* The chemical shifts of these bases were referenced with respect to the solvent.

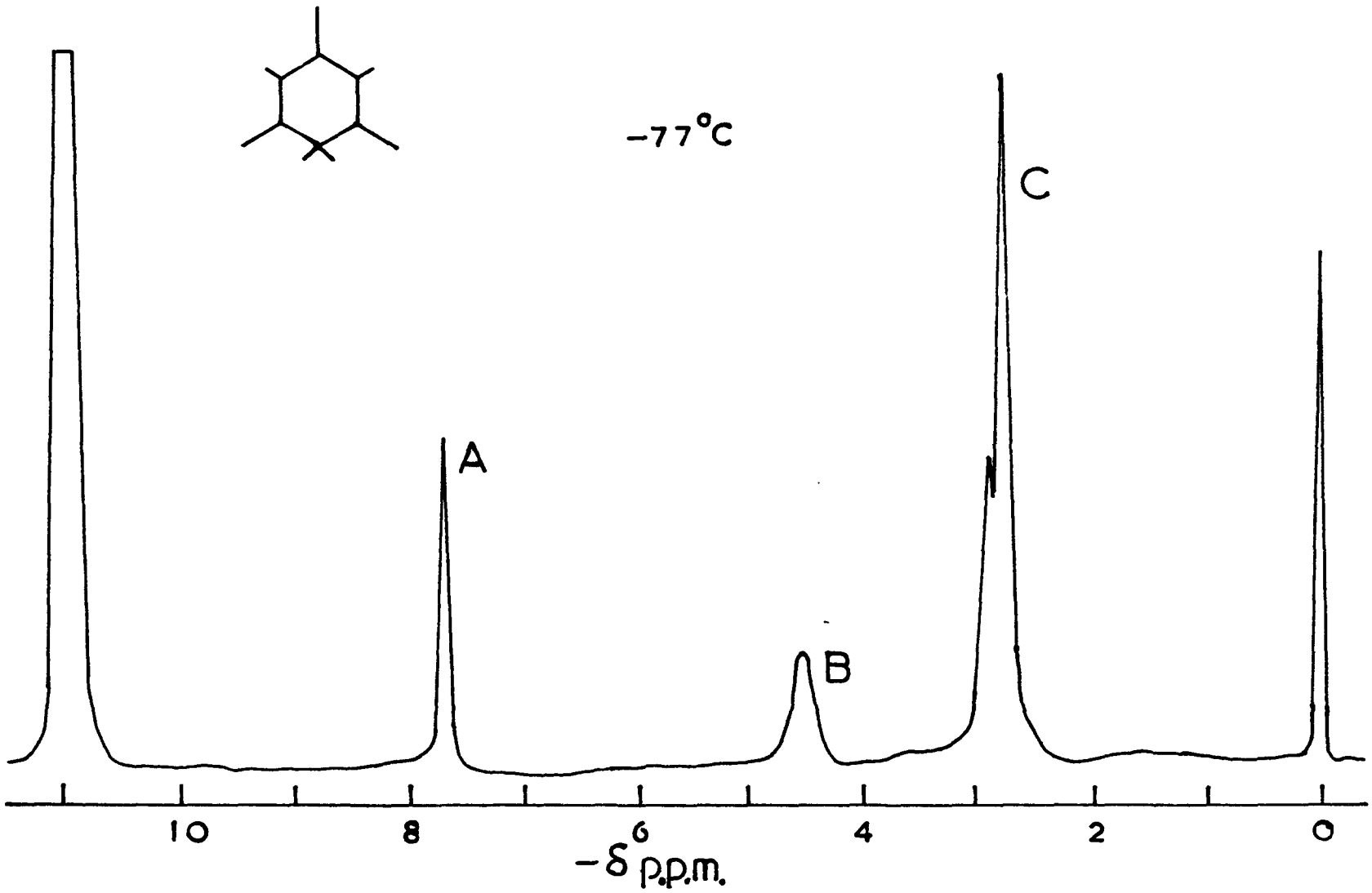


Fig. 17 N.m.r. SPECTRUM OF A SOLUTION OF MESITYLENE (6.16 mole %) IN FLUOROSULPHURIC ACID.

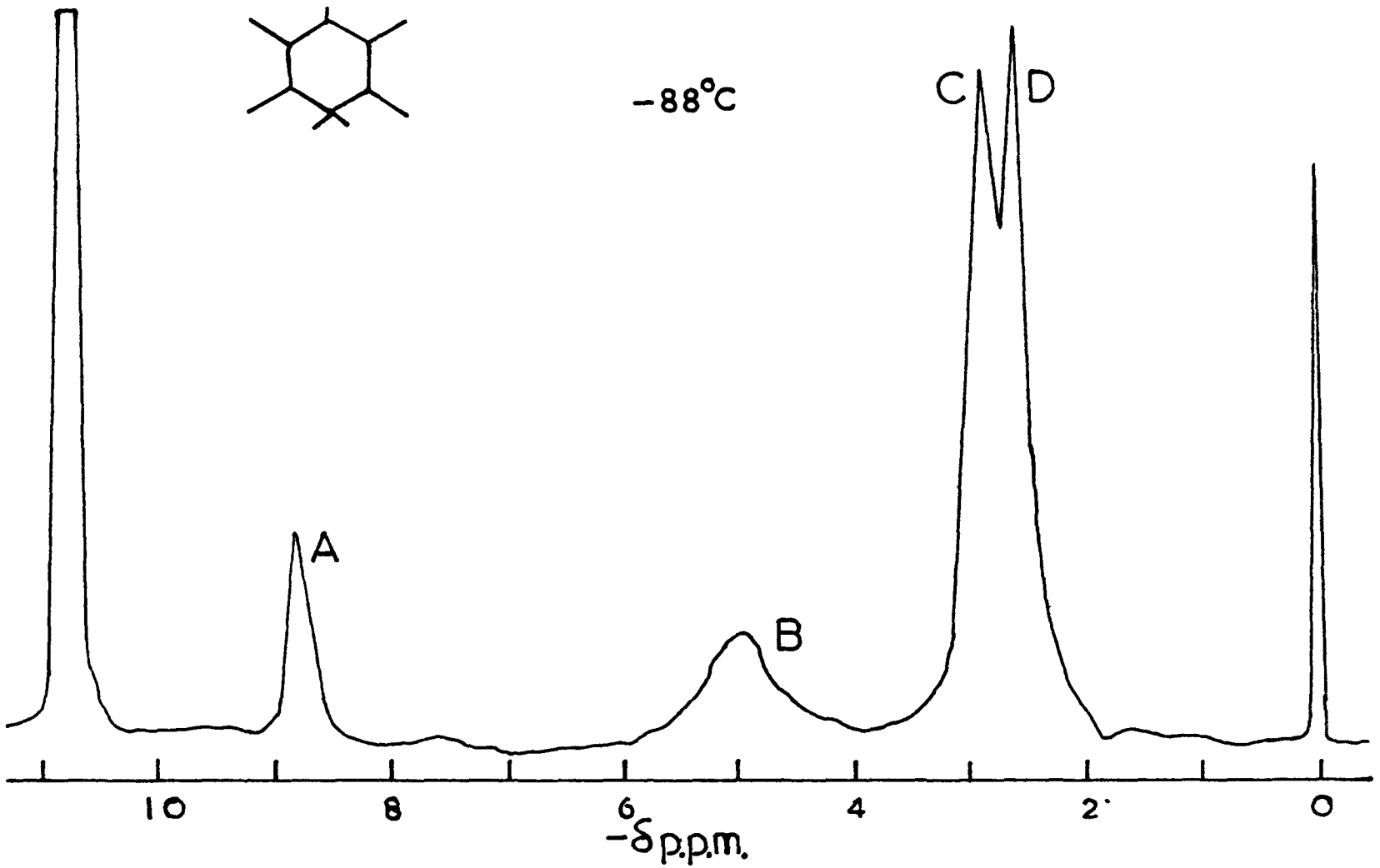


Fig. 18 N.m.r. SPECTRUM OF A SOLUTION OF DURENE (1.12 mole %) IN FLUOROSULPHURIC ACID.

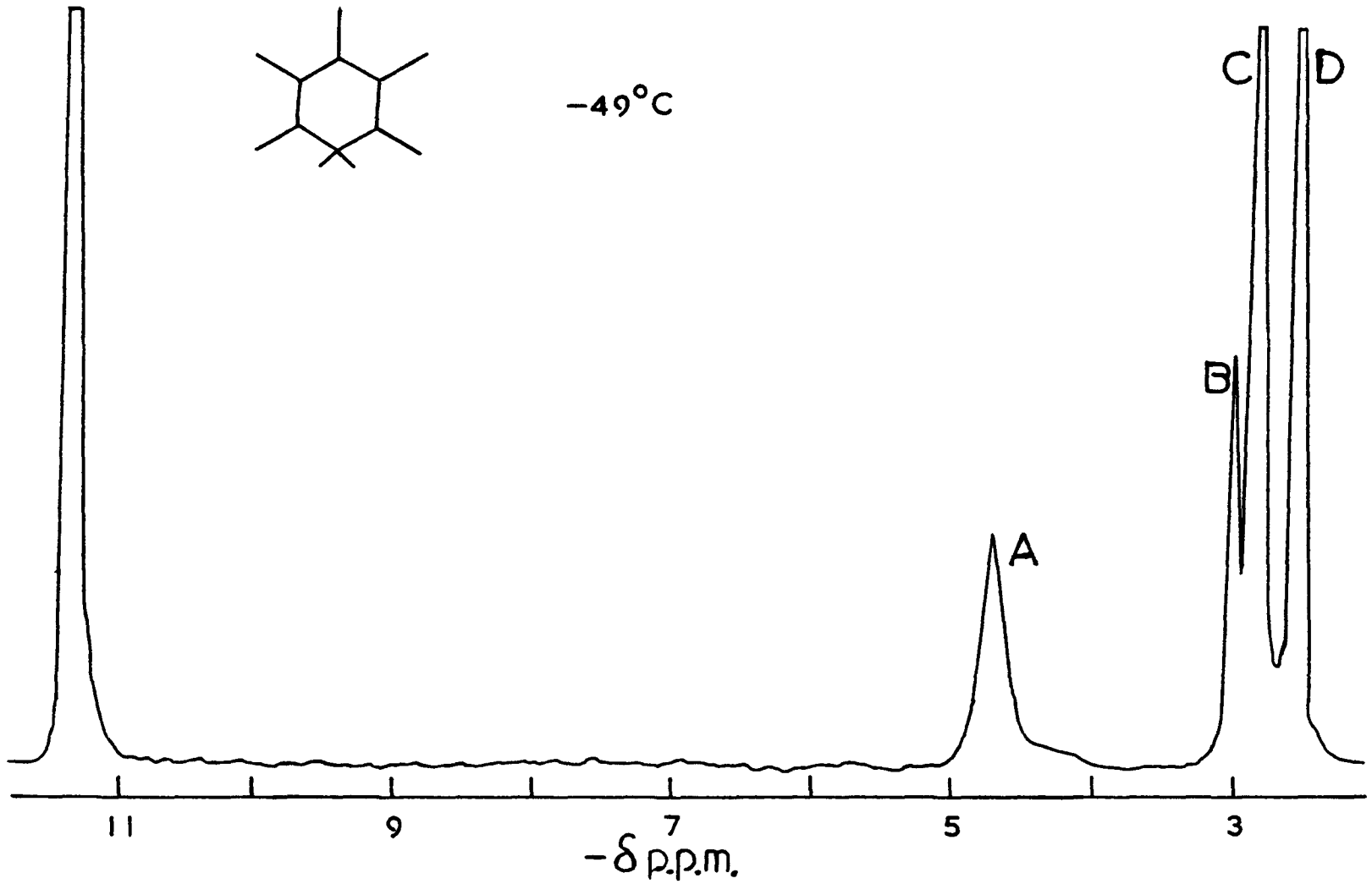


Fig. 19 N.m.r. SPECTRUM OF PENTAMETHYLBENZENE (2.82 mole %) IN FLUOROSULPHURIC ACID. PEAK A WAS RECORDED AT A HIGHER POWER LEVEL THAN PEAKS B, C, AND D.

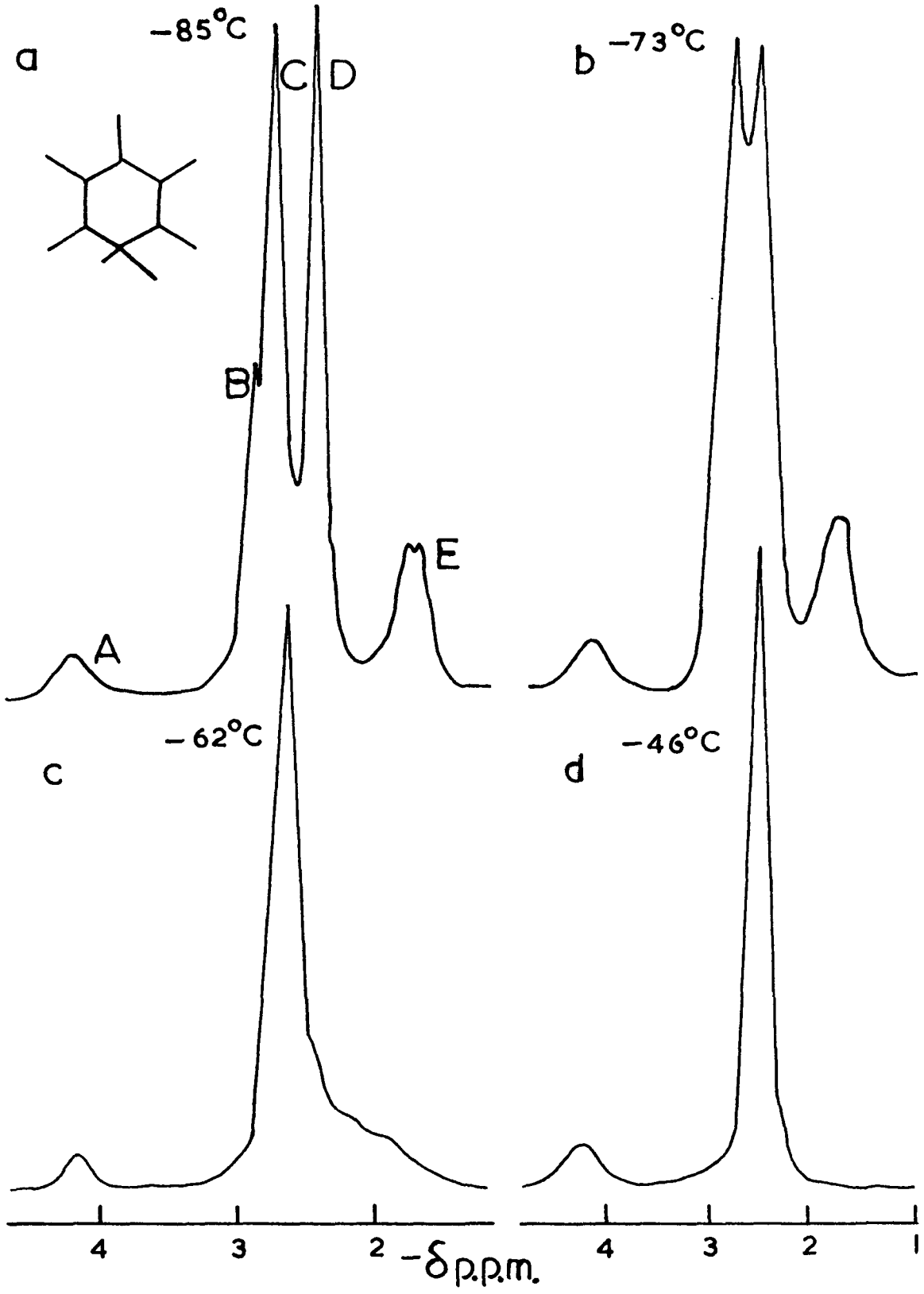


Fig. 20 N.m.r. SPECTRA OF A SOLUTION OF HEXAMETHYLBENZENE (2.7 mole %) IN FLUOROSULPHURIC ACID.

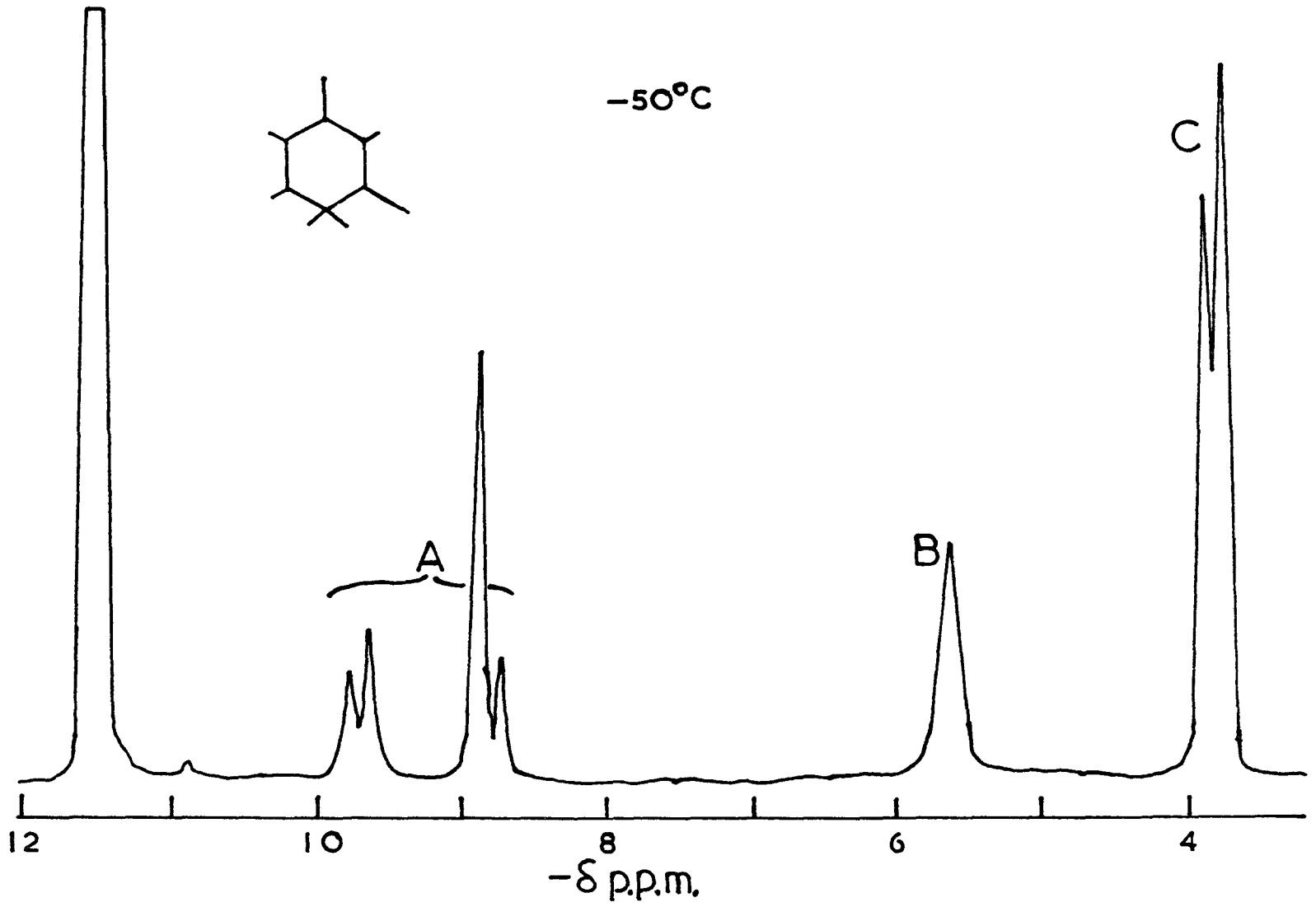


Fig. 21 N.m.r. SPECTRA OF A SOLUTION OF M-XYLENE IN FLUOROSULPHURIC ACID CONTAINING 12 MOLE % ANTIMONY PENTAFLUORIDE.

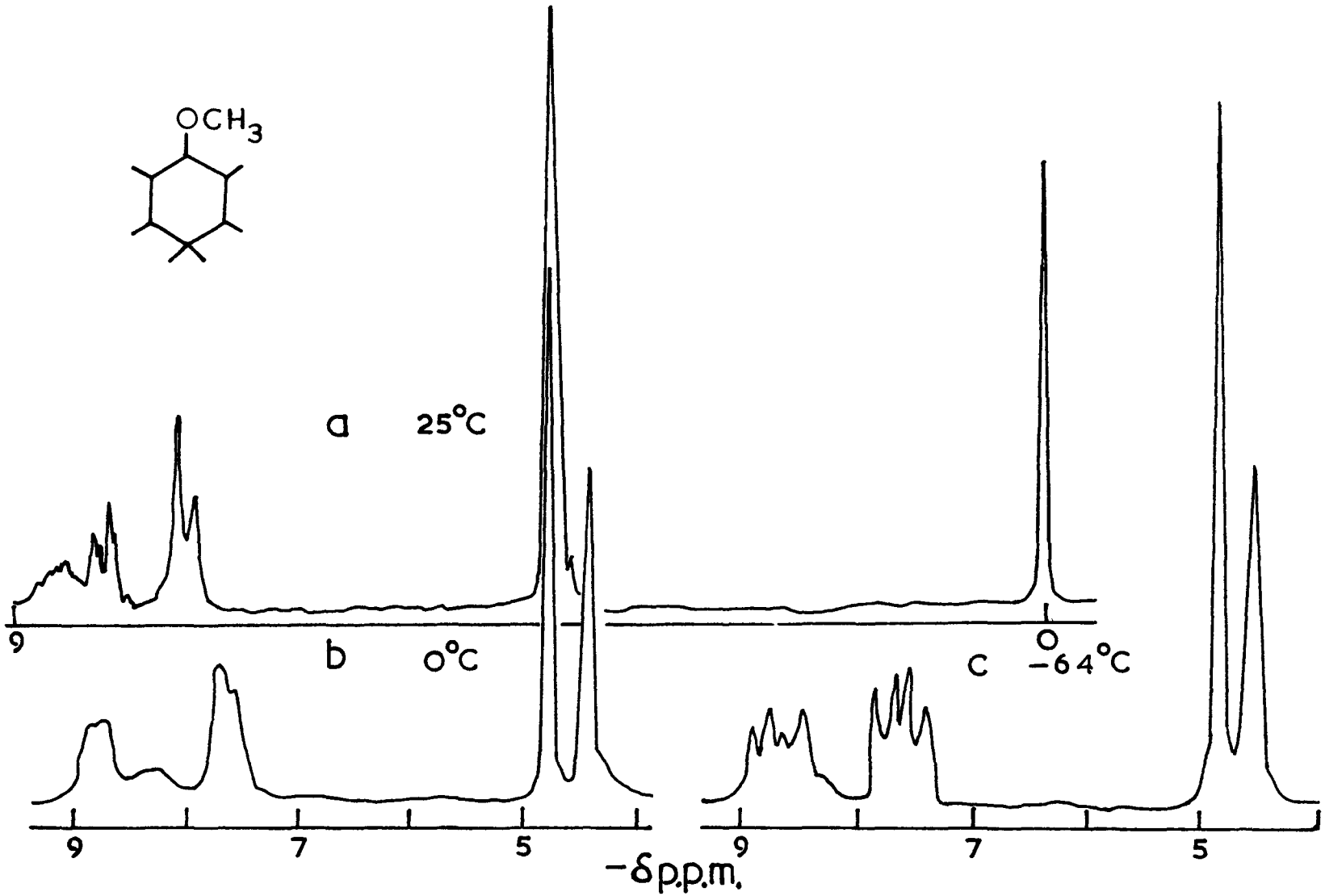


Fig. 22 N.m.r. SPECTRA OF A SOLUTION OF ANISOLE IN FLUOROSULPHURIC ACID.

(3) RATES OF PROTON EXCHANGE

On raising the temperature of the solution the lifetime of the conjugate acid decreases and the spectrum changes accordingly. The methyl spectrum collapses to a single line in all cases except pentamethylbenzene, which is the only case for which proton exchange does not lead to equivalence of the o-, m-, and p-CH_3 groups, the "methylene" (or $CH.CH_3$) and phenyl peaks broaden and eventually merge into the baseline and finally the solvent line broadens somewhat. The collapse of the methyl peaks of the conjugate acid of hexamethylbenzene with increasing rate of proton exchange is illustrated in Fig. 20. The o-CH_3 group is the first to collapse since it has the smallest chemical shift, and the methyl group on the site of protonation is the last since it has the largest chemical shift from the other methyl peaks. These observations may be attributed to proton exchange by one or more of the processes (4.1), (4.2), and (4.3).

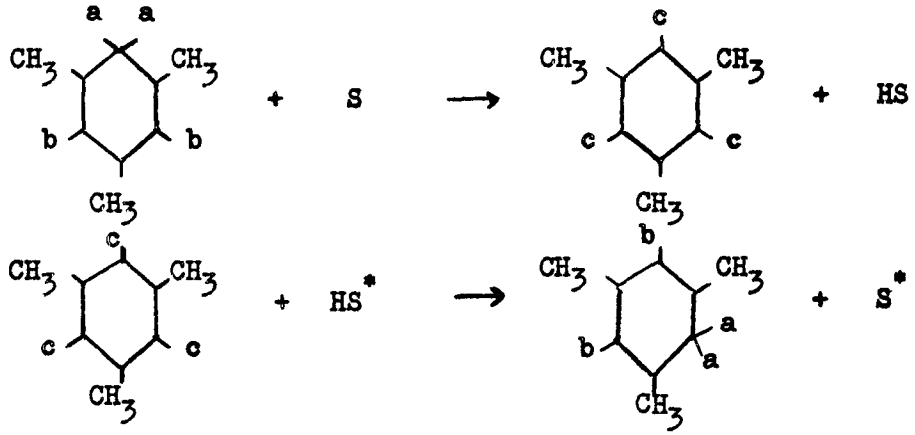
The lifetime of the proton in the CH_2 or $CH.CH_3$ group of the conjugate acid can be obtained from the widths of the CH and CH_2 (or $CH.CH_3$) signals. Under conditions where these signals can be observed the lifetime of the conjugate acid is large compared with the inverse of the separation of exchangeable sites and the condition for slow exchange may be applied. The broadened signal arising from protons at a site A has a width ($1/T'_{2A}$) given by the equation (3.3)

$$1/T'_{2A} = 1/T_{2A} + 1/\tau_A \qquad (3.3)$$

where τ_A is the lifetime of the proton on site A and $1/T_{2A}$ is the natural line width in the absence of exchange.

The relation between the lifetime of any particular proton in

a hydrocarbon conjugate acid and the lifetime of the conjugate acid τ depends on the conditions under which exchange occurs and on the particular hydrocarbon under consideration. For example, for mesitylene when the concentration of free base is negligibly small the necessary relation may be derived in the following manner. Exchange between the two proton sites a and b occurs by a slow rate determining proton loss to a solvent molecule S followed by rapid addition of another proton from the solvent.



Then if $1/\tau_{as}$ and $1/\tau_{ac}$ are the probabilities of an a proton becoming an s proton or a c proton respectively

$$1/\tau_{as} = 1/2\tau \ , \quad 1/\tau_{ac} = 1/2\tau$$

Since 2/3rds of the c protons are rapidly reconverted to b protons

$$1/\tau_{ab} = 2/3\tau_{as} = 1/3\tau$$

Hence $1/\tau_{CH_2} = 1/\tau_{ab} + 1/\tau_{as} = 5/6\tau$

Now $1/\tau_{bc} = \tau$ and since 1/3 of the c protons are rapidly reconverted to a protons

$$1/\tau_{ba} = 1/3\tau_{bc} = 1/3\tau$$

Hence $1/\tau_{CH} = 1/\tau_{ba} = 1/3\tau$

Thus for mesitylene

$$1/\tau_{CH} = 1/3\tau, \quad 1/\tau_{CH_2} = 5/6\tau \tag{4.4a}$$

The corresponding relations for the other hydrocarbons under the same conditions are

Durene $$1/\tau_{CH} = 1/2\tau, \quad 1/\tau_{CH_2} = 3/4\tau \tag{4.4b}$$

Hexamethylbenzene $$1/\tau_{CH_3} = 1/\tau \tag{4.4c}$$

Pentamethylbenzene $$1/\tau_{CH_2} = 1/2\tau \tag{4.4d}$$

m-Xylene $$1/\tau_{CH_2} = 3/4\tau \tag{4.4e}$$

The first order rate constant for proton loss by the conjugate acid is given by (3.4).

$$k = 1/\tau \tag{3.4}$$

In order to obtain a value for τ from the measured line widths it is necessary to know $1/T_2$. The CH and CH_2 line widths for mesitylene are plotted against the temperature in Fig. 23. They decrease with decreasing temperature and eventually reach a constant limiting value. At very low temperatures the CH_2 but not the CH line widths increase again somewhat. This may possibly be attributed to a decrease in the relaxation time as a consequence of an increase in η/T where η is the viscosity and T is the absolute temperature. The theory of relaxation mechanisms indicates that $1/T_1$, the inverse of the spin-lattice relaxation time, should be proportional to η/T and Bloembergen et al.[91] have shown this to be true for ethyl alcohol. The equations relating the intra- and intermolecular contributions to the spin-lattice relaxation time are given below, (4.5; 4.6).

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{2\pi\,\eta\,a^3\hbar^2\gamma^4}{b^6 kT} \tag{4.5}$$

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{3\pi^2\,\eta\,N_0\hbar^2\gamma^4}{kT} \tag{4.6}$$

Under conditions where the molecules are rotating rapidly, as in liquids, the spin-lattice relaxation time T_1 becomes equal to the spin-spin relaxation time T_2; hence $1/T_2$ is proportional to η/T. The effect of temperature upon the viscosity of fluorosulphuric acid is not known so that a correction to the inverse of the relaxation time $1/T_2$ due to change in η/T with temperature could not be made. However a partial correction for the effect of temperature alone was made according to (4.7)

$$\frac{1}{T_{2b}} = \frac{1}{T_{2a}} \cdot \frac{Ta}{Tb} \qquad (4.7)$$

where T_{2a} is the relaxation time at the lowest temperature T_a, when no further changes in the spectrum are produced; T_{2b} is the relaxation time at the higher temperature T_b, at which the exchange rate is being measured. The calculated relaxation times, together with the measured line-widths and log of the calculated lifetimes of the conjugate acid are given in Tables VI-X.

The line width of the CH_2 peak is in all cases considerably greater than that of the CH peak. This may be due to unresolved spin-spin coupling in the CH_2 signal or to the protons of the methylene group having a shorter relaxation time which might possibly be attributed to these protons being involved in rather strong hydrogen bonding with the solvent. The line widths of the CH and CH_2 peaks in SbF_5/HSO_3F solutions are greater than for solutions in HSO_3F alone which is consistent with the greater viscosity of these solutions.

It is clear from Fig. 23 that the line widths are dependent on the concentration of the hydrocarbon base. An increase in the

concentration of hydrocarbon results in an increase in the CH and CH_2 line widths and a decrease in the temperature at which broadening is first observed. Evidently the rate of proton exchange increases with increasing concentration of the hydrocarbon base. As the ionisation of the hydrocarbon produces fluorosulphate ion which increases the basicity of the solvent, the increase in exchange rate is attributed to this increase in solvent basicity. A detailed comparison of the rates of proton exchange at -20° of the compounds studied is given in Table XI. In the case of pentamethylbenzene and m-xylene this rate was calculated only from the broadening of the CH_2 peak; for hexamethylbenzene from the broadening of the $\underline{CH}.CH_3$ peak and for mesitylene from both the CH and CH_2 peaks: the rate in the case of durene was calculated only from the CH_2 signal. The reason why the CH peak was not used will be explained later.

The rate increases in every case with increase in the concentration of the hydrocarbon. The suggestion that this may be attributed to the effect of the increased concentration of fluorosulphate ion, resulting from the protonation of the hydrocarbon, is confirmed by the effect of added fluorosulphate ion in increasing the rate in the case of pentamethylbenzene and the effect of added SbF_5 in reducing the rate in the cases of mesitylene, durene, hexamethylbenzene, and m- xylene[72]. In this respect these results differ substantially from those of MacLean and Mackor[20] who claim that the rate of proton exchange for hexamethylbenzene, durene, and prehnitene are independent of the concentration of the BF_3 in the HF/BF_3 solvent and conclude that in these cases exchange occurs by the intramolecular process (4.3). It was found in fact that

the addition of SbF_5 to a solution of hexamethylbenzene in fluorosulphuric acid increases the lifetime of the conjugate acid to such an extent that the CH peak does not broaden sufficiently, even at 25°, to enable a lifetime to be measured.

For the compounds studied in this investigation these results clearly exclude the possibility that (4.3) is the only process by which exchange occurs. The solvent line broadens somewhat as the CH and CH_2 lines broaden with increasing temperature, especially when the concentration of base is appreciable. Results shown in Table XII illustrate this fact. Because of the high concentration of the solvent in the solutions the amount of broadening of the solvent peak is not great enough to enable exchange rates to be calculated, but nevertheless these results clearly indicate that exchange cannot occur only by process (4.2) because this does not involve the solvent. In addition the concentration of free base was very small (not detected by n.m.r. techniques) which makes it unlikely that exchange via process (4.2) could be fast enough to compete to any appreciable extent with (4.1). It is therefore concluded that proton exchange occurs mainly via the solvent although one cannot entirely rule out the possibility that there might be some exchange by (4.2) and (4.3) under suitable conditions.

TABLE VI

LINE WIDTHS, RELAXATION TIMES, AND RATE CONSTANTS FOR SOLUTIONS OF MESITYLENE IN FLUOROSULPHURIC ACID

Temp. °C	CH			CH_2		
	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/τ	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/τ
Conc. of mesitylene 1.93 mole %						
-36.5	17.6	13.2	1.123	42.4	34.8	0.962
-35	21.2	13.1	1.386	46.3	34.6	1.150
-30	25.7	12.8	1.587	56.8	33.9	1.440
-25	34.3	12.6	1.815	77.0	33.2	1.720
-21.5	42.0	12.4	1.949	87.9	32.7	1.821
Conc. of mesitylene 3.59 mole %						
-40	21.8	12.6	1.441	52.6	33.0	1.372
-33.5	25.1	12.3	1.800	72.1	32.1	1.780
-28.5	48.2	12.0	2.036	101.8	31.4	1.927
-24.5	65.1	11.8	2.203	141.1	30.9	2.120
Conc. of mesitylene 3.71 mole %						
-50	-	-	-	42.1	37.1	0.778
-40	27.0	14.2	1.585	54.4	35.5	1.356
-25	83.2	13.3	1.322	-	-	-

TABLE VI (Cont'd.)

Temp. °C	CH			CH_2		
	$1/T_2'$	$1/T_2$	log.1/T	$1/T_2'$	$1/T_2$	log.1/T
	sec^{-1}	sec^{-1}		sec^{-1}	sec^{-1}	
Conc. of mesitylene 6.16 mole %						
-57	16.0	11.6	1.126	40.5	37.8	0.511
-45	26.4	11.0	1.665	66.6	35.8	1.567
-35	65.3	10.5	2.216	149.5	34.3	2.141
-20.5	153.3	9.9	2.634	-	-	-
-12	262.0	9.6	2.879	-	-	-
Conc. of mesitylene 5.79 mole %				(SbF_5 4.29 mole %)		
-33	23.2	17.8	1.212	50.3	42.7	0.960
-26	26.4	17.3	1.435	62.2	41.5	1.396
-13	58.7	16.4	2.103	130.7	39.4	2.040
- 8	95.2	16.1	2.375	170.6	38.6	2.200
4	185.3	15.4	2.707	-	-	-

TABLE VII

LINE WIDTHS, RELAXATION TIMES AND RATE CONSTANTS FOR SOLUTIONS OF DURENE IN FLUOROSULPHURIC ACID

Temp.°C	CH			CH_2		
	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/T	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/T
Conc. of durene 1.12 mole %						
-87.5	34.6	30.7	0.888	-	-	-
-82	48.1	29.8	1.562	64.7	60.1	0.789
-77.8	64.7	29.2	1.852	69.4	58.9	1.151
-74	97.4	28.6	2.139	86.4	57.7	1.583
-72	88.0	28.3	2.077	90.8	57.1	1.652
-68.5	-	-	-	129.4	56.5	1.986
-64.5	-	-	-	171.2	55.1	2.190
Conc. of durene 1.74 mole % (SbF_5 4.42 mole %)						
-80	58.4	29.3	1.743	-	-	-
-77.5	62.2	29.0	1.798	68.2	62.5	0.921
-75	76.0	28.6	1.957	71.0	61.1	1.119
-70.5	105.6	28.0	2.175	85.1	59.8	1.529
-64.5	134.5	27.2	2.318	101.8	58.0	1.766
-61	185.3	26.7	2.490	126.6	57.1	1.967
-58.5	-	-	-	156.5	56.4	2.125
-56	-	-	-	166.5	55.8	2.169

TABLE VII (Cont'd.)

Temp. °C	CH			CH_2		
	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/T	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/T
Conc. of durene 1.49 mole % (SbF_5 9.04 mole %)						
-75	49.8	38.0	1.370	-	-	-
-69.5	72.4	37.0	1.850	70.3	64.1	0.914
-65	115.6	36.2	2.201	80.0	62.7	1.361
-60.4	209.5	35.4	2.542	102.3	61.3	1.737
-57	-	-	-	129.0	60.4	1.961
-54.5	-	-	-	153.7	59.7	2.098

TABLE VIII

LINE WIDTHS, RELAXATION TIMES AND RATE CONSTANTS FOR SOLUTIONS OF HEXAMETHYLBENZENE IN FLUOROSULPHURIC ACID

Temp. °C	$1/T_2'$ sec^{-1}	$CH.CH_3$ $1/T_2$ sec^{-1}	$\log.1/\tau$
Conc. of hexamethylbenzene 2.74 mole %			
-50	46.2	44.0	0.342
-25	47.1	39.6	0.879
0	122.8	35.9	1.939
Conc. of hexamethylbenzene 4.73 mole %			
-22	64.7	41.2	1.371
-17	79.8	40.5	1.594
-13	93.3	39.9	1.728
-10	123.5	39.3	1.925
- 4	175.0	38.5	2.135
Conc. of hexamethylbenzene 5.67 mole %			
-30	51.8	41.6	1.010
-25	63.8	40.8	1.362
-18.5	81.7	39.8	1.622
-11	153.6	38.6	2.061
Conc. of hexamethylbenzene 8.21 mole %			
-43	45.7	40.5	0.715
-36.5	55.8	39.5	1.212
-34.5	63.6	39.1	1.389
-31	76.2	38.5	1.577
-27.5	98.6	38.0	1.783
-25	111.8	37.6	1.871

TABLE IX

LINE WIDTHS, RELAXATION TIMES AND RATE CONSTANTS FOR SOLUTIONS OF PENTAMETHYLBENZENE IN FLUOROSULPHURIC ACID

Temp. °C	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/τ
Conc. of pentamethylbenzene 4.01 mole %			
-40	47.1	36.9	1.312
-30	61.6	36.1	1.692
-25	72.9	35.2	1.877
-16	106.2	34.0	2.159
Conc. of pentamethylbenzene 2.82 mole % (KSO_3F 3.39 mole %)			
-35	65.6	38.4	1.736
-30.5	78.9	37.7	1.905
-25	102.7	36.9	2.110
-18	159.0	35.9	2.391

TABLE X

LINE WIDTHS, RELAXATION TIMES AND RATE CONSTANTS FOR SOLUTIONS OF m-XYLENE IN FLUOROSULPHURIC ACID

Temp. °C	$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log.1/τ
Conc. of m-xylene 7.82 mole % (SbF_5 11.35 mole %)			
-31.5	41.5	35.8	0.882
-23	50.6	34.3	1.332
-20	57.8	34.1	1.500
-13	82.6	33.1	1.819
- 9	100.5	32.7	1.957
- 7	119.4	32.4	2.076

TABLE XI

RATE CONSTANTS FOR PROTON EXCHANGE AT -20°

Base	(Mole %)	SbF_5 (Mole %)	k (sec^{-1})
Mesitylene	1.93	-	96.9
	3.59	-	243.1
	3.71	-	276.5
	6.16	-	843.0
	5.79	4.29	53.7
Durene	1.12	-	1.06×10^5
	1.48	9.04	1.04×10^4
	1.74	4.42	3.44×10^4
Pentamethylbenzene	2.82*	-	200.0
	4.01	-	108.0
Hexamethylbenzene	2.73	-	9.8
	4.73	-	27.5
	5.67	-	38.9
	8.21	-	154.9
	2.85	4.42	†
m-xylene	7.82	11.55	28.0

* This solution also contained 3.39 mole % potassium fluorosulphate.

† The rate of exchange was too slow to measure.

TABLE XII

BROADENING OF THE SOLVENT LINE WITH INCREASING TEMPERATURE

Base	Conc. mole %	Temp. °C	Solvent line width c.p.s.
Mesitylene	3.58	-77	2.2
		-24.5	4.4
	5.79	-26	4.6
	(4.29 SbF_5)	4	9.2
Durene	1.34	-89	4.0
	(4.42 SbF_5)	-56	6.6
Hexamethyl-	4.73	-41	3.2
benzene		- 4	5.4
	8.21	-69.5	1.8
		-25	4.5

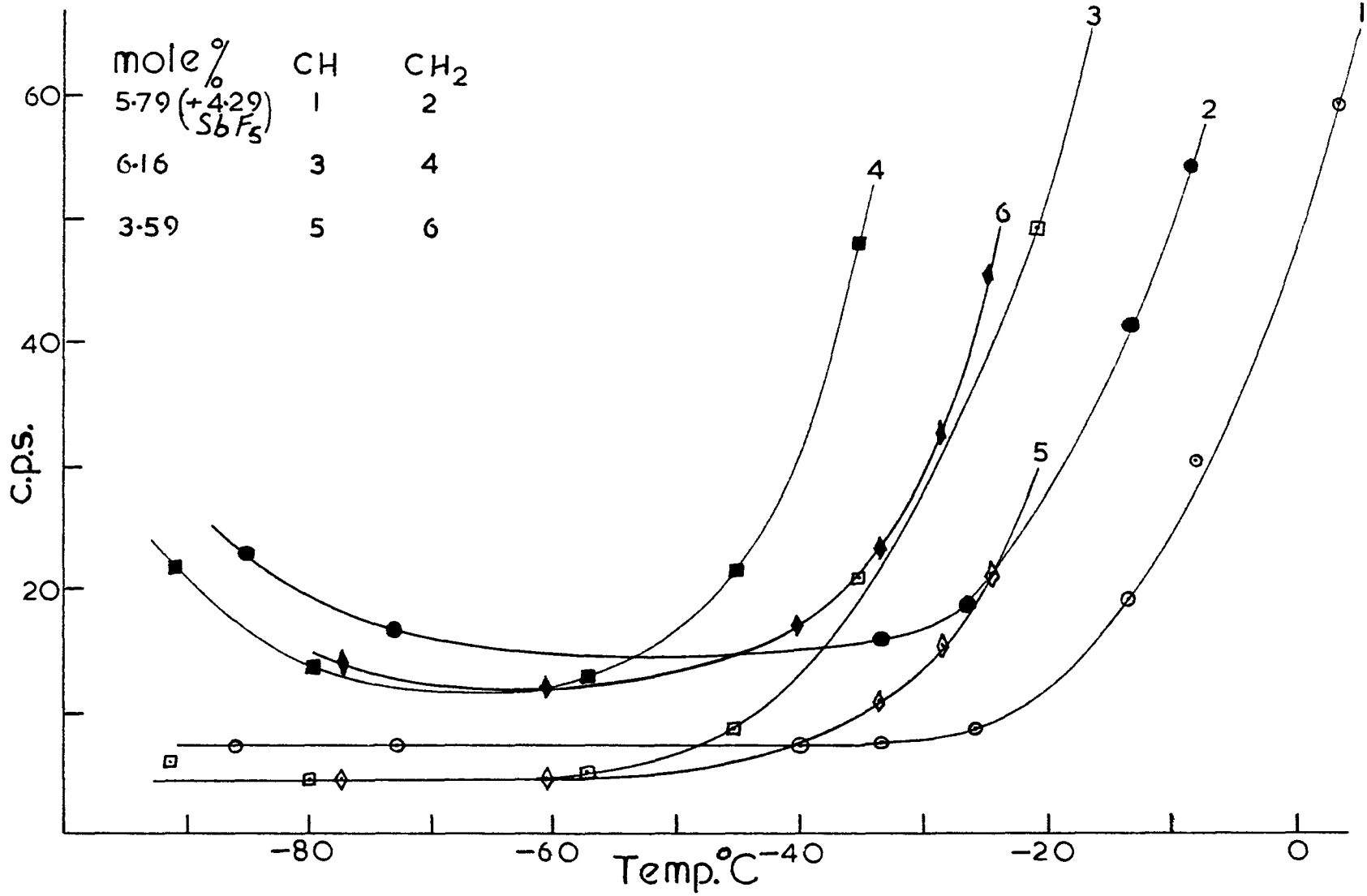


Fig. 23 SOLUTIONS OF MESITYLENE IN FLUOROSULPHURIC ACID: LINE WIDTHS OF CH AND CH_2 PEAKS.

(4) ACTIVATION ENERGIES

The dependence of the rate of proton exchange on the temperature can be expressed by the Arrhenius equation

$$k = k_0 \ e^{-E/RT} \qquad (4.8)$$

Plots of log k against 1/T are shown in Figs. 24-27 for solutions of mesitylene, durene, hexamethylbenzene, pentamethylbenzene and m-xylene in fluorosulphuric acid. For mesitylene (Fig. 24) it can be seen that the rates obtained from the broadening of the CH and from the CH_2 lines are the same within experimental error. This provides some confirmation of the values chosen for $1/T_2$.

Fig. 25 shows a similar plot for the base durene. Except in one case the lines are reasonably parallel. For durene it was found that the rate constant calculated from the CH line broadening was much greater than that obtained from the CH_2 line broadening. This greater rate of exchange may not be due solely to the exchange of the "methylene" protons but could be partly due to the rearrangement of the methyl groups. Durene and prehnitene are both known to rearrange to the more stable 1,2, 3,5-tetramethylbenzene [20].

The results obtained from Figs. 24-27 are summarised in Table XIII. It can be seen that, except for pentamethylbenzene, the activation energies fall in the range 13-15 kcals. and are much higher than the values obtained by MacLean and Mackor for HF/BF_3 solutions which are in the range 7-8.5 kcals. This is possibly a reflection of the smaller basicity of the fluorosulphuric acid solvent system.

TABLE XIII

ACTIVATION ENERGIES (E) AND FREQUENCY FACTORS (k_o) FOR METHYLBENZENES IN FLUOROSULPHURIC ACID

Base		SbF_5	Log k_o	E
	(Mole %)	(Mole %)		(K cals/mole)
Mesitylene	1.93	-	13.72	13.6
	3.59	-	13.91	13.3
	3.71	-	13.82	13.2
	6.16	-	14.38	13.8
	5.79	4.29	13.89	14.1
Durene	1.12	-	17.92	14.9
	1.48	9.04	17.23	15.3
	1.74	4.42	16.20	13.5
Pentamethylbenzene	4.01	-	10.65	9.9
	2.82*	-	11.52	10.4
Hexamethylbenzene	2.73	-	12.95	13.7
	4.73	-	13.42	13.9
	5.67	-	14.51	15.0
	8.21	-	15.60	15.5
m-xylene	7.82	11.55	13.72	14.2

* This solution also contained 3.39 mole % potassium fluorosulphate.

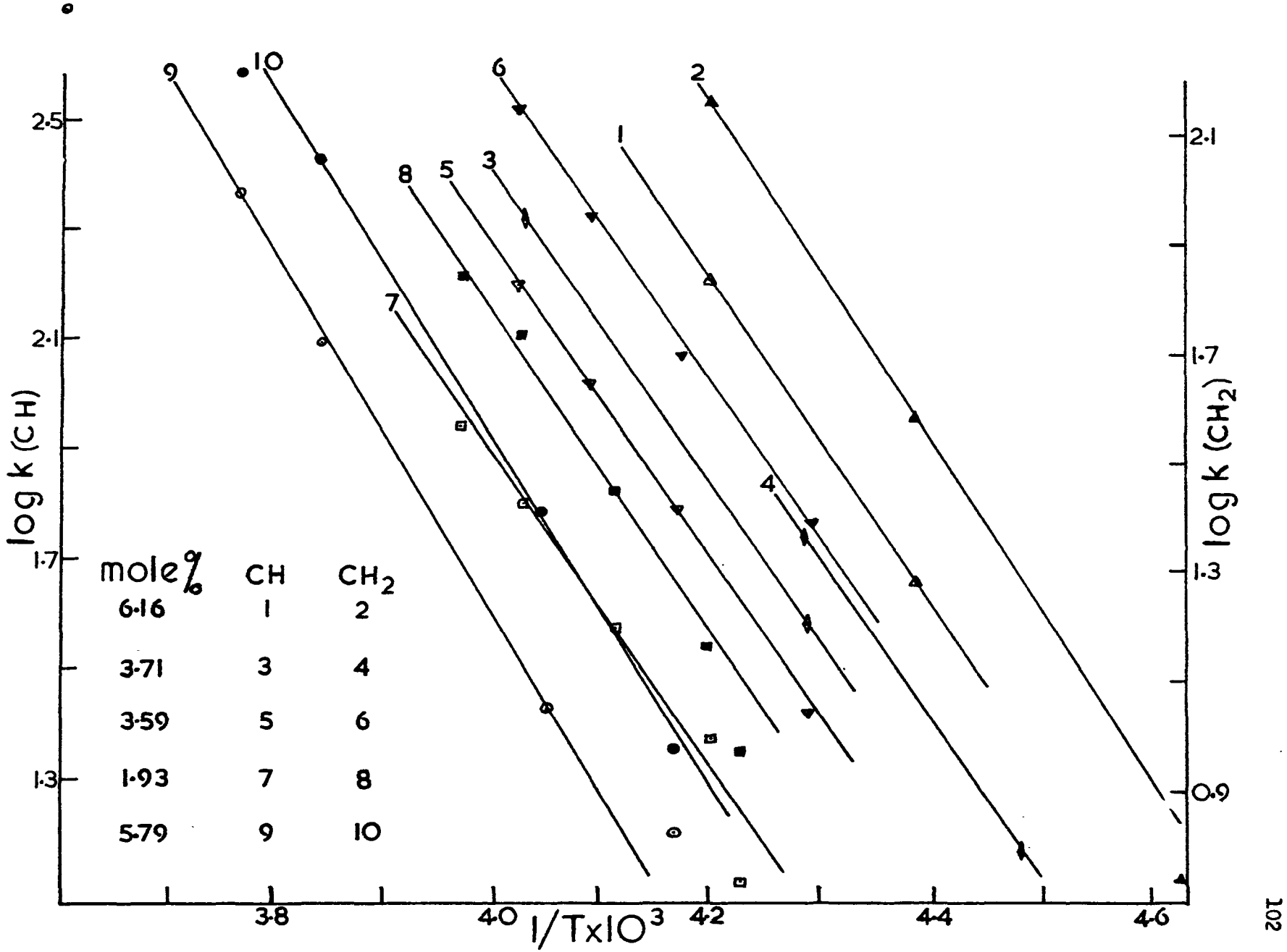


Fig. 24 SOLUTIONS OF MESITYLENE IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

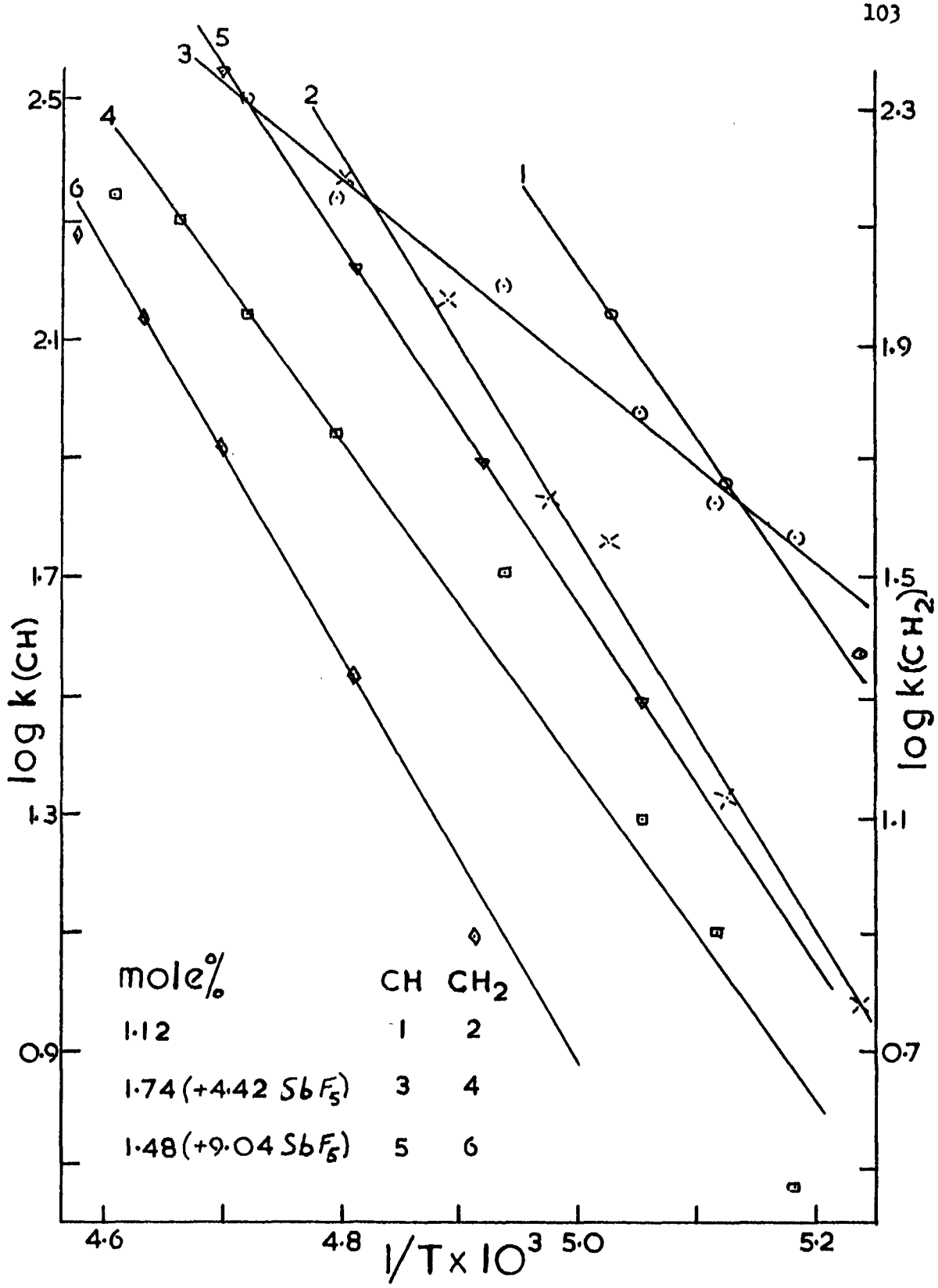


Fig. 25 SOLUTIONS OF DURENE IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

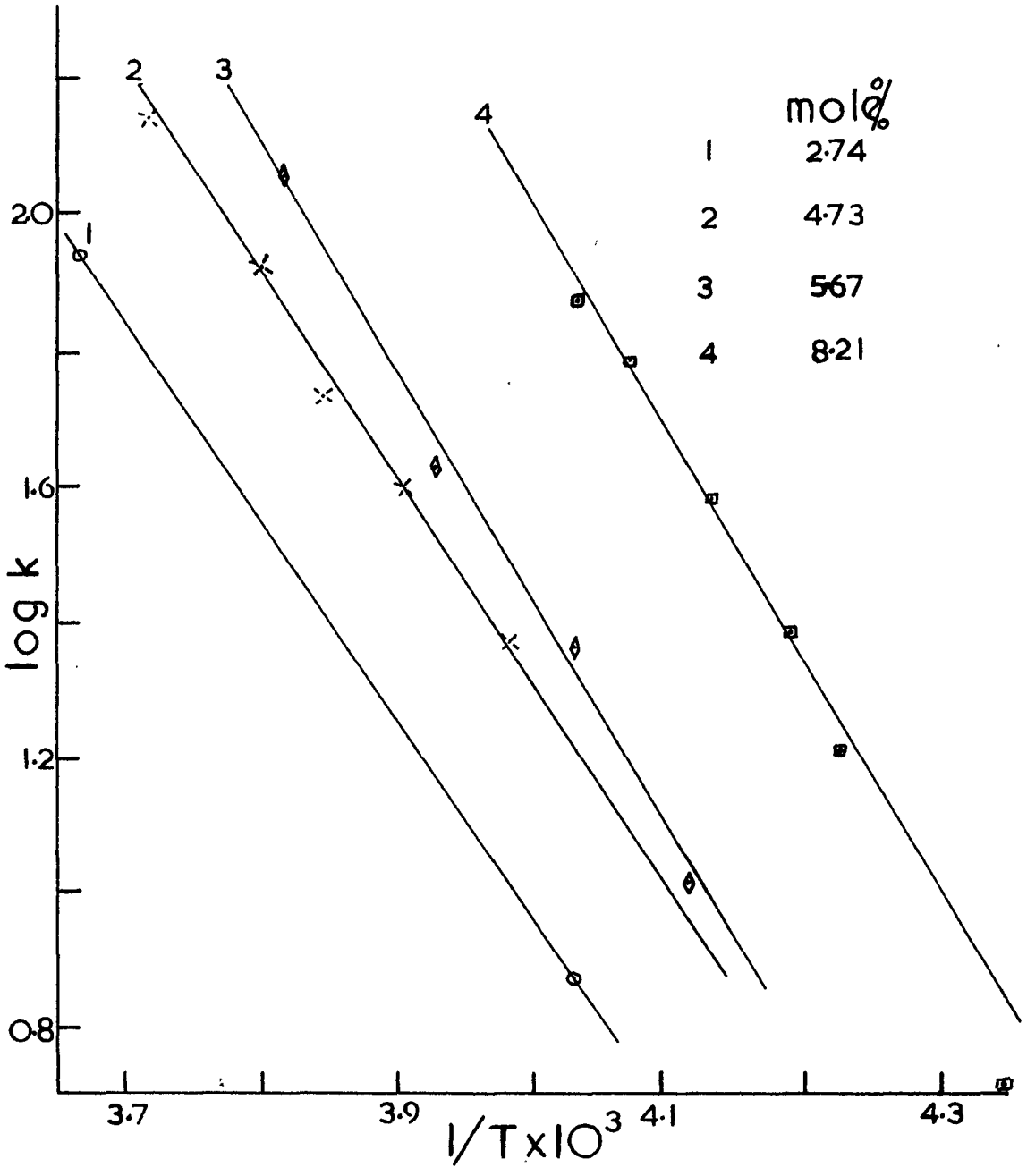


Fig. 26 SOLUTIONS OF HEXAMETHYLBENZENE IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

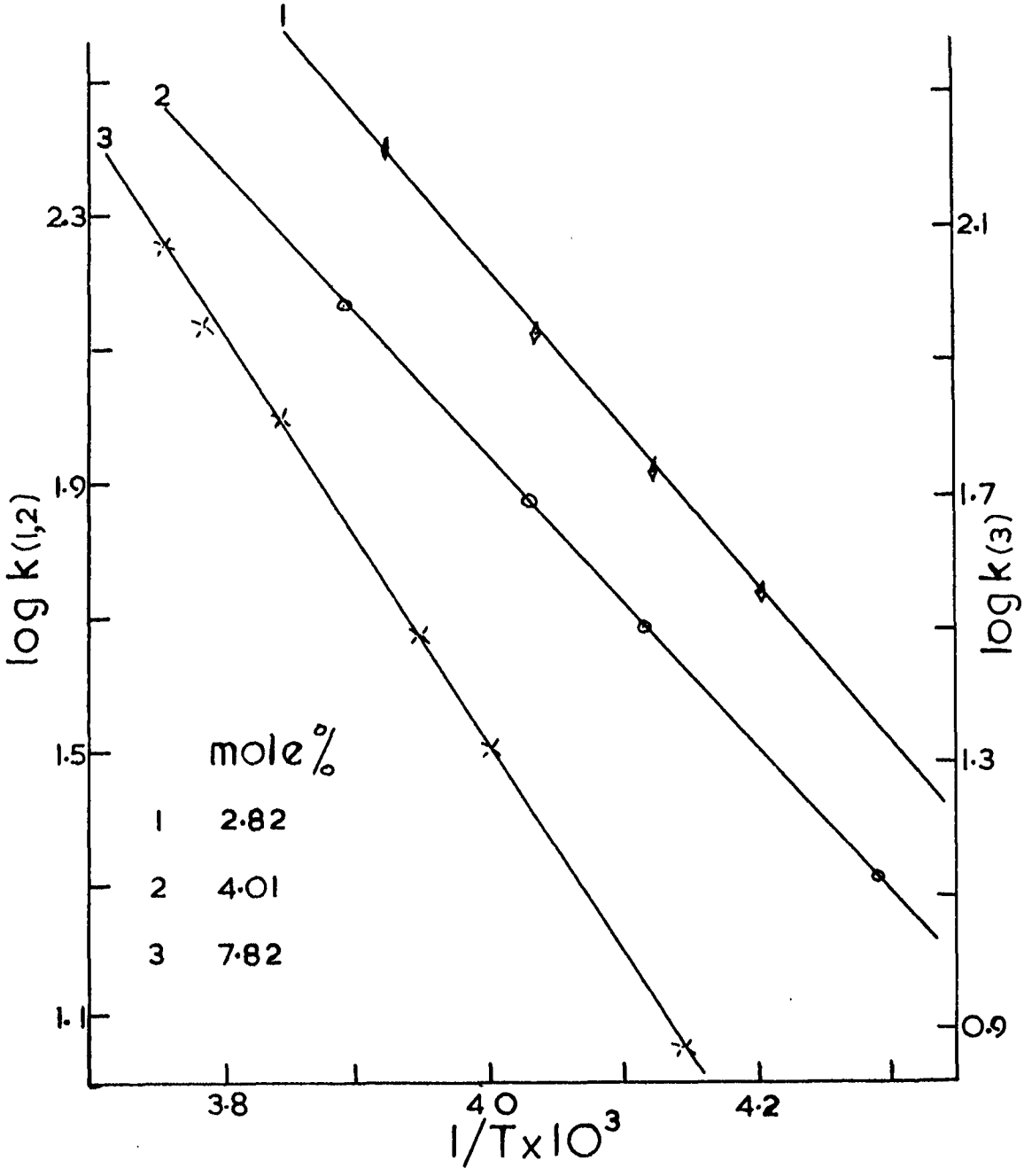


Fig. 27 SOLUTIONS OF PENTAMETHYLBENZENE (1,2) AND M-XYLENE (3) IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

(5) DISCUSSION

Since there are some notable differences between the results of MacLean and Mackor on solutions in HF and the results of this investigation on fluorosulphuric acid solutions, some comments are made on their work.

MacLean and Mackor[20] have calculated the rate of proton exchange for hexamethylbenzene by comparing experimentally obtained spectra with theoretical line shapes calculated from the Bloch equations including exchange. The assumption was made that the proton only jumps between adjacent carbon atoms: this presupposes the mechanism proposed. No reason was given for the choice of 2.2 c.p.s. for the line width of the methyl signals and the ortho methyl signal was assigned a width of 4.4 c.p.s. in order to account for the spin-spin coupling $J_{AC} \simeq 1$ c.p.s. This value for the ortho methyl signal appears to be too large for two peaks separated by only 1c.p.s.; nor is the assumption that all methyl peaks have the same width necessarily a good one.

The Dutch workers[20] also state that "whether a proton exchange reaction is intra or intermolecular can in general not be conclusively determined from the shape of the spectra", yet later they say that the spectrum of a solution of hexamethylbenzene in HF/BF_3 at -30° provides conclusive evidence that the exchange is intramolecular. It is remarkable that this spectrum recorded under conditions of rapid exchange shows spin-spin splittings which are better resolved than the supposed quartet for the $\underline{CH}.CH_3$ peak when exchange is extremely slow[19]. They claim that the exchange processes for hexamethylbenzene, durene, and prehnitine are independent of concentration of base and of BF_3 and

therefore exchange intramolecularly. However results are quoted for only two different concentrations of hexamethylbenzene, and only one concentration for each of the other two bases. In addition durene is reported as exchanging at nearly the same rate as hexamethylbenzene even though it is a much weaker base [84]. In the fluorosulphuric acid system, the exchange rate for durene is much faster than it is for hexamethylbenzene. In fact the rates calculated at -20° (Table XI) increase roughly in the same order as the basicities of the bases decrease.

A noticeable feature of the spectra of MacLean and Mackor [20] is that in the cases where an intermolecular process is proposed, free base is present, but in the cases where an intramolecular exchange is postulated there is no free base present. It seems surprising that the bases were not examined under similar conditions. In the experiments with HSO_3F under no conditions was there any free base present suggesting once again that HSO_3F is much more acidic than HF/BF_3. The calculations by MacLean and Mackor based on the acid line width must also be regarded with suspicion since the large $H^1 - F^{19}$ spin-spin coupling constant may have a considerable effect on the acid line width over the temperature range studied. In the presence of appreciable quantities of free base it is conceivable that exchange process (4.2) may contribute to some extent but in the fluorosulphuric acid system where the concentration of base was very small all of the exchange must occur via process (4.1).

In conclusion it was found that for all the methylbenzenes in fluorosulphuric acid the predominant exchange process is an intermolecular one between the conjugate acid and the solvent. The high

activation energies found for the proton transfer probably reflect the low basicity of the solvent rather than being typical of the CH_2 group as suggested by MacLean and Mackor. It is quite likely that some of the differences between the two systems are due to differences in the solvents, but the methylbenzene-HF/BF_3 system needs to be reinvestigated under more uniform conditions.

CHAPTER V

PROTONATION OF OXYGEN BASES

(1) INTRODUCTION

Many organic oxygen bases are known to be fully ionised in strong acid solution. Gillespie and Leisten[92] have reviewed the literature up to 1951 which shows that ketones and most carboxylic acids behave as simple bases

$$B + H_2SO_4 \longrightarrow BH^+ + HSO_4^- \qquad (5.1)$$

in 100% sulphuric acid. It has been shown however that alcohols are esterified by sulphuric acid and that certain carboxylic acid ionise according to the equation

$$RCOOH + 2H_2SO_4 \longrightarrow RC{=}\overset{+}{O} + 2HSO_4^- + H_3\overset{+}{O} \qquad (5.2)$$

A review by Paul and Long[93], on Hammett acidity function determinations, lists the pK_{BH^+} values for a number of organic oxygen bases. Edward and coworkers[26] have used the changes produced in the n.m.r. spectra of alcohols and ethers upon protonation to measure pK_{BH^+} for these bases. In no case did they observe an n.m.r. spectrum due to the captured proton. MacLean and Mackor[24] were the first to observe the spectra of the conjugate acids of acetone, ethyl alcohol and water in solution in anhydrous hydrogen fluoride saturated with boron trifluoride at -75°.

(2) NUCLEAR MAGNETIC RESONANCE SPECTRA OF OXYGEN BASES IN FLUOROSULPHURIC ACID

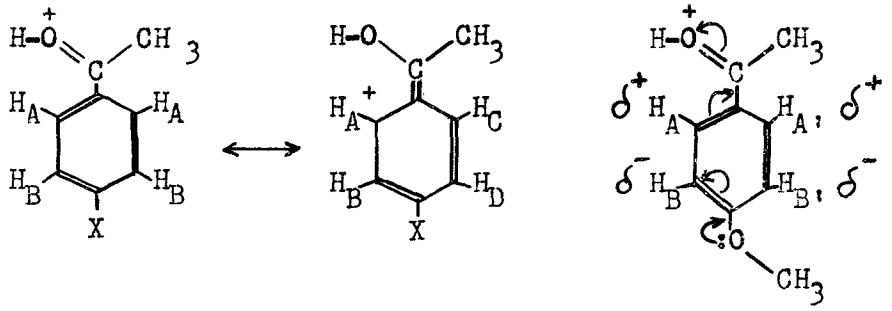
In view of the successful observation of the n.m.r. spectra of the conjugate acids of amides and methylbenzenes in fluorosulphuric acid solution, a study of some oxygen bases was carried out in this solvent.

Ketones

A series of para-substituted acetophenones were dissolved in fluorosulphuric acid and the n.m.r. spectra of these solutions recorded at various temperatures. In all cases it was possible to observe the spectrum of the conjugate acid, although in the case of p-nitroacetophenone at -88° the $=OH^+$ peak had a width of 12.4 c.p.s. indicating that exchange was still occurring. For the other acetophenones the $=OH^+$ line width reached a minimum value above -38° indicating that exchange was extremely slow. The chemical shifts of the peaks in the n.m.r. spectra of the conjugate acids of these bases are recorded in Table XIV. A notable feature of these low temperature spectra is the very large chemical shift of the captured proton from T.M.S. indicating a very small shielding at this proton. No spin-spin coupling was observed between the captured proton and the methyl protons of the ketone.

The n.m.r. spectra of the phenyl region of these bases is shown in Fig. 28. This would be expected to be of the A_2B_2 or ABCD type, but except for acetophenone and p-fluoroacetophenone it apparently approximates to an AB quartet and shows a typical change in shape as the ratio δ/J changes. One would expect that protonation of the carbonyl oxygen would lead to an increased contribution from II with the result that the $HO.C.CH_3$ group would become coplanar with the ring and an ABCD spectrum

would be expected. The apparent AB spectrum must be due to negligible cross ring spin-spin coupling with the result that there are two AB quartets with the same chemical shifts. Acetophenone would be expected



I II III

to give a complicated pattern for the ring part of the spectrum since there are three different groups of protons all of which can spin-spin interact (Fig. 28a). The ring portion of the spectrum of the conjugate acid of p-fluoroacetophenone (Fig. 28b) is complicated due to spin-spin coupling of the ring protons with the para-fluorine which has a spin of $\frac{1}{2}$.

Fig. 28 and Table XIV illustrate the effect a change of substituent can have on the n.m.r. pattern produced by the aromatic protons and on the position of the resonance due to the captured proton. The $\overset{+}{HO}.C.CH_3$ would be expected to be strongly electron withdrawing at the ortho-positions, whereas the OCH_3 group is electron donating at ortho-positions: thus in the conjugate acid of p-methoxyacetophenone (III) the A protons have quite a different chemical shift from the B protons. As the substituent para to the ketone group is made less electron donating and becomes more electron withdrawing, it competes more and more with the ketone group for the electron density of the ring, with the result that the two A and the two B protons become more and more equivalent. In p-nitroacetophenone the chemical shifts of the A and B protons are almost the same, indicating

that the electron withdrawing powers of the NO_2 and $HO.\overset{+}{C}.CH_3$ groups are comparable.

When the para substituent is strongly electron donating, eg. OCH_3, the $=OH^+$ peak is at higher field than when there is a strongly electron attracting group in the para position eg. NO_2. Stewart and Yates[94] have measured the pK_{BH^+} values for a number of substituted acetophenones and attempted to correlate pK_{BH^+} with σ, the Hammett substituent constant. The substituents which gave negative deviations from their plot were all para substituents which can donate electrons by resonance. A σ^+ value has been developed for these substituents where a positive charge is developed in conjugation with the group[95]. A plot of pK_{BH^+} against σ^+ gave a good correlation for the substituted acetophenones except for para-OCH_3. It is thought that although the para-OCH_3 group is strongly electron donating by resonance, it is not quite as strong as the σ^+ value predicts presumably because of strong hydrogen bonding with the solvent. In Table XV and Figs. 29, 30 the chemical shifts obtained for the captured proton of the conjugate acids are compared with the pK_{BH^+} and σ^+ values given by Stewart and Yates[94]. Fig. 29 shows that there is a good correlation between chemical shift and the pK_{BH^+} for the conjugate acids: likewise there is a good correlation between the chemical shift and the σ^+ value (Fig. 30) for the p-substituent except for the p-OCH_3 group.

N.m.r. spectra of the conjugate acids of acetone and benzophenone have also been obtained and the chemical shifts are given in Tables XVI and XVII. The spectra of the conjugate acid of acetone will be discussed in Chapter VII. In a solution of benzophenone in an SbF_5/HSO_3F mixture the

resonance due to the captured proton is clearly visible at 25° although exchange is still occurring (the $=\overset{+}{O}H$ peak becomes sharper on lowering the temperature). The chemical shifts reported in Table XVII are relative to the solvent. An attempt was made to use methanesulphonylfluoride as an internal reference, but as the temperature was lowered an additional methyl doublet appeared which moved away from the original CH_3SO_2F doublet. It seems likely that some of the "reference" is coordinating with the SbF_5 thus giving rise to two doublets. It was therefore felt that CH_3SO_2F was probably not a reliable reference.

Ethyl Alcohol and Water

The chemical shifts obtained for solutions of ethyl alcohol and water are given in Table XVI.

It can be seen that protonation of ethyl alcohol results in a shift of all the peaks to lower field: this is caused by withdrawal of electron density from the molecule to counteract the positive charge placed at the site of protonation. By cooling the solution to low temperature the spectrum of the conjugate acid was obtained. The areas of the three peaks observed at -95° were in the ratio 1.75: 1.89: 3.00 indicating that the extra proton was attached to the oxygen atom. There was no evidence which suggested that any ethyl fluoride had been formed by the reaction

$$CH_3CH_2OH + HSO_3F \longrightarrow CH_3CH_2F + H_2SO_4 \qquad (5.3)$$

Formation of ethyl fluoride would result in a spectrum containing only two peaks i.e. CH_3 and CH_2 in addition to the solvent line $HSO_3F + H_2SO_4$. It was not possible to observe any fine structure in the $\overset{+}{O}H_2$: in HF/BF_3 solution it has been observed as a triplet[24] due to coupling with the methylene protons. The chemical shift between the CH_2 and CH_3 peaks is

found to be increased considerably in the conjugate acid spectrum compared to the unprotonated form. This fact has been used by Edward and co-workers[26] to measure the pK_{BH^+} for this and other bases containing ethyl groups attached to the basic atom.

In a solution of water in HSO_3F, or in SbF_5/HSO_3F, it was not possible to detect a peak due to H_3O^+. A possible reason for this could be hydrolysis according to (5.4)

$$H_2O + HSO_3F \rightleftharpoons HF + H_2SO_4 \qquad (5.4)$$

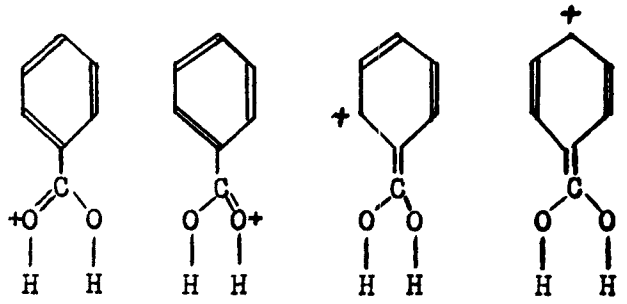
and rapid exchange of the HF and H_2SO_4 protons with the solvent. However Senior[96] has shown that the equilibrium (5.4) lies far to the left and that protonation is the only significant reaction. MacLean and Mackor[24] observed a peak which they attributed to H_3O^+ which occurs at slightly lower field (0.57 p.p.m.) than the peak due to OH_2^+ in protonated ethyl alcohol. Addition of this shift (0.57 p.p.m.) to the value found for OH_2^+ in HSO_3F solutions at -95° gives a value for the expected chemical shift of H_3O^+ in HSO_3F solutions of about -10.5 p.p.m. which is very close to the observed value for the chemical shift of the HSO_3F protons at -95°. In viewof the fact that the solvent peak is invariably broad at these temperatures it seems reasonable to suppose that the peak due to H_3O^+ is overlapped by the solvent line and is therefore not observed.

Other Oxygen Bases

Solutions of dimethylsulphoxide in fluorosulphuric acid have only one peak in their n.m.r. spectra at 25°. Upon lowering the temperature a new peak appears, at -7.08 p.p.m. from T.M.S. (Table XVI), which is quite sharp at -98° indicating that at this temperature exchange is slow. The relative areas of the two peaks were found to be 0.67: 6.00: the

reason for the unexpectedly high ratio is unknown. The absence of any spin-spin coupling in the methyl signal and the chemical shift of the captured proton, indicates that protonation occurs on oxygen rather than on sulphur. A proton on sulphur would be expected to give a signal at $\delta \ll$ -5.5 p.p.m. from T.M.S. (see Chapter III) which would have a quartet structure as a consequence of spin-spin coupling with the CH_3 protons since they would be separated by only three bonds.

The resonance due to the proton captured by benzoic acid in an SbF_5/HSO_3F solution was observed at low temperatures. In addition to the peaks arising from the phenyl protons only one other peak was visible in the spectrum, apart from the solvent. This peak was located in the same region of the spectrum as the $=OH^+$ peaks in the spectra of protonated ketones (Tables XV-XVII) and can therefore be attributed to a proton attached to the carbonyl oxygen, rather than to protonation of the OH oxygen to $-\underset{\underset{O}{\|}}{C}-OH_2^+$. This latter structure might be expected to give a signal in the same region of the spectrum as the OH_2^+ of protonated ethyl alcohol i.e. -10 p.p.m. from T.M.S. or +1.5 p.p.m. from HSO_3F. Protonation of the carbonyl oxygen would give rise to an ion with the resonance structures IV-VII in which the two OH groups are equivalent.



IV V VI VII

Stewart and Yates[97] have found a close correlation between the basicities of a number of benzoic acids and their acetophenone analogues which also indicates that the carbonyl oxygen is the site of protonation in benzoic acids. It was confirmed that protonation is on oxygen by measuring the relative areas of the peaks which were found to be in the ratio 2.0: 4.96. Only the chemical shifts of the more prominent phenyl peaks are given in Table XVII since the patterns are complex.

The spectrum of nitromesitylene in CCl_4 consists of a single line A due to the phenyl and two overlapping lines B, C due to the ortho and para methyl groups. In a strongly acidic solution, at low temperatures, a new peak D appears at -4.07 p.p.m. from the solvent: the relative areas were found to be D: A: B + C:: 0.95: 1.81: 9.00. The chemical shift between the nonequivalent methyl groups increases from 3.2 c.p.s. in CCl_4 to 13.2 c.p.s. in the acid solution. The absence of any peaks in the "methylene" region of the spectrum, which would be produced by protonation of the aromatic ring (Chapter IV), the area measurements and the fact that the new peak appears in the position now well established for an $=OH^+$ proton (Tables XV-XVII), indicate that protonation takes place on one of the oxygen atoms of the nitro group.

TABLE XIV

CHEMICAL SHIFTS OF THE CONJUGATE ACIDS OF PARA-SUBSTITUTED ACETOPHENONES

p-subst.	Temp. °C	OH^+	$-\delta$ (p.p.m.) from ext. T.M.S. HSO_3F	Phenyl				$OC.CH_3$	X
NO_2	-84	15.33	11.32			8.87		3.66	
Cl	-79	13.52	11.16	8.67	8.53	7.95	7.82	3.42	
H	-82	13.46							
F	-71	13.34	11.14	8.77	7.76	7.63	7.51	3.44	
CH_3	-46	12.85	11.04	8.63	8.49	7.83	7.70	3.37	2.74
OCH_3	-81	12.46	11.26	8.85	8.72	7.61	7.48	3.34	4.38

TABLE XV

CHEMICAL SHIFTS OF OH^+, pK_{BH^+}, AND σ^+ VALUES FOR PARA-SUBSTITUTED ACETOPHENONES

p-subst.	$-\delta$ p.p.m. of $-OH^+$	$-pK_{BH^+}$	σ^+
NO_2	15.33	7.94	+0.79
Cl	13.52	6.52	+0.114
H	13.46	6.15	0.00
F	13.34	6.06	-0.073
CH_3	12.85	5.47	-0.371
OCH_3	12.46	4.81	-0.778

TABLE XVI

CHEMICAL SHIFTS OF THE CONJUGATE ACIDS OF SOME OXYGEN BASES

Base	Solvent	Temp. °C	$-\delta^{+}$(p.p.m.) from ext. T.M.S. OH	HSO_3F	CH_2	CH_3
Acetone	$CDCl_3$	25	-	-	-	2.17
	SbF_5/HSO_3F	25	14.45		-	3.25
Ethyl alcohol	$CDCl_3$	25	2.58	-	3.70	1.22
	HSO_3F	25	-	10.92	4.95	1.83
		-82	10.35	11.65	4.83	1.72
		-95	9.89	11.78 (32)	4.85	1.74
Dimethyl sulphoxide	$CDCl_3$	25	-	-	-	2.62
	HSO_3F	-98	7.08	11.37	-	3.31
Water		25	5.20	-	-	-
	SbF_5/HSO_3F	-80	-	11.24 (14)	-	-
		-90		11.3 (136)	-	-

The figures in ( ) denote the line width.

TABLE XVII

CHEMICAL SHIFTS OF THE CONJUGATE ACIDS OF SOME OXYGEN BASES

Base	Solvent	Temp. °C	δ_{OH^+} (p.p.m.) from the solvent	phenyl				CH_3	
Benzophenone	SbF_5/HSO_3F	25	-1.80	2.09	2.20	2.33	2.46		
		0	-1.75	2.20	2.31	2.46	2.57		
		-26	-1.72	2.30	2.41	2.55	2.67		
Benzoic acid	SbF_5/HSO_3F	9	-1.56	1.59	2.04	2.42			
		-4	-1.59	2.14	2.47				
		-75.5	-1.39	2.42	2.82				
Nitromesitylene	SbF_5/HSO_3F	-95	-4.07	3.21				7.92	8.14

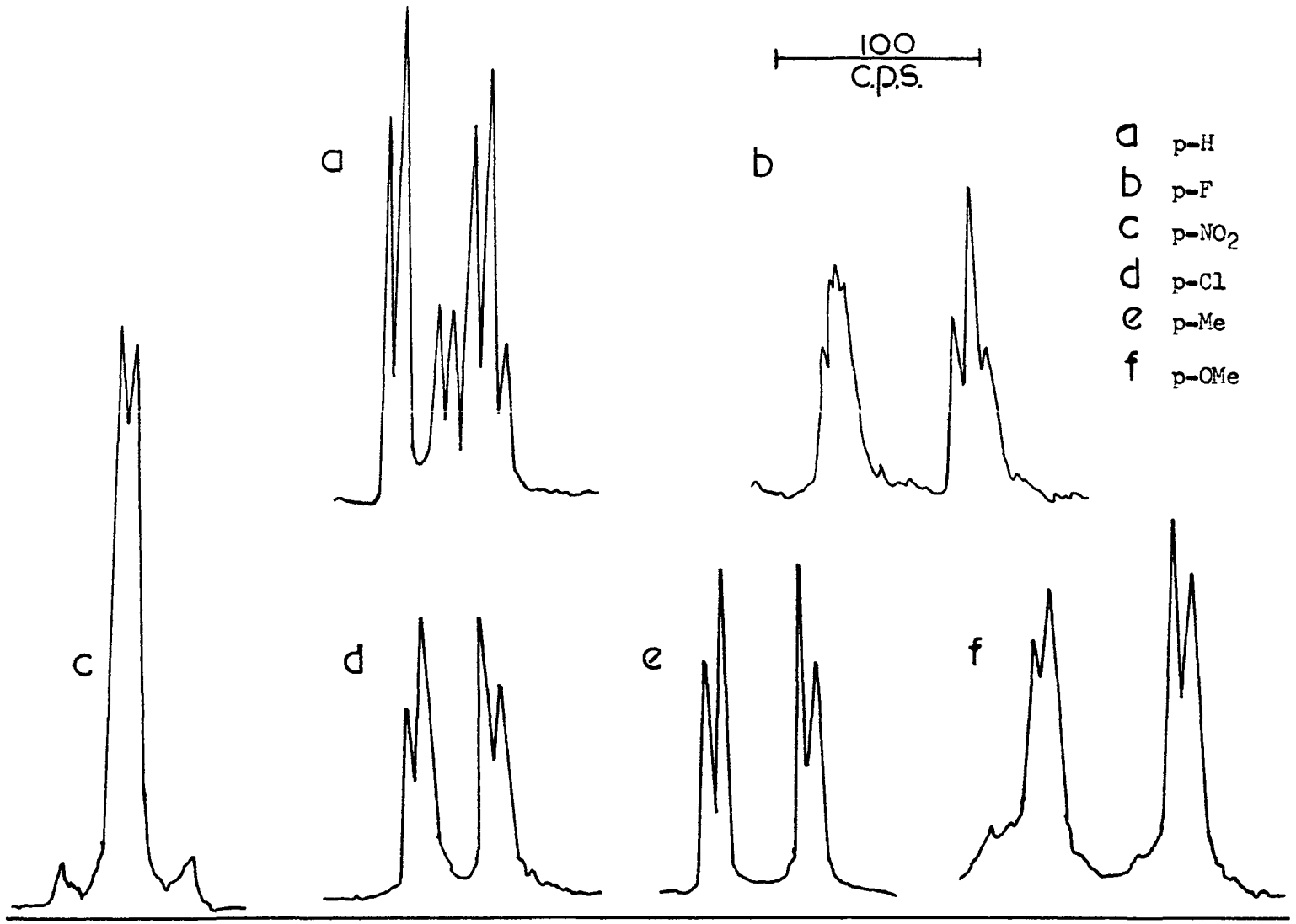


Fig. 28 SOLUTIONS OF ACETOPHENONES IN FLUOROSULPHURIC ACID: AROMATIC PROTON SPECTRA.

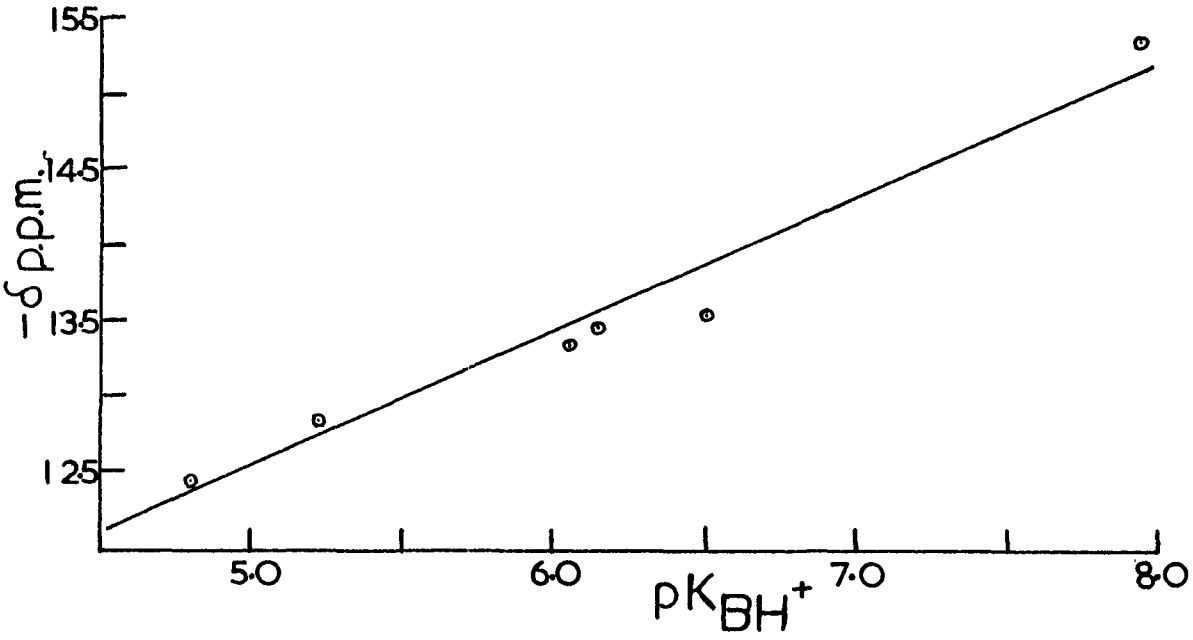


Fig. 29 SOLUTIONS OF ACETOPHENONES IN FLUOROSULPHURIC ACID: =OH$^+$ PROTON CHEMICAL SHIFTS AGAINST pK$_{BH^+}$.

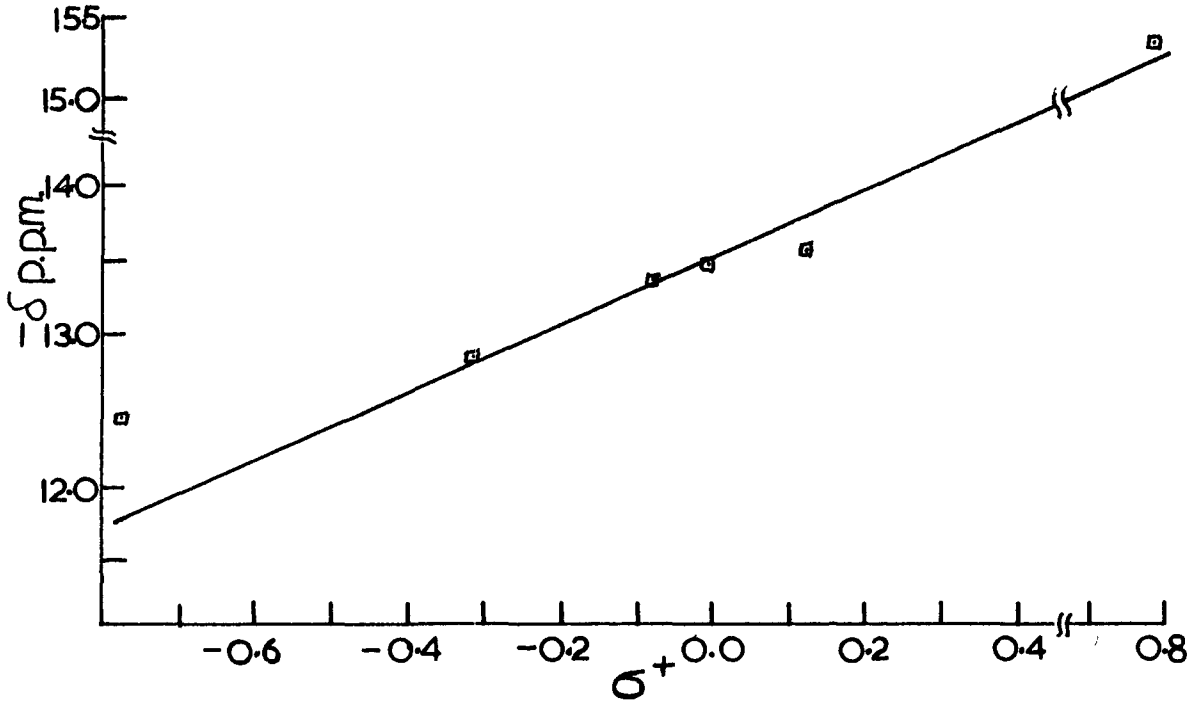


Fig. 30 SOLUTIONS OF ACETOPHENONES IN FLUOROSULPHURIC ACID: =OH$^+$ PROTON CHEMICAL SHIFTS AGAINST σ^+.

(3) RATES OF PROTON EXCHANGE AND ACTIVATION ENERGIES

Raising the temperature of solutions of these oxygen bases in HSO_3F results in a broadening of the $=OH^+$ peak due to a decrease in the lifetime of the conjugate acid. Since there is no overlapping of the $=OH^+$ and the solvent peaks the conditions for slow exchange may be applied and equation (3.3) may be used to calculate the rate of proton exchange. Values for $1/T_2$, the line width in the absence of exchange, were obtained for benzophenone and benzoic acid by the same method as used in Chapter IV for the methylbenzene exchange studies. For solutions of acetophenones in HSO_3F the following method was used to obtain $1/T_2$ which eliminates the uncertainty of the η/T correction applied in Chapter IV. Charman, Vinard, and Kreevoy[8], during the course of a study on the rates of proton abstraction from monosubstituted acetylenes, developed, from the Bloch equations as generalised by McConnell[3], an expression which relates the rate of proton exchange to peak heights (5.5)

$$\frac{1}{\tau} = \frac{V^{\infty}-V}{V.T_2} \qquad (5.5)$$

where V^{∞} is the height of the peak in the absence of exchange and V the height at an exchange rate $1/\tau$. Since $1/T_2'$ in equation (3.3) and τ^{∞} and V in equation (5.5) are all measurable quantities there are only two unknowns, $1/\tau$ and $1/T_2$, for any particular temperature: since there are two equations (3.3) and (5.5) relating these quantities, the relaxation time for a particular temperature can be calculated and hence the rate of exchange at that temperature. From the results of these studies activation energies were calculated by means of the Arrhenius equation (4.6).

Table XVIII gives the measured line widths at various temperatures, as well as the calculated rate of proton loss from the conjugate acids of benzophenone and benzoic acid. In Fig. 31 a plot of log k against 1/T gives a straight line for the conjugate acid of benzophenone, but a similar plot for the conjugate acid of benzoic acid shows deviations from a straight line which are much greater than the experimental error. The reason for this is unknown. The plot suggests that there are two exchange processes operating, but protonation at either the C=O oxygen or the COH oxygen would result in equivalence of the two protons and only one exchange process should be observed.

Data for the acetophenones is given in Table XIX. The values obtained for $1/T_2$ for p-nitroacetophenone could not be obtained using equations (3.3) and (5.5) because it was not possible to stop the exchange process completely for this base and hence V^{∞} was not obtainable. The value for $1/T_2$ at the lowest temperature at which a line width was recorded (-88°) was taken from an experiment in which p-methylacetophenone was used as the base and where exchange at -88° was negligible and therefore (3.3) reduces to $1/T_2' = 1/T_2$. Plots of log k against 1/T (Fig. 32) for these acetophenones give reasonable straight lines from which the activation energies and frequency factors were obtained. These values are given in Table XX. It is seen that the activation energies fall in the range 11-12 k.cals. except for p-nitroacetophenone which was 7.7 k.cals. Whether or not this large difference between p-nitroacetophenone and the other ketones studied is real, or is due to the choice of an incorrect value for T_2, could perhaps be answered by carrying out a comparable investigation in a solvent which is more acidic than

HSO_3F so that proton exchange by the conjugate acid of p-nitroacetophenone could be stopped completely. The small differences in the activation energies for the other bases are not considered to be significant.

It was hoped to obtain a correlation between the rates of proton loss and pK_{BH^+} and σ^+ values for these bases. However it can be seen (Fig. 32 and Table XX) that although there is a general trend of increasing rate of proton exchange with decreasing basicity, the conjugate acids of acetophenone and p-methoxyacetophenone exchange faster than would be expected from their published basicities[94]. Differences in the concentrations of the bases may partly account for this. In the case of p-methoxyacetophenone the calculated rate may not be correct since the conditions for slow exchange may not apply as the $=OH^+$ peak is much closer to the solvent peak than it is for the other bases studied (Table XV), and when exchange becomes appreciable some merging of the $=OH^+$ and the solvent lines is apparent. Under these conditions the assumption of the slow exchange condition (3.3) may not strictly apply and a more detailed calculation may be necessary. Use of another acidic solvent, where the acid protons are further removed from the $=OH^+$ resonance to ensure that conditions for slow exchange applied in all cases, might give a better correlation between the rate of exchange and pK_{BH^+}.

TABLE XVIII

LINE WIDTHS AND EXCHANGE RATES FOR BENZOPHENONE AND BENZOIC ACID SOLUTIONS

	$1/T_2'$ sec^{-1}	log $1/\tau$	$1/\tau x\ 10^3$
Benzophenone			
	17.6	0.539	3.854
	27.6	1.016	3.663
	39.0	1.395	3.546
	45.9	1.501	3.472
	59.4	1.656	3.407
	75.7	1.789	3.356
Benzoic acid			
	16.7	0.643	3.718
	34.6	1.348	3.677
	81.1	1.838	3.617
	99.9	1.943	3.584
	127.5	2.062	3.546

TABLE XIX

LINE WIDTHS, RELAXATION TIMES, AND EXCHANGE RATES FOR PARA-SUBSTITUTED ACETOPHENONES IN FLUOROSULPHURIC ACID

$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log $1/\tau$	$1/\tau \times 10^3$
p-nitroacetophenone			
39.0	18.2	1.319	5.405
44.1	18.0	1.415	5.361
50.5	17.8	1.514	5.291
72.8	17.3	1.737	5.155
p-chloroacetophenone			
24.2	15.2	0.952	4.785
31.1	14.9	1.209	4.673
33.5	14.4	1.282	4.640
41.9	14.4	1.440	4.587
57.4	13.5	1.643	4.505
acetophenone			
18.9	9.8	0.961	4.919
22.8	9.1	1.138	4.847
35.3	7.6	1.443	4.708
45.8	7.7	1.581	4.669
61.5	7.0	1.736	4.583
p-fluoroacetophenone			
20.8	14.7	0.785	4.728
26.1	15.1	1.041	4.651
30.0	14.5	1.191	4.598
44.4	14.2	1.480	4.505
67.4	13.6	1.731	4.405

TABLE XIX (Contd.)

$1/T_2'$ sec^{-1}	$1/T_2$ sec^{-1}	log $1/T$	$1/Tx\ 10^3$
p-methylacetophenone			
16.2	13.3	0.468	4.831
21.1	12.1	0.936	4.684
26.4	10.8	1.193	4.566
36.2	9.9	1.418	4.484
49.4	9.3	1.603	4.405
68.8	7.5	1.789	4.329
p-methoxyacetophenone			
14.2	9.4	0.682	4.831
18.4	9.0	0.970	4.747
22.4	8.5	1.142	4.678
32.5	7.6	1.396	4.574
49.0	6.5	1.629	4.464

TABLE XX

RATE DATA FOR SOLUTIONS OF KETONES IN FLUOROSULPHURIC ACID

Base	Conc. mole %	E k.cals./ mole	log k_o	log k (-60°)	$-pK_{BH^+}$
p-nitro-acetophenone	3.28	7.6	10.89	3.10	7.94
p-chloro-acetophenone	2.93	11.4	12.89	1.17	6.52
acetophenone	3.36	11.1	12.64	1.49	6.15
p-fluoro-acetophenone	2.94	12.9	14.14	0.90	6.06
p-methyl-acetophenone	3.22	11.4	12.57	0.87	5.47
p-methoxy-acetophenone	3.10	11.6	12.97	1.08	4.81
benzophenone	3.15	11.2	14.97	-	6.16

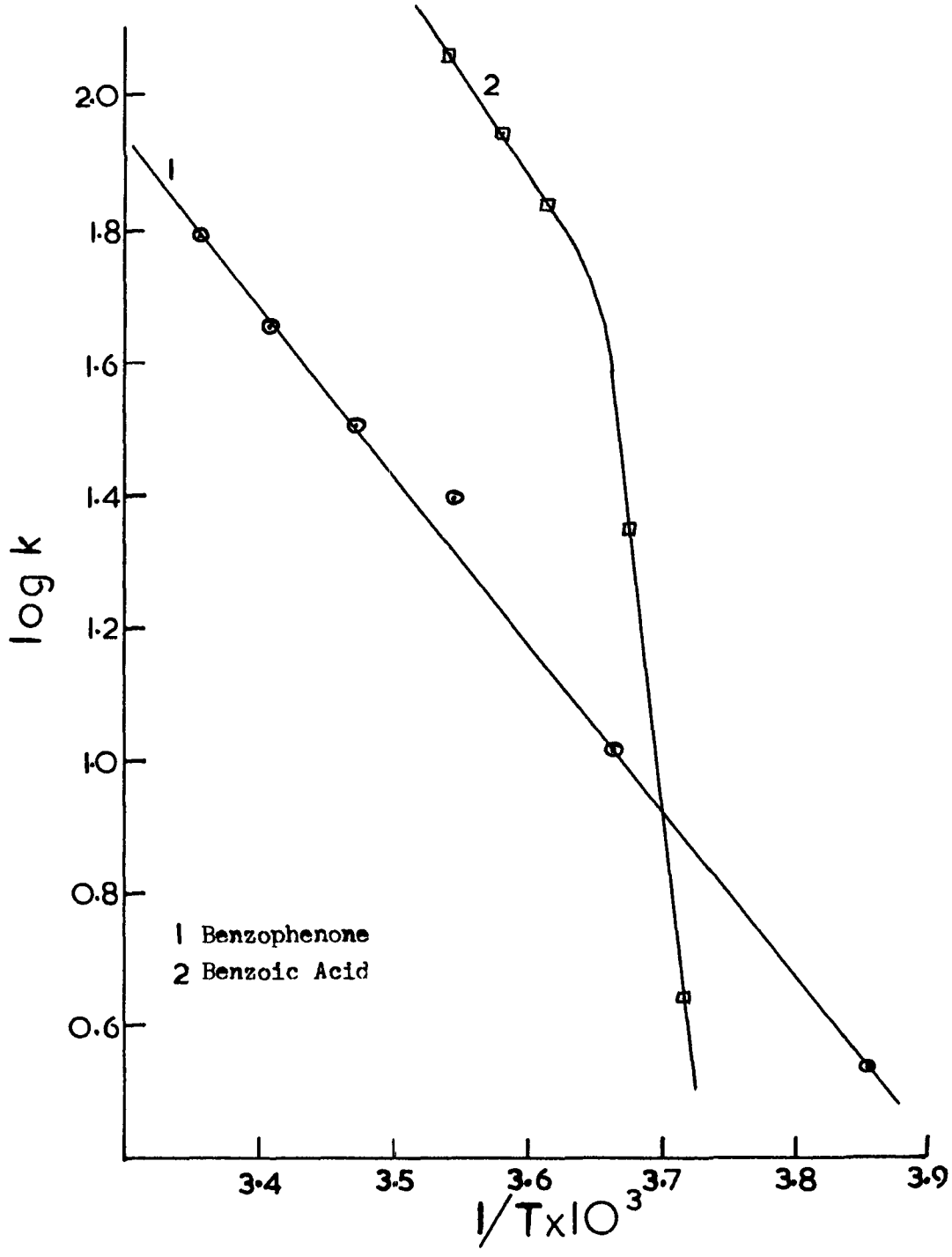


Fig. 31 SOLUTIONS OF BENZOPHENONE AND BENZOIC ACID IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

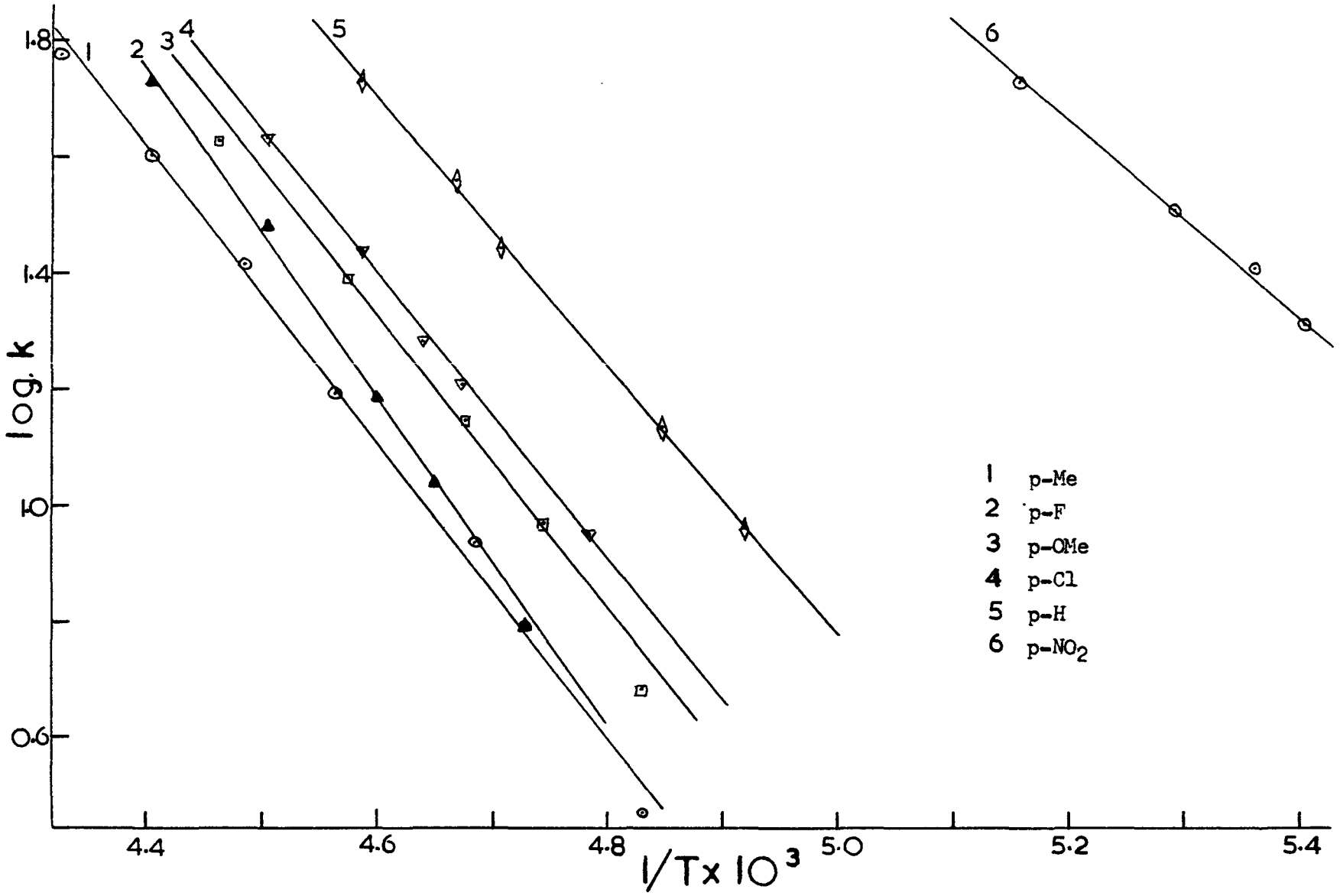


Fig. 32 SOLUTIONS OF ACETOPHENONES IN FLUOROSULPHURIC ACID: LOG k AGAINST 1/T.

CHAPTER VI

PROTONATION OF NITROGEN, PHOSPHORUS, AND ARSENIC BASES

(1) INTRODUCTION

N.m.r. techniques have been used to study the protolysis of methylammonium ions in aqueous solution. Grunwald and coworkers[9,10] have obtained quantitative information about the rate and mechanism of proton transfer, between the solvent water molecules and the methylammonium ions. They followed the collapse of the structure of the methyl peak, due to spin-spin coupling with the captured proton, with increasing pH, and also the broadening of the water line. Other workers[11,98,99] have carried out similar studies. Connor and Loewenstein[12] have used n.m.r. methods to measure the activation energies of proton transfer in solutions of NH_4^+ and $CH_3NH_3^+$ in water. Jardetzky and Jardetzky[100], and Bovey and Tiers[101] have examined the proton spectra of amino acids in acid solution and obtained information on their structures.

In this investigation the solvents used are much more acidic than those mentioned above, and in order that exchange processes could be studied much weaker bases had to be used. These bases were mostly substituted anilines of the type used in the measurement of the Hammett acidity function by the spectrophotometric method. By varying the number and types of substituents in the aromatic ring and on the nitrogen, a large variation in pK_{BH^+} can be obtained.

The protonation of this type of base has been relatively little studied by n.m.r. methods. Isobe et al.[14] have examined aniline in glacial acetic acid and observed that the phenyl spectrum, which is complex in an organic solvent, collapses to a single line on protonation. Reynolds and Schaefer[15] recently measured the exchange rate and activation energy of exchange for N,N-dimethylaniline in trifluoracetic acid solution, by observation of the collapse with increasing temperature of the methyl doublet, produced by spin-spin coupling with the captured proton.

(2) PROTONATION OF NITROGEN BASES

Anilines

Most of the anilines studied have been shown by means of cryoscopic studies to ionise by adding a single proton in 100% sulphuric acid, even 2,4,6-trinitroaniline which has a $pK_{BH^+} = -9.41$, is extensively protonated in 100% sulphuric acid. Although a base may be effectively 100% protonated in solution, the lifetime of the conjugate acid may not be sufficient for its n.m.r. spectrum to be recorded. For example, the NH_3^+ peak of the conjugate acid of p-nitroaniline (pK_{BH^+} +0.99) is not visible in solution in trifluoracetic acid (H_0 -3.0) although the concentration of the protonated form is approximately 10^4 times greater than the concentration of the unprotonated form. This phenomenon has also been found for other types of base, but at a sufficiently low temperature the exchange process is slowed down enough so that it is possible to observe the spectrum of the conjugate acid.

In the case of the substituted anilines it is also found that the exchange rate can be changed by altering the acidity of the medium. p-nitroaniline was the strongest base used in this study, and it was found to exchange rapidly with the solvent in CF_3COOH and in 40 mole % H_2SO_4/H_2O solutions. By adding sulphuric acid to both these solutions proton exchange is slowed down and the spectrum of the conjugate acid can be obtained. For weaker bases it is necessary to increase the acidity of the solution accordingly in order to record the conjugate acid spectrum. N.m.r. spectra have been recorded for solutions in mixtures of H_2O/H_2SO_4, CF_3COOH/H_2SO_4, CH_3NO_2/H_2SO_4, and HSO_3F/H_2SO_4 and the chemical shifts are recorded in Tables XXI-XXXIII. Corrections for the bulk diamagnetic

susceptibilities of the solution and the external reference were made in all cases.

The rate of proton exchange was followed in a general way by observation of the reappearance of the peak due to the protons attached to nitrogen. Protonation of the nitrogen bases results in the disappearance of the NH signal as a consequence of rapid exchange with the solvent and it reappears only when the rate of exchange becomes slower than the inverse of the separation of the two exchangeable sites. As the exchange process becomes slower the chemical shift between the two exchanging sites becomes greater. When the rate of exchange is negligible any further increase in the acidity produces no change in the chemical shift between the two sites other than that due to a solvent effect. This is illustrated in Fig. 33 where the chemical shifts of the protons attached to nitrogen are plotted against mole % H_2SO_4 (or HSO_3F). Detection of a signal due to a proton on nitrogen is often difficult due to the fact that the proton signal is frequently very broad as a result of interaction with the quadrupole moment of the nitrogen nucleus[75,103]. In addition the signal is also somewhat broadened by the exchange process and becomes sharper as the exchange is slowed down. An attempt is made in a later chapter (VII) to correlate the appearance of the NH peak with the H_o of the solution.

For N-methyl substituted amines it is possible to follow the proton transfer by observation of the structure of the CH_3 peak. For example, N-methyl-4-chloro-2-nitroaniline, in an organic solvent, shows a doublet structure for the CH_3 resonance. Upon dissolving the base in CF_3COOH protonation occurs and the doublet structure collapses to a single

line. This broadens as the concentration of H_2SO_4 is increased and eventually becomes a triplet due to spin-spin coupling with the NH_2^+ protons when exchange becomes negligible. The spin-spin coupling constant between the CH_3 and NH protons is usually of the order of 5 c.p.s. The relation between the structure of the CH_3 group resonance in the spectra of N-methylanilines and the acidity of the solution is discussed in Chapter VII.

From Tables XXI-XXXIII it is seen that protonation of the base results in all the peaks in the spectrum being shifted to lower field. This is the result of the positive charge on the nitrogen atom which reduces the shielding at the other hydrogen atoms by varying amounts. The effect is most noticeable for the protons of the aromatic ring. The chemical shifts of the ortho and para protons are most affected by protonation, as a result of conjugation in the aromatic ring, and the shifts of the meta protons the least. This results in a partial collapse of the phenyl part of the spectrum, although in no case was a complete collapse to a single line observed as found previously for aniline[14]. No attempt has been made to analyse the phenyl portion of these spectra in order to obtain chemical shifts and spin-spin coupling constants.

Pyridine

The protonation of pyridine has been investigated by Isobe et al.[13] who found that it was protonated in acetic acid but that there was rapid exchange occurring. Smith and Schneider[16] have studied pyridine in trifluoracetic acid and observed a triplet due to the proton captured by the nitrogen. The triplet structure is the result of spin-spin coupling between the captured proton and the nitrogen. The quadrupole moment of

the nitrogen nucleus is apparently not too effective in relaxing the N^{14}-H spin-spin coupling which suggests that the nitrogen is in a fairly symmetrical environment. This phenomenon has been discussed by Roberts[75] and others[103].

The resonance due to the NH^+ proton was found by Smith and Schneider[16], and also in this investigation, to occur at very low field for a proton attached to nitrogen. This low value has been compared[16] with that of the NH proton in pyrrole, a correction for the ring current effect made, and the electron density around the pyridinium ion calculated from this and the chemical shifts of the other ring protons. These workers suggest that the broadening of the β and γ protons on protonation is the result of a slow proton exchange between the NH^+ proton and the solvent.

The n.m.r. spectrum of pyridine in a number of solvents having widely different acidities was recorded and the chemical shifts of the more prominent peaks are given in Table XXXIV. On going from trifluoracetic acid (H_0 -3.0) to the much stronger fluorosulphuric acid (H_0 -13.8) the resonance of the NH^+ proton is shifted 1.45 p.p.m. to higher field, and the N^{14}-H spin-spin coupling remains unchanged at 67$\pm$ 1 c.p.s. Fig. 34 shows the ring part of the spectrum in solutions of differing acidity: the signal from the β protons is relatively little changed in the different solvents whereas the signals from the α and γ protons move together. These facts do not appear to be in accord with Smith and Schneider's[16] explanation of a slow proton exchange as the cause of the increased width of the β and γ peaks on protonation. Any slow exchange would surely be completely stopped by increasing the H_0

from -3.0 to -13.8 but in spite of this the β and γ proton peaks remain broad. Furthermore J_{N-H} remains unchanged with increasing acidity. It seems clear that the broadness of the β and γ peaks in the ion is not due to any residual exchange, but may either be due to the overlapping of a large number of resonance lines which cannot be resolved, or to the nuclear quadrupole relaxation of the N^{14} nucleus operating at positions in the molecule several bonds removed from the nitrogen nucleus. A spin-spin decoupling experiment in which the proton spectrum is observed while the nitrogen nucleus is being irradiated with a strong radio-frequency magnetic field which causes frequent transitions of the states of the N^{14} nucleus thus effectively decoupling it from the rest of the system, might enable this problem to be solved. It might also be possible to achieve spin-spin decoupling by observing the proton spectrum of pyridine in HSO_3F solution at low temperatures (-85°) since this was achieved in the case of acetamide (Chapter III).

TABLE XXI

CHEMICAL SHIFTS OF p-NITROANILINE IN H_2O/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift Solvent	δ (p.p.m.) from ext. H_2SO_4 ref. NH_3^+	Phenyl			
76.63	-0.59	2.17	2.03	2.17	2.77	2.93
75.45	-0.61	2.32	2.04	2.13	2.78	2.92
62.30	-0.67	2.14	1.99	2.14	2.73	2.88
48.18	-0.38	1.96	1.96	2.10	2.68	2.83
40.66	0.02		1.96	2.11	2.68	2.83
38.60	0.15		1.96	2.12	2.68	2.82
30.96	0.77		1.95	2.11	2.66	2.79
28.30	1.03		1.95	2.09	2.65	2.80

Conc. of base 1.1 mole %

TABLE XXII

CHEMICAL SHIFTS OF p-NITROANILINE IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift solvent	δ(p.p.m.) from ext. H_2SO_4 ref. NH_3^+		phenyl		
100.00	0.0	2.51	2.10	2.25	2.85	3.00
78.97	-0.13	2.45	2.16	2.31	2.89	3.04
44.77	-0.30	2.34	2.23	2.37	2.90	3.05
30.28	-0.37	2.26	2.26	2.40	2.91	3.06
25.98	-0.38	2.25	2.29	2.44	2.92	3.10
17.46	-0.44	2.16	2.31	2.45	2.96	3.11
14.80	-0.48	2.16	2.34	2.48	2.97	3.11
13.81	-0.49	2.10	2.31	2.46	2.94	3.09
12.37	-0.51	2.08	2.30	2.48	2.96	3.11
10.95	-0.53	2.05	2.32	2.47	2.96	3.11
8.19	-0.55	2.03	2.33	2.48	2.97	3.12
5.92	-0.59	2.00	2.35	2.49	2.97	3.12
4.74	-0.56	1.99	2.39	2.54	3.02	3.17
4.38	-0.61	1.96	2.37	2.52	3.00	3.15
2.27	-0.65	1.87	2.38	2.53	3.01	3.16
0.00	-0.65	-	2.35	2.50	3.02	3.17

Conc. of base 1.8 mole %

TABLE XXIII

CHEMICAL SHIFTS OF p-NITROANILINE IN CH_3NO_2/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift solvent	NH_3^+	δ(p.p.m.) from ext. phenyl			H_2SO_4 ref.	CH_3NO_2
100.00	-0.02	2.50	2.10	2.25	2.85	3.00	-
87.37	-0.22	2.38	2.08	2.22	2.81	2.95	6.16
81.40	-0.30	2.35	2.07	2.22	2.80	2.95	6.17
76.81	-0.37	2.31	2.07	2.21	2.78	2.92	6.16
66.36	-0.38	2.30	2.07	2.26	2.76	2.90	6.38
55.05	-0.41	2.29	2.14	2.29	2.79	2.94	6.19
46.56	-0.40	2.26	2.15	2.26	2.80	2.94	6.21
41.89	-0.34	2.25	2.15	2.29	2.78	2.92	6.23
37.21	-0.26	2.22	2.17	2.32	2.80	2.95	6.27
29.47	-0.19	2.20	2.20	2.35	2.81	2.97	6.32
23.54	-0.17	2.11	2.18	2.33	2.79	2.93	6.35
17.70	-0.12	2.14	2.22	2.37	2.83	2.98	6.35
17.46	-0.09	2.12	2.23	2.38	2.83	2.98	6.35
13.90	-0.03	2.03	2.23	2.38	2.83	2.98	6.43
9.14	-0.11	-	2.26	2.42	2.86	3.01	6.38
8.46	-0.10	-	2.26	2.41	2.86	3.00	6.44
0.00	-		2.72	2.87	4.03	4.16	6.45

Conc. of base 1.2 mole %

TABLE XXIV

CHEMICAL SHIFTS OF 4-CHLORO-2-NITROANILINE IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift Solvent	NH_3^+	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl				
100.00	0.0	2.06	2.21	2.64	2.80	2.95	3.08
71.74	-0.13	1.98	2.28	2.71	2.82	2.95	3.06
66.25	-0.17	1.97	2.30	2.70	2.86	2.94	3.09
37.96	-0.29	1.87	2.36	2.77		2.95	3.12
24.52	-0.39	1.81	2.41			2.97	
21.10	-0.42	1.82	2.41			2.98	
18.15	-0.46	1.76	2.43			2.99	
12.08	-0.52	1.65	2.45			3.00	
0.00	-0.60	-	2.52			3.11	
(CH_3NO_2)		4.31	2.44	3.35	3.51	3.76	3.91

Conc. of base 1.5 mole %

TABLE XXV

CHEMICAL SHIFTS OF 2-CHLORO-4-NITROANILINE IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shifts solvent	NH_3	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl			
100.00	0.0	2.33	2.13	2.32	2.73	2.88
74.48	-0.14	2.26	2.20	2.36	2.75	2.90
61.42	-0.20	2.23	2.23	2.39	2.76	2.92
50.73	-0.25	2.19	2.24	2.40	2.77	2.92
31.63	-0.32	2.13	2.33	2.48	2.83	2.96
26.26	-0.37	2.08	2.33	2.48	2.83	2.95
23.42	-0.40	2.04	2.32	2.49	2.80	2.95
11.95	-0.51	-	2.37	2.53	2.83	2.97
0.00	-0.61	-	2.43	2.64	2.98	3.13
(CH_3NO_2)		5.52	2.66	2.89	3.82	3.98

Conc. of base 1.6 mole %

TABLE XXVI

CHEMICAL SHIFTS OF N-METHYL-2-CHLORO-4-NITROANILINE IN H_2O/H_2SO_4 SOLUTIONS

Mole %	Chemical shift, δ(p.p.m.) from ext. H_2SO_4 ref.							
	solvent	NH_2^+	phenyl				$N.CH_3$	J (c.p.s.)
68.25	-0.67	~2.02	2.02	2.18	2.62	2.77	7.21	
63.28	-0.68	~2.02	2.02	2.19	2.61	2.76	7.20	
61.28	-0.67	~1.99	2.00	2.16	2.60	2.76	7.19	
57.82	-0.63	~1.95	1.98	2.16	2.58	2.73	7.19	
52.61	-0.54	-	1.99	2.17	2.56	2.73	7.17	
47.21	-0.33	-	2.01	2.18	2.59	2.74	7.18	
HSO_3F	0.29	~2.01	2.01	2.18	2.65	2.96	7.35	5.65

Conc. of base 1.2 mole %

TABLE XXVII

CHEMICAL SHIFTS OF N-METHYL-2-CHLORO-4-NITROANILINE IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift, δ(p.p.m.) from ext. H_2SO_4 ref.							
	solvent	NH_2^+	phenyl				$N.CH_3$	J (c.p.s.)
42.08	-0.31	2.08	2.28	2.41	2.77	2.91	7.38	-
34.45	-0.37	2.09	2.25	2.36	2.76	2.91	7.38	-
18.72	-0.45	2.03	2.31	2.47	2.80	2.93	7.41	-
10.83	-0.53	1.91	2.35	2.51	2.89	2.96	7.43	-
4.37	-0.50	-	2.37	2.53	2.82	2.96	7.43	-

Conc. of base 1.6 mole %

TABLE XXVIII

CHEMICAL SHIFTS OF N-METHYL-4-CHLORO-2-NITROANILINE

IN H_2O/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift Solvent	NH_2^+	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl					N.CH_3	J(c.p.s.)
69.71	-0.66	1.55	2.10	2.50	2.64	2.79	2.94	7.23	Not
62.38	-0.65	1.54	2.11	2.50	2.62	2.80	2.94	7.23	resolved
58.33	-0.64	1.40	2.07	2.45	2.60	2.76	2.89	7.16	
49.51	-0.44	1.34	2.04	2.45	2.57	2.72	2.86	7.17	
47.19	-0.36	-	2.02	2.39	2.56	2.67	2.84	7.15	
40.80	-0.01	-	2.04	2.43	2.57	2.70	2.82	7.16	

Conc. of base 1.6 mole %.

TABLE XXIX

CHEMICAL SHIFTS OF N-METHYL-4-CHLORO-2-NITROANILINE

IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift† solvent	NH_2^+	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl					$N.CH_3$	J (c.p.s.)
100.00	-0.02	1.76	2.21	2.61	2.76	2.91	3.08	7.33	4.08
87.06	-0.08	1.71	2.26	2.64	2.80	2.95	3.09	7.39	
59.15	-0.20	1.71	2.36	2.77	2.91	3.02	3.17	7.37	4.42
42.64	-0.28	1.67	2.41	2.79	2.94	3.02	3.15	7.41	5.10
23.49	-0.39	1.55	2.46	2.86	3.02	3.07	3.22	7.49	
21.92	-0.41	1.52	2.41			2.98		7.57	
18.05	-0.44	1.49	2.44			2.99		7.45	
11.02	-0.52	1.36	2.45			3.01		7.45	
7.18	-0.56	-	2.46			3.01		7.47	
0.00	-	-	2.50			3.06		7.53	
(CH_3NO_2)	-	-	2.73	3.24	3.39	3.75	3.89	7.73	4.59

Conc. of base 1.8 mole %.

TABLE XXX

CHEMICAL SHIFTS OF N-METHYL-2,4-DINITROANILINE IN

H_2SO_4/HSO_3F SOLUTIONS

Mole % HSO_3F	Chemical shift† solvent	NH_2	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl					$N.CH_3$	J (c.p.s.)
100.00	0.33	-	1.36	1.77	1.92	2.56	2.73	7.26	5.6
74.63	0.17	1.76	1.42	1.82	1.99	2.62	2.77	7.30	5.5
56.96	0.09	1.70	1.41	1.82	1.96	2.62	2.76	7.32	5.2
33.82	0.03	1.57	1.38	1.77	1.92	2.55	2.71	7.27	-
27.53	0.02	1.65	1.46	1.76	1.99	2.62	2.77	7.26	-
17.77	0.00	1.58	1.41	1.80	1.94	2.67	2.72	7.26	-
8.80	0.00	-	1.39	1.72	1.93	2.55	2.69	7.25	-
0.00	-0.02	-	1.36	1.75	1.89	2.52	2.67	7.28	-

Conc. of base 1.4 mole %.

TABLE XXXI

CHEMICAL SHIFTS OF N,N-DIMETHYL-2,4-DINITROANILINE

IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift solvent	δ(p.p.m.) from ext. H_2SO_4 ref. phenyl					$N(CH_3)_2$	J_{CH_3-H}
100.00	-0.02	1.39	1.71	1.85	2.38	2.52	7.12	3.1
89.67	-0.05	1.40	1.72	1.88	2.38	2.54	7.16	4.25
54.41	-0.22	1.46	1.77	1.92	2.38	2.53	7.14	4.53
47.61	-0.27	1.56	1.85	2.00	2.46	2.61	7.22	4.41
22.45	-0.40	1.54	1.81	1.97	2.39	2.55	7.13	4.76
3.08	-0.62	1.62	1.93	2.09	2.43	2.59	7.21	0.0
0.62	-0.59	1.62	1.93	2.08	2.42	2.57	7.19	0.0
(CH_3NO_2)		2.24	2.57	2.73	3.56	3.71	7.73	0.0

NH^+ peak not detected even in 100% H_2SO_4.

Conc. of base 1.2 mole %

TABLE XXXII

CHEMICAL SHIFTS OF N,N-DIMETHYL-2,4,6-TRINITROANILINE IN H_2SO_4/HSO_3F SOLUTIONS

Mole % HSO_3F	Chemical shift δ(p.p.m.) from ext. H_2SO_4 ref. solvent	NH^+	phenyl	$N.CH_3$	J CH_3NH^+ (c.p.s.)
100.00	0.39	-0.62	1.31	6.96	5.00
66.09	0.12	-0.62	1.33	7.00	5.05
46.41	0.06	-0.43	1.46	6.99	4.47
25.73	0.02	-0.52	1.33	6.98	4.74
0.00	-0.02	-0.43	1.31	6.96	-

Conc. of base 1.3 mole %.

TABLE XXXIII

CHEMICAL SHIFTS OF N,N-DIMETHYL-2,4,6-TRINITROANILINE IN CF_3COOH/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift δ(p.p.m.) from ext. H_2SO_4 ref. solvent	NH^+	phenyl	$N.CH_3$	$J_{CH_3NH^+}$ (c.p.s.)
87.83	-0.07	-	1.34	6.97	3.67
67.25	-0.16	-	1.44	6.97	-
57.67	-0.21	-	1.46	7.02	-
51.76	-0.22	-	1.40	6.97	-
33.14	-0.31	-	1.57	7.11	-
20.48	-0.42	-	1.68	7.18	-

Conc. of base 1.2 mole %.

TABLE XXXIV

CHEMICAL SHIFTS OF PYRIDINE IN ACID SOLUTIONS

Solvent	Chemical shift - δ(p.p.m.) from int. T.M.S. ref. solvent	aromatic protons				NH^+	J_{NH^+} (c.p.s.)
CF_3COOH	11.96	8.98 8.32	8.89 8.21	8.78 8.10	8.65	13.89	67
CF_3COOH cont. 32.5 mole % H_2SO_4	10.83	8.42 7.77	8.33 7.67	8.23 7.56	8.10	12.62	68
H_2SO_4 *	10.49	8.33 7.73	8.23 7.62	8.20 7.51	8.09	12.07	68

Solvent	Chemical shift δ(p.p.m.) from ext. H_2SO_4 ref. solvent	aromatic protons				NH^+	J_{NH^+} (c.p.s.)
CF_3COOH	-1.19	1.85 2.51	1.93 2.62	2.06 2.73	2.35	-3.04	68
H_2SO_4 cont. 28.45 mole % CF_3COOH	-0.43	1.89 2.15	1.99 2.48	2.02 2.57	2.07 2.68	-2.06	66
HSO_3F*	-0.31	2.01 2.59	2.13 2.69	2.25 2.81		-1.59	67

* The high field component of the NH^+ triplet is not visible in these solutions since it has the same chemical shift as the solvent.

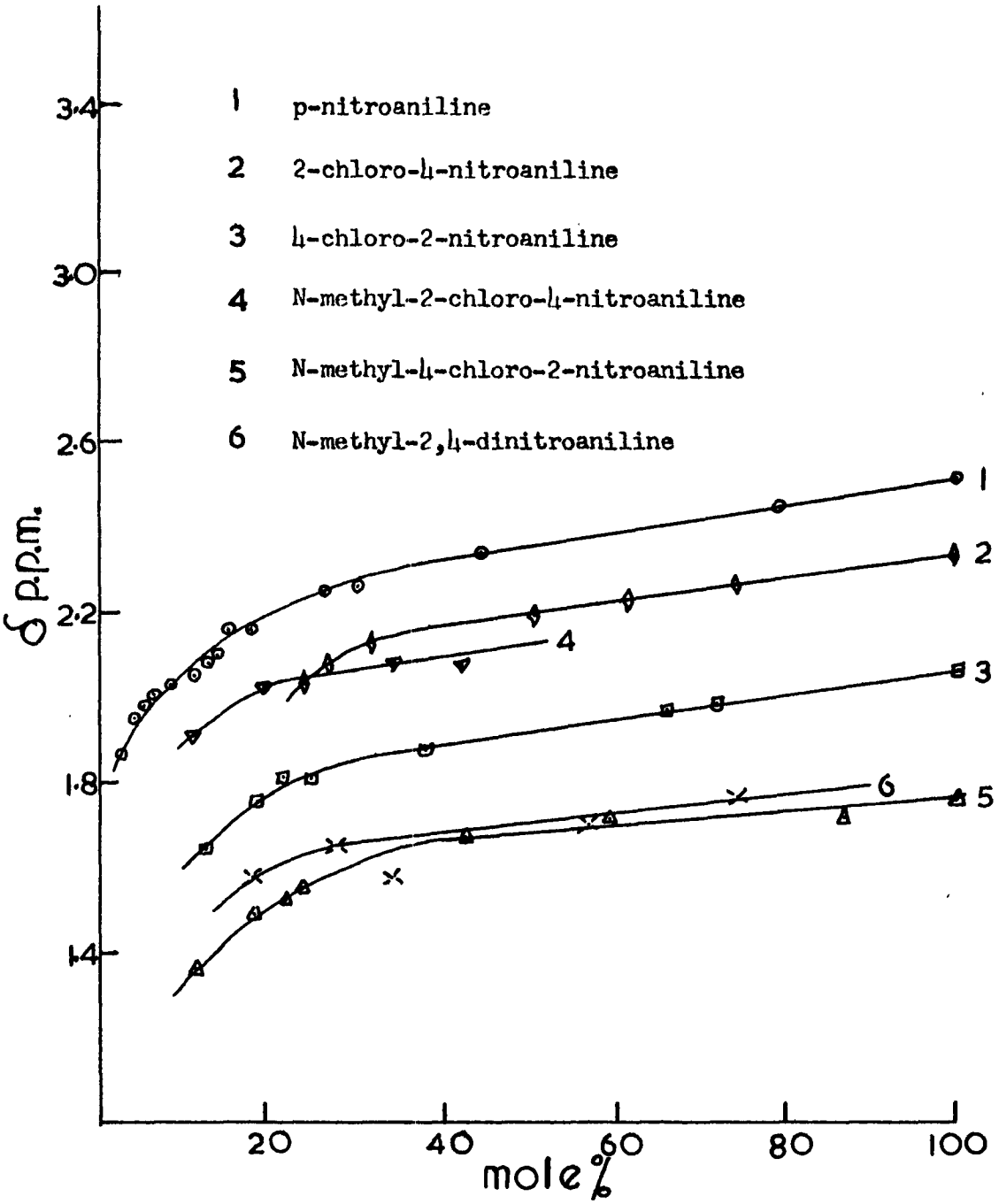


Fig. 33 SOLUTIONS OF ANILINES: NH^+ PROTON CHEMICAL SHIFTS AGAINST CONCENTRATION OF H_2SO_4 OR HSO_3F.

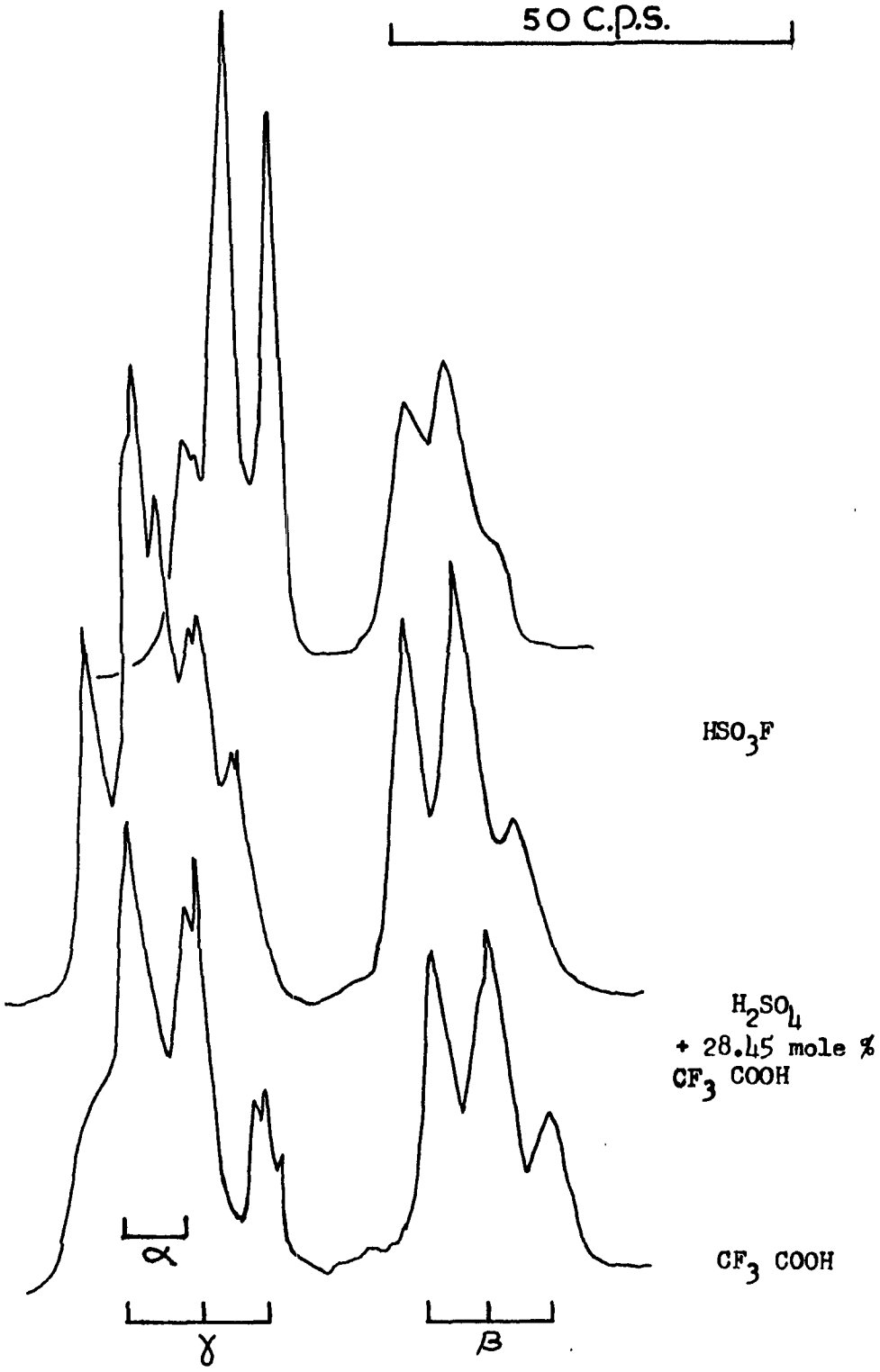


Fig. 34 RING PROTON SPECTRA OF PYRIDINE IN SOLUTIONS OF VARYING ACIDITY .

(3) PROTONATION OF TRIPHENYLPHOSPHINE AND TRIPHENYLARSINE

The rate and mechanism of proton exchange in aqueous solutions of the trimethylphosphonium ion have been determined by n.m.r. techniques[25]. Observation of the collapse of the fine structure in both the methyl and P-H proton resonances with increasing pH enabled a pK_a of 8.80 to be determined. It was found that the doublet, due to spin-spin coupling of the P^{31} with the attached proton, did not collapse to a single line but each component merely broadened and merged into the baseline with increasing rate of exchange.

Examination of a solution of triphenylphosphine in 100% sulphuric acid by n.m.r. showed that protonation had occurred, the proton being attached to the phosphorus atom. That this is the site of protonation is evidenced by the fact that the resonance due to the captured proton is a doublet of J=509 c.p.s. The doublet structure persists even in quite dilute aqueous acid and is also present in CH_3NO_2/H_2SO_4 with a concentration of H_2SO_4 greater than 3.57 mole %. When exchange became rapid the individual components of the doublet broadened and merged with the baseline. The chemical shifts of the main peaks in the spectrum are given in Tables XXXV-XXXVI.

In view of the ease of protonation of triphenylphosphine an attempt was made to observe the spectrum of the conjugate acid of triphenylarsine. However no extra peaks were visible in the n.m.r. spectrum in H_2SO_4 or HSO_3F solutions. Even cooling the solution in HSO_3F to -90° produced no extra peaks. This may be due to the fact that the As nucleus has spin 3/2 and a quadrupole moment which would probably broaden the signal of a proton attached to As to such an extent that it can not be detected.

TABLE XXXV

CHEMICAL SHIFTS FOR TRIPHENYLPHOSPHINE IN H_2O/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shift δ(p.p.m.) from ext. H_2SO_4 ref. solvent	phenyl			P-H	J_{P-H} (c.p.s.)
100.00	0.0	2.89	2.99	3.08	2.53	509.0
73.94	-0.60	2.88		3.07	2.41	503.7
59.56	-0.63	2.89		3.08	2.36	505.3
43.63	-0.17	2.90		3.08	2.28	508.7
37.50	0.25			3.14	2.26	512.4
35.45	0.39			3.12	2.25	512.4
30.71	0.80			3.15	2.21	509.6

Conc. of base 1.2 mole %.

TABLE XXXVI

CHEMICAL SHIFTS FOR TRIPHENYLPHOSPHINE IN CH_3NO_2/H_2SO_4 SOLUTIONS

Mole % H_2SO_4	Chemical shifts - δ(p.p.m.) from ext. T.M.S. solvent	P-H	phenyl			CH_3NO_2
13.72	10.84	13.00	7.77	7.89	7.94	4.38
12.32	10.87	12.99	7.77	7.89	7.94	4.37
5.47	11.02	13.04	7.79	7.91	7.96	4.37
4.47	11.14	13.05	7.82	7.93	7.99	4.37
3.57	10.90	13.07	7.79	7.89	7.96	4.37
2.76	11.15	-	7.79	7.90	7.96	4.35
1.82	10.28	-	7.77	7.87	7.95	4.35

Conc. of base 1.1 mole %.

CHAPTER VII

DETERMINATION OF pK_{BH^+} AND H_o VALUES

(1) INTRODUCTION

In recent years two groups of workers[26,30] have attempted to use n.m.r. techniques to determine indicator ratios of bases in acid solutions. As mentioned in Chapter V, Edward et al.[26] followed the protonation of ethyl alcohol in acid solution by means of the change, with H_o, of the chemical shift between the CH_2 and CH_3 proton resonances. A plot of $\delta_{CH_3} - \delta_{CH_2}$ versus H_o gave a sigmoid type curve with a point of inflection which corresponded to the pK_{BH^+} of the indicator. This method although giving reasonable results, suffers from the disadvantage that the solvent effects on the proton chemical shifts are often of the same order as the effect of protonation.

A similar technique has been used by Taft and Levins[30] who measured the F^{19} chemical shift produced by protonating *para*-substituted fluorobenzenes. In this case the solvent effects are small compared with the chemical shifts produced on protonation and this method appeared to be promising as a means of measuring the H_o of strong acid solutions.

Some Russian workers[31] have calculated H_o for the hydrofluoroic system from F^{19} chemical shifts. Their agreement with

independent results for this system may be fortuitous as their interpretation of the chemical shifts has been questioned[32].

The n.m.r. studies carried out in this work have suggested some other methods which might be applicable to the measurement of H_o. These are discussed in the following sections. In order that some of these results could be interpreted it was necessary to extend the H_o measurements of Barr[27] on the SbF_5/HSO_3F system to much higher concentrations of SbF_5. As stated in Chapter I this necessitates the measurement of ξ_{ion}, ξ_B and ξ for a series of suitable bases. The measurements carried out by Barr[27] indicated that HSO_3F has an H_o of -12.85. It is obvious that the substituted aniline bases used by Hammett[28] are much too strong to be used in this system and it was necessary to use much weaker bases. Brand and coworkers[104], who measured H_o for oleums, used a series of substituted nitrobenzenes and this type of base has also been used in this investigation.

(2) MEASUREMENT OF IONISATION RATIOS, pK_{BH^+}, AND H_o BY THE SPECTROPHOTOMETRIC METHOD

The ionisation ratios were calculated by equation (1.21). The extinction coefficients were measured at the wave-length of the absorption maximum of the bases and not at the wave-length at which ε_{ion} is measured, since there is generally a solvent effect which shifts the absorption maxima towards shorter wave-lengths with increasing acidity.

The bases used in this investigation were:- 2,4-dinitrotoluene; 1-chloro-2,4-dinitrobenzene; 1-fluoro-2,4-dinitrobenzene; 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene. The present results in conjunction with those of Barr[27] and some unpublished measurements of Gillespie et al.[105], are used to extend the acidity function of HSO_3F solutions from 100% HSO_3F to HSO_3F containing 6 mole % SbF_5. In addition the pK_{BH^+} values for the above mentioned bases were calculated in the cases where they were not known. Extinction coefficients and ionisation ratios for these bases are given in Tables XXXVII-XLVI.

Figs. 35-39 show the spectra of these bases in HSO_3F solutions containing different amounts of KSO_3F, H_2SO_4, and SbF_5. Brand and coworkers[104] were unable to obtain experimental values for ε_{ion} for 2,4-dinitrotoluene and weaker bases, and as a result had to resort to calculation in order to obtain ε_{ion} and pK_{BH^+}. In the fluorosulphuric acid system it has been possible to completely protonate all of the bases by addition of suitable quantities of antimony pentafluoride.

The value ε_{ion} = 13900 for 2,4-dinitrotoluene used by Brand

is retained in this investigation; ε_{ion} for 1-fluoro-2,4-dinitrobenzene was found to be 11570 at 330 mμ ; ε_{ion} for 1-chloro-2,4-dinitrobenzene is taken as 12590 at 360 mμ (Gillespie et al.[105]); ε_{ion} for 2,4,6-trinitrotoluene was found to be 10440 at 325 mμ. This latter value was the average of ε_{max} at 325 mμ in two HSO_3F solutions containing 0.523 and 1.725 mole % SbF_5 respectively. Since ε_{max} in the latter solution had a slightly lower value than in the 0.523 mole % solution it was concluded that protonation was complete in the 0.523 mole % SbF solution and the differences in ε_{max} were due to experimental error.

Since there seems to be some disagreement over the correct value for the pK_{BH^+} of 2,4-dinitrotoluene (Brand[104] gives -12.6 while Paul and Long[93] give -12.95), it was thought that an independent value might be calculated from the results of Barr[27] for H_2SO_4/HSO_3F solutions. Using his data for m-chloronitrobenzene (pK_{BH^+} = -12.21) and 2,4-dinitrotoluene in H_2SO_4/HSO_3F solutions, the pK_{BH^+} for 2,4-dinitrotoluene was found to be -13.06. This agrees well with the value due to Paul and Long[93]. The values of log $\frac{C_{BH^+}}{C_B}$ for the indicator 1-fluoro-2,4-dinitrobenzene obtained in this investigation in H_2SO_4/HSO_3F are shown in Fig. 40 plotted together with Barr's data for the other bases. The overlap is not very good but nevertheless it is possible to calculate a value for the pK_{BH^+} of 1-fluoro-2,4-dinitrobenzene. This value was then used in conjunction with the indicator ratios obtained for the other bases in HSO_3F containing KSO_3F or SbF_5 (Fig. 41) in order to obtain their pK_{BH^+} values and also to extend the H_o

measurements to higher SbF_5 concentrations. Tables XLII-XLVI show the indicator ratios, pK_{BH^+}s for the bases and H_0 values for fluorosulphuric acid containing up to 6 mole % SbF_5. The values obtained for H_0 for solutions of KSO_3F and SbF_5 in HSO_3F are shown in Fig. 42. It has been shown by Barr[27] that ionisation ratios cannot be measured directly in 100% HSO_3F as the concentration of the indicator used is larger than the concentration of the ions produced by autoprotolysis. The value of H_0 for 100% HSO_3F was obtained by interpolation from the plot in Fig. 42 and was found to be -13.8: Barr[27] found a value of -12.9. One possible reason for this difference could be the fact that the spectrophotometer used by Barr could only scan the spectrum down to 330 mμ and since the peak maximum in SbF_5/HSO_3F solutions occurs at 315 mμ Barr's extinction coefficients might be too low, resulting in a low interpolated value for 100% HSO_3F.

It is seen from Table XXXVII that in a solution of HSO_3F containing 0.165 mole % SbF_5 the extinction coefficient at 315 mμ for 2,4-dinitrotoluene is higher than ε_{ion} used in the calculations of indicator ratios for this base. Gillespie et al.[105] have found that higher concentrations of SbF_5 produce still higher values of ε but at a wave-length of 310 mμ. These workers found that a new peak appears in the spectrum of 1-chloro-2,4-dinitrobenzene at 310 mμ when the concentration of SbF_5 is increased beyond the value necessary to completely protonate this base: the peak due to the protonated form of this base occurs at 360 mμ. The same effect is noticed in the case of 1-fluoro-2,4-dinitrobenzene, though to a lesser extent since very high concentrations of SbF_5 were not used. In view of the

appearance of this peak at 310 mμ in solutions containing high concentrations of SbF_5 it is believed that the values chosen for ε_{ion} for these dinitrobenzenes are correct even though they are not the maximum values. This peak at 310 mμ is not observed for mononitro bases but only for dinitro bases. It seems reasonable that this new peak might be the result of protonation of the nitracidium ion, i.e. diprotonation of the dinitrobenzene, as a result of the extremely high acidity of the solutions. Alternatively the peak at 310 mμ might be the result of association of the nitracidium ion with SbF_5 as the SbF_5 concentration becomes appreciable.

TABLE XXXVII

EXTINCTION COEFFICIENTS OF 2,4-DINITROTOLUENE IN FLUOROSULPHURIC ACID SOLUTIONS

Wave-length (mμ)	Concentration mole %		
	KSO_3F	H_2SO_4	SbF_5
	0.156	0.461	0.165
	Extinction coefficient		
260	13390	9510	5830
270	13240	8450	6570
280	12190	6730	8040
290	10410	5360	9970
300	8720	5350	12330
310	7820	7100	14160
320	7660	9490	14360
330	7720	11080	13400
340	7290	11280	12270
350	6350	10360	10690
360	5370	8720	8540
370	4090	6550	6180
380	2870	4300	3900
390	1870	2490	2090
400	1290	1370	1090
ε	7660	11330	14530

TABLE XXXVIII

EXTINCTION COEFFICIENTS OF 1-FLUORO-2,4-DINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

Wave-length ($m\mu$)	Concentration mole % KSO_3F				SbF_5	
	0.156	0.047	0.022	0.079	0.165	0.523
	Extinction coefficient					
260	13750	12640	11650	6070	7160	5260
270	12230	10430	10120	4910	4880	5300
280	9840	8180	8230	4210	4610	6480
290	7490	6340	6130	4530	5440	8790
300	5360	5340	4930	5730	7080	10700
310	3820	4820	4370	7520	9210	11910
320	2980	4660	4410	9360	10890	12360
330	2560	4470	4520	10290	11570	12070
340	2210	4070	4270	10030	10970	10890
350	1830	3340	3470	8430	9210	8850
360	1350	2490	2530	6040	6170	5960
370	940	1620	1490	3560	3570	2780
380	600	1000	800	1620	1590	1670
390	450	630	390	680	540	730
400	-	480	-	220	140	340
ε_{330}	2560	4470	4520	10290	11570	

TABLE XXXVIII (Contd.)

EXTINCTION COEFFICIENTS OF 1-FLUORO-2,4-DINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

Wave-length (mμ)	Concentration mole % H_2SO_4 54.95	4.938	0.580	0.343
	Extinction coefficient			
260	-	13800	11590	10450
270	-	11010	9050	8110
280	-	8300	6940	6220
290	5480	6270	5310	5000
300	3650	4980	4630	4800
310	2320	3990	4530	5000
320	1460	3430	4730	5470
330	1030	3050	4830	5620
340	740	2640	4490	5190
350	530	2070	3730	4280
360	330	1600	2540	2890
370	160	1050	1420	1620
380	-	480	650	760
390	-	320	240	310
ε_{330}	1030	3050	4830	5620

TABLE XXXIX

EXTINCTION COEFFICIENTS OF 1-CHLORO-2,4-DINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

Wavelength (mμ)	Concentration mole % KSO_3F 0.047	KSO_3F 0.022	H_2SO_4 0.416
	Extinction coefficient		
260	11020	10100	9550
270	10950	10220	9190
280	10160	9450	8340
290	8850	7930	7100
300	7130	6230	5910
310	5800	5040	5370
320	4960	4540	5260
330	4440	4440	5370
340	4170	4510	5670
350	4170	4740	6080
360	4150	4910	6220
370	3790	4580	5770
380	2910	3560	4440
390	1880	2250	2720
400	1020	1170	1380
ε_{360}	4150	4910	6220

TABLE XL

EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE IN FLUOROSULPHURIC ACID SOLUTIONS

	Concentration mole %					
	KSO_3F		SbF_5			
Wave-length (mμ)	0.156	0.047	0.079	0.165	0.523	1.725
	Extinction coefficient					
260	13510	14440	10770	7900	6970	7450
270	10480	11560	8590	5690	5370	6620
280	7530	8540	6460	4560	4900	6650
290	5170	6070	5240	4950	5810	7520
300	3740	4690	4910	6670	7530	8980
310	2970	3800	5120	8350	9290	10020
320	2360	3080	5330	9350	10410	10340
330	1930	2610	5070	9110	10290	9850
340	1580	2260	4360	7680	9070	8150
350	1250	1930	3330	5720	7410	6540
360	950	1510	2390	3950	5320	4720
370	830	1180	1640	2380	3680	3230
380	590	875	1010	1260	2210	2070
ε_{325}	2120	2840	5330	9410	10540	10340

TABLE XL (Contd.)

EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE IN FLUOROSULPHURIC ACID SOLUTIONS

Wave-length (mμ)	Concentration mole % H_2SO_4 100.00	4.938	0.343
	Extinction coefficient		
260	11300	14580	13470
270	8370	11360	10420
280	5120	8150	7230
290	2910	5790	4860
300	1940	4630	3820
310	1470	3650	3160
320	1110	2890	2580
330	840	2290	1930
340	660	1780	1270
350	430	1420	690
ε_{325}	960	2190	2240

TABLE XLI

EXTINCTION COEFFICIENTS OF 1,3,5-TRINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

	Concentration mole %	
	H_2SO_4	SbF_5
	0.343	0.260
Wave-length (mμ)	Extinction coefficient	
260	12040	7570
270	6420	5690
280	3260	5800
290	2060	7080
300	1470	8110
310	880	7930
320	700	6230
330	-	4330
340	-	2900
350	-	1880
360	-	1250
370	-	910
380	-	420
ε_{305}	1200	8200

TABLE XLII

INDICATOR RATIOS, pK_{BH^+} AND H_o VALUES FOR 2,4-DINITROTOLUENE IN HSO_3F SOLUTIONS

ε_B = 1700	ε_{ion} = 13900		pK_{BH^+} = -13.06
Conc. mole %	ε	$\log \frac{C_{BH^+}}{C_B}$	H_o
0.156 (KSO_3F)	7660	-0.20	-12.86
0.461 (H_2SO_4)	11330	0.57	-13.63

TABLE XLIII

INDICATOR RATIOS, pK_{BH^+} AND H_o VALUES FOR 1-FLUORO-2,4-DINITROBENZENE IN HSO_3F SOLUTIONS

ε_B = 920	ε_{ion} = 11570		pK_{BH^+} = -13.84
Conc. mole %	ε	$\log \frac{C_{BH^+}}{C_B}$	H_o
0.156 (KSO_3F)	2560	-0.74	-13.10
0.047 "	4470	-0.30	-13.54
0.022 "	4520	-0.29	-13.55
0.079 (SbF_5)	10290	0.86	-14.70
54.95 (H_2SO_4)	1030	-1.99	-11.85
4.938 "	3050	-0.60	-13.24
0.580 "	4830	-0.24	-13.60
0.343 "	5620	-0.10	-13.74

TABLE XLIV

INDICATOR RATIOS, pK_{BH^+} AND H_o VALUES FOR 1-CHLORO-2,4-DINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

ε_B = 590	ε_{ion} = 12590		pK_{BH^+} = -13.88
Conc. mole %	ε	$\log \frac{C_{BH^+}}{C_B}$	H_o
0.047 (KSO_3F)	4150	-0.38	-13.50
0.022 "	4910	-0.25	-13.53
0.416 (H_2SO_4)	6220	-0.05	-13.83

TABLE XLV

INDICATOR RATIOS, pK_{BH^+} AND H_o VALUES FOR 2,4,6-TRINITROTOLUENE IN FLUOROSULPHURIC ACID

ε_B = 960	ε_{ion} = 10440		pK_{BH^+} = -14.32
Conc. mole %	ε	$\log \frac{C_{BH^+}}{C_B}$	H_o
0.156 (KSO_3F)	2120	-0.86	-13.46
0.047 "	2840	-0.61	-13.71
0.079 (SbF_5)	5330	-0.07	-14.25
0.165 "	9410	0.91	-15.23
4.938 (H_2SO_4)	2190	-0.83	-13.49
0.343 "	2240	-0.81	-13.51

TABLE XLVI

INDICATOR RATIOS, pK_{BH^+} AND H_o FOR 1,3,5-TRINITROBENZENE IN FLUOROSULPHURIC ACID

ε_B = 800 ε_{ion} = 14000 pK_{BH^+} = -15.1

Conc. mole %	ε	$\log \frac{C_{BH^+}}{C_B}$	H_o
0.343 (H_2SO_4)	1200	-1.51	-13.59
0.260 (SbF_5)	8200	0.11	-15.21
Results of Gillespie et al.[105]			
0.475 (SbF_5)	6600	-0.11	-14.99
1.163 "	8940	0.21	-15.31
3.452 "	10420	0.43	-15.53
6.335 "	11200	0.57	-15.67

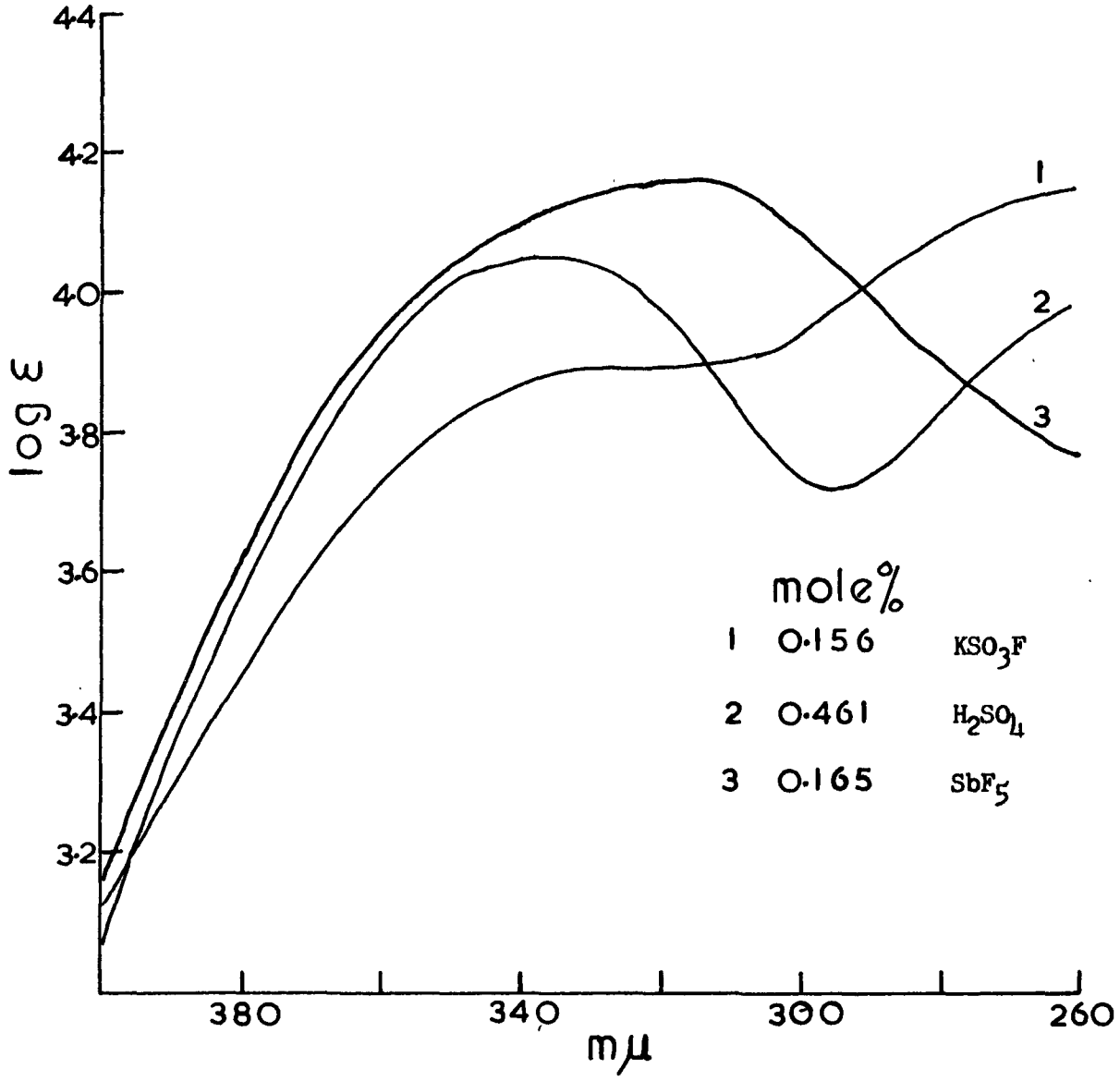


Fig. 35 SOLUTIONS OF 2,4-DINITROTOLUENE: ABSORPTION SPECTRA.

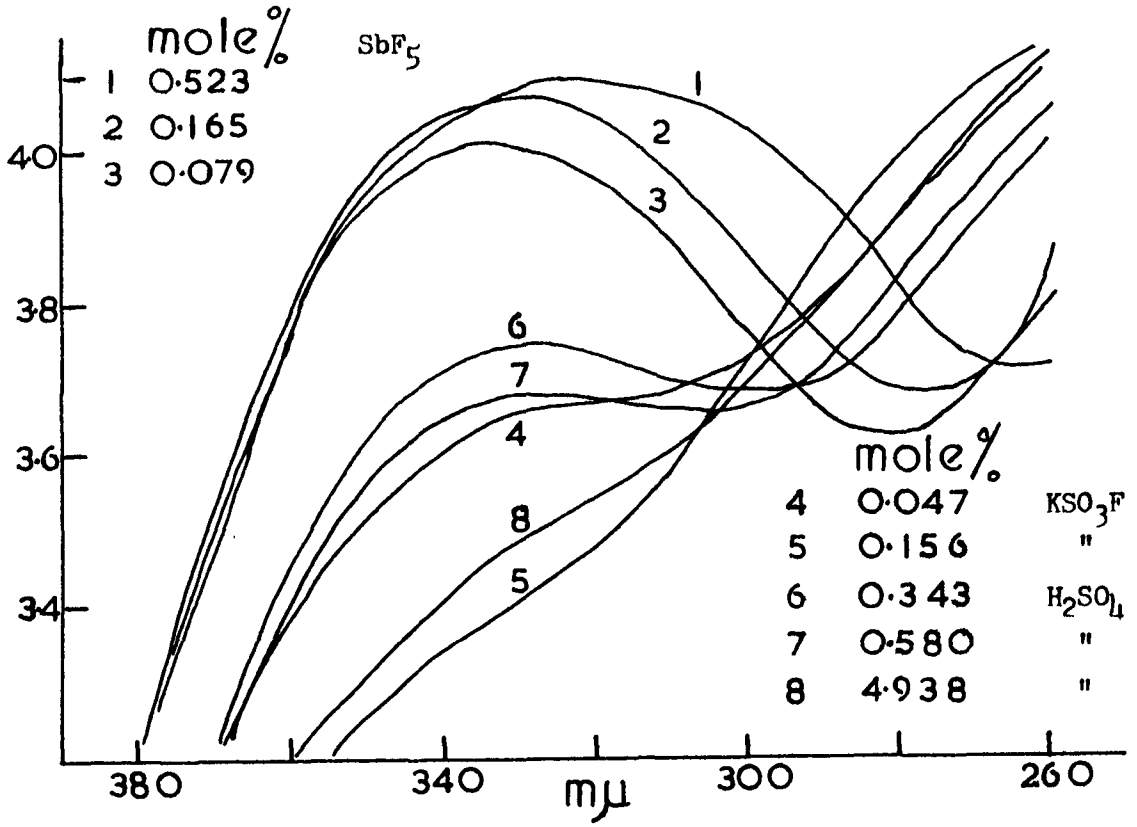


Fig. 36 SOLUTIONS OF 1-FLUORO-2,4-DINITROBENZENE: ABSORPTION SPECTRA.

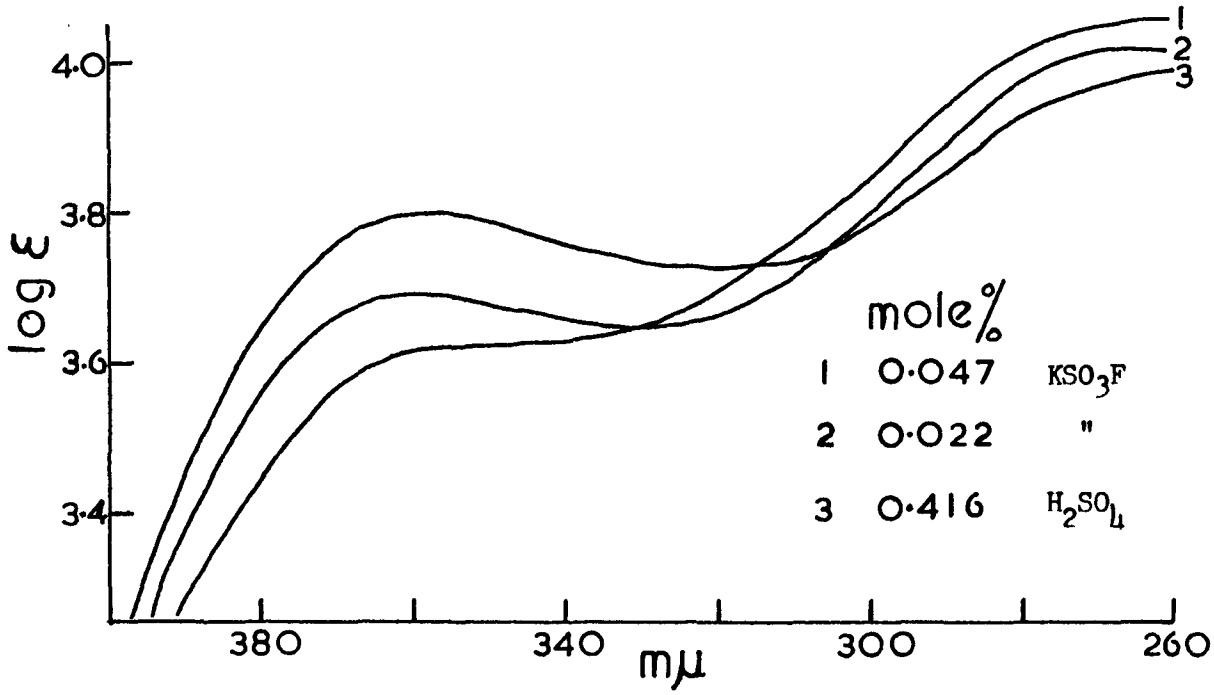


Fig. 37 SOLUTIONS OF 1-CHLORO-2,4-DINITROBENZENE: ABSORPTION SPECTRA.

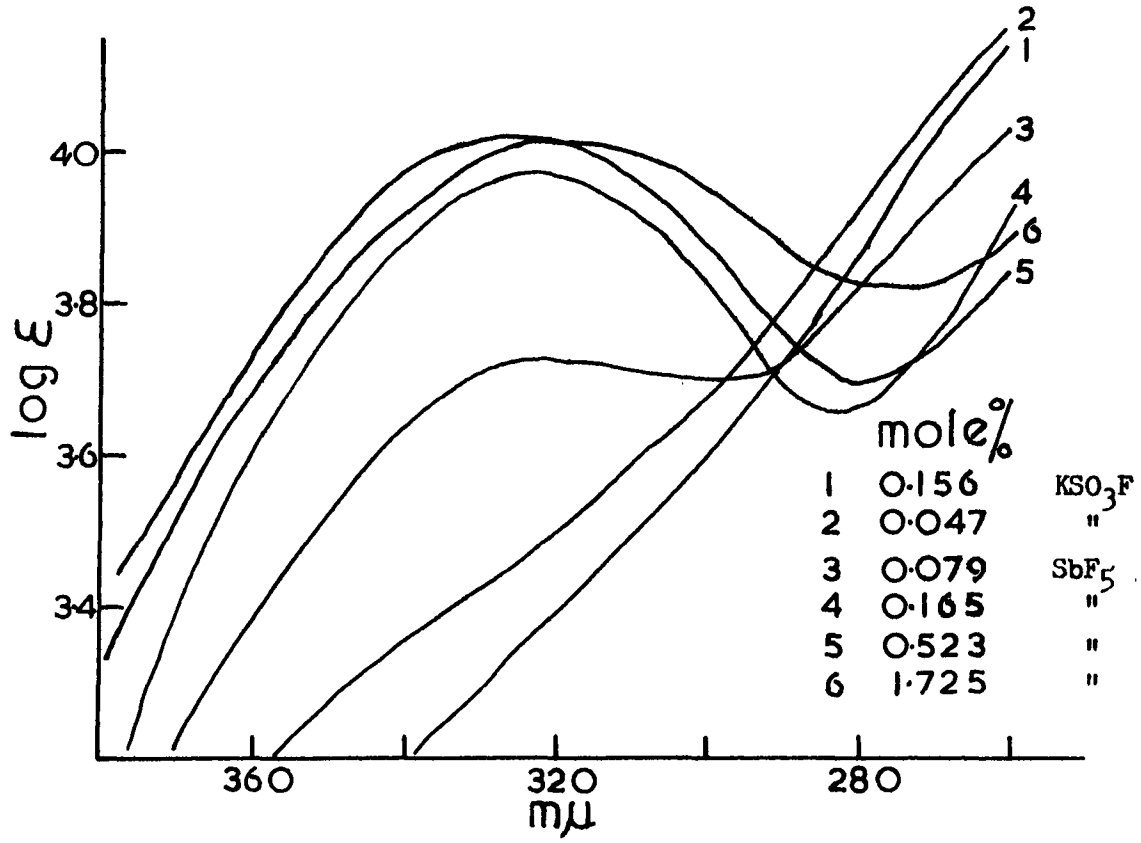


Fig. 38 SOLUTIONS OF 2,4,6-TRINITROTOLUENE: ABSORPTION SPECTRA.

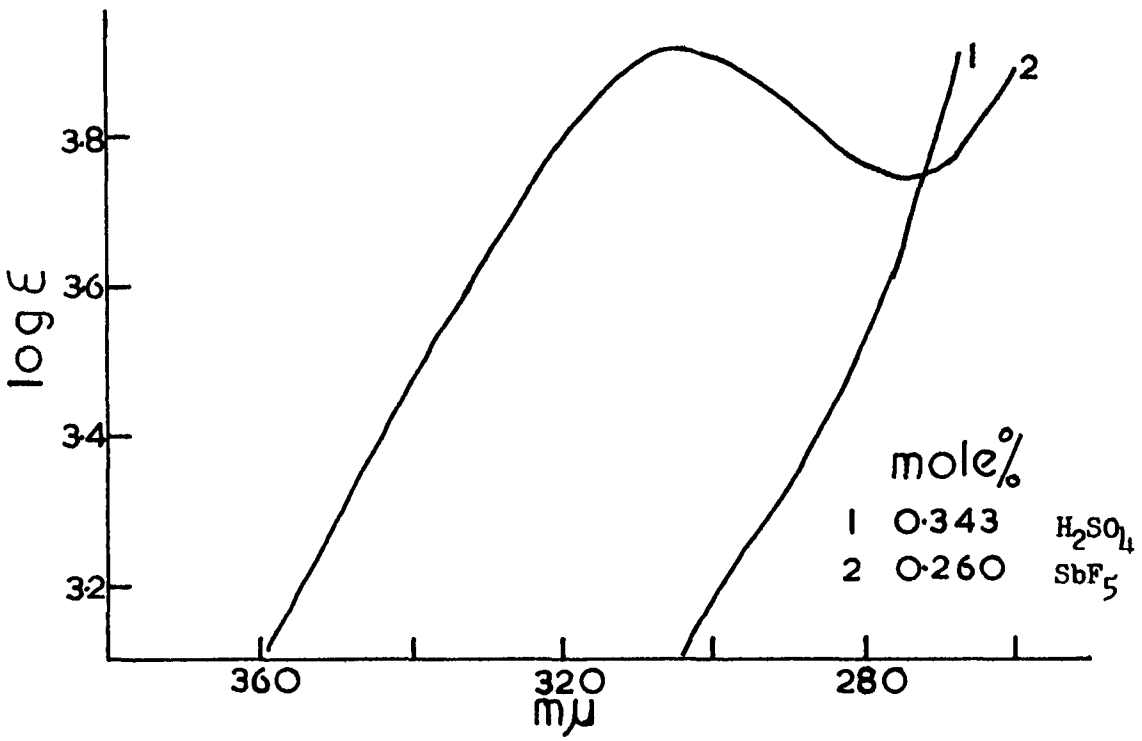


Fig. 39 SOLUTIONS OF 1,3,5-TRINITROBENZENE: ABSORPTION SPECTRA.

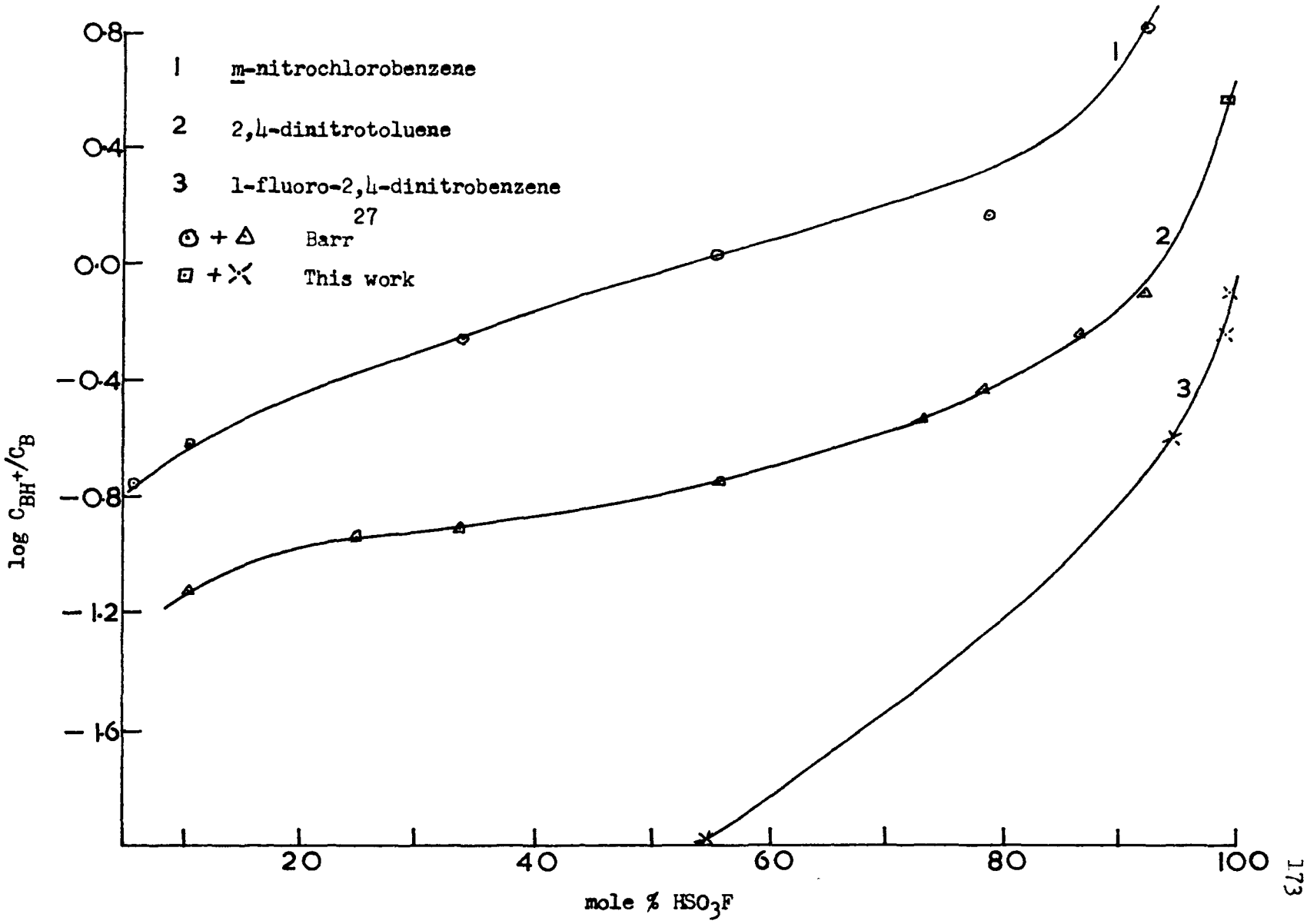


Fig. 40 SOLUTIONS OF NITROBENZENES IN H_2SO_4/HSO_3F: IONISATION RATIOS.

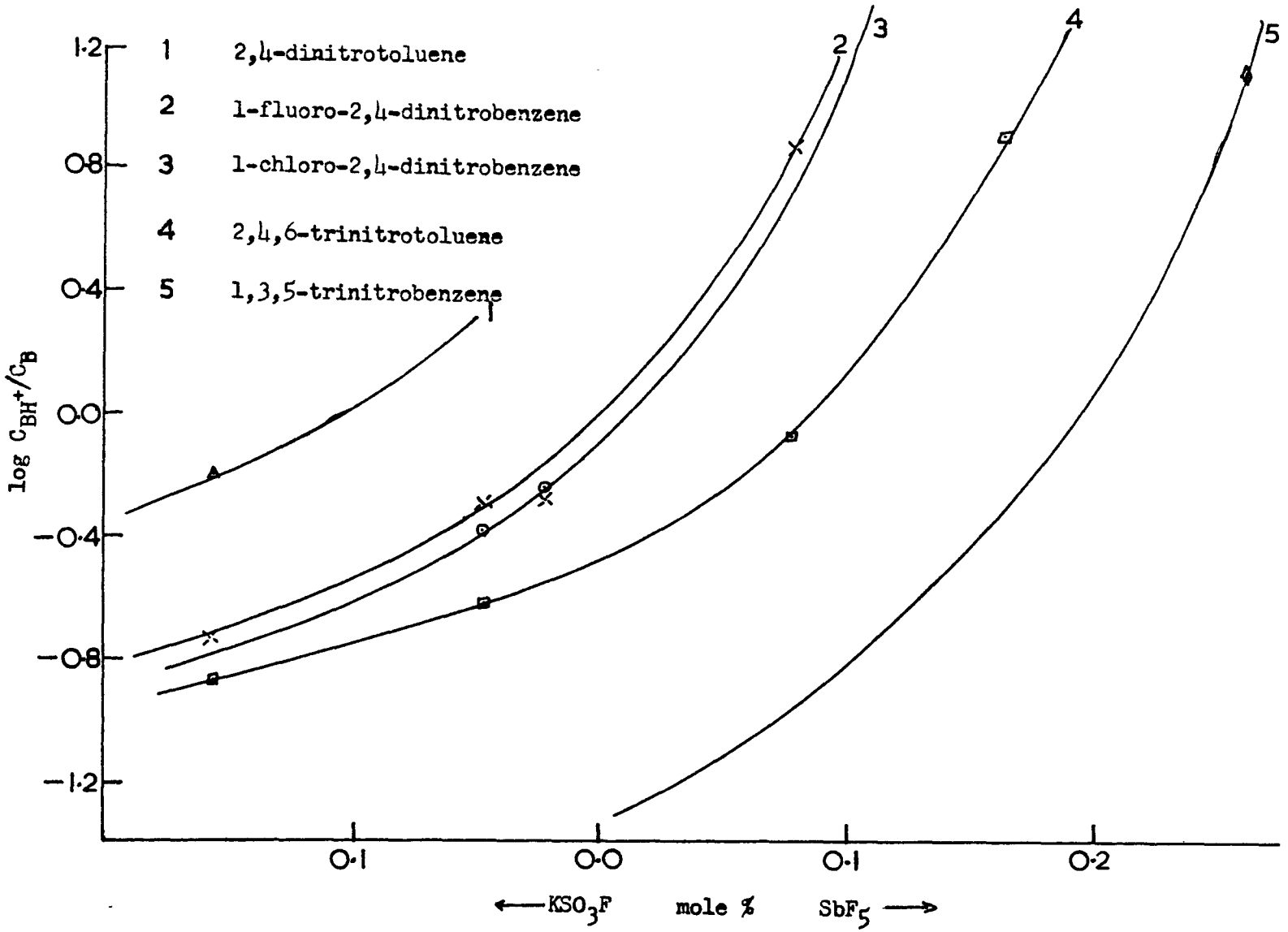


Fig. 41 SOLUTIONS OF NITROBENZENES IN KSO_3F/HSO_3F AND SbF_5/HSO_3F: IONISATION RATIOS.

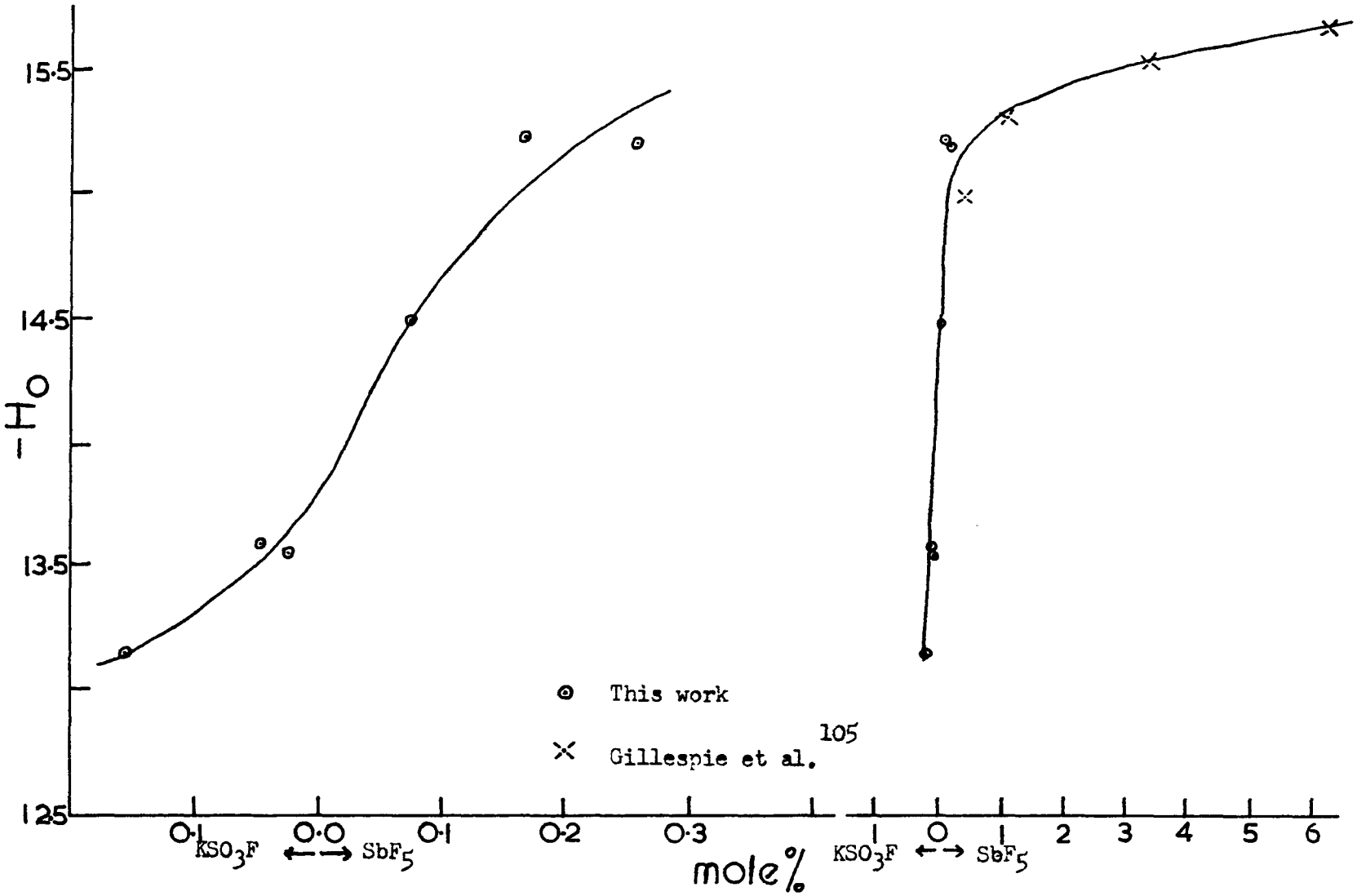


Fig. 42 H_o FOR SOLUTIONS OF KSO_3F AND SbF_5 IN FLUOROSULPHURIC ACID.

(3) CORRELATION OF THE N.M.R. DATA ON ANILINES WITH H_o

It was reported in Chapter VI that by increasing the concentration of sulphuric acid in solutions of anilines in H_2O, CH_3NO_2, and CF_3COOH it is possible to slow down the exchange process so that the spectrum of the conjugate acid can be recorded. Since the appearance of the NH_X^+ resonance occurs at a different acid concentration for each base it was thought that there might be a relation between the acidity at which the NH_X^+ resonance is first visible and the pK_{BH^+} of the base. It is seen from Table XLVII that the value of $-H_o$ at which the NH_X^+ resonance is first observed does in fact increase as the basicity of the aniline decreases. However the detection of the NH_X^+ resonance is not always easy because of the broadness of the signal due to the N^{14} quadrupole moment[75]. In view of this, the further development of these studies as a means of determining H_o was deemed to be unprofitable.

TABLE XLVII

SOLUTIONS OF ANILINES: RELATIONSHIP BETWEEN pK_{BH^+} AND H_o

Base	pK_{BH^+}	$-H_o$*	Solvent system
p-nitroaniline	+1.02	6.25	CF_3SOOH/H_2SO_4
2-chloro-4-nitroaniline		8.75	"
4-chloro-2-nitroaniline	-1.03	7.96	"
N-methyl-2-chloro-4-nitroaniline		7.96	"
N-methyl-4-chloro-2-nitroaniline	-1.49	7.86	"
N-methyl-2,4-dinitroaniline		11.65	HSO_3F/H_2SO_4

* The value of H_o at which the NH_X^+ resonance is first observed.

As the exchange process is slowed down by increasing the acidity of the solution the $N.CH_3$ peak of N-methyl anilines is found to change quite rapidly from a single sharp peak, to a broadened peak and finally when exchange is very slow, into apeak with a multiplet structure depending upon the number of protons attached to the nitrogen of the conjugate acid. This change occurs over quite a narrow H_o range. A plot of the line width of the $N.CH_3$ peak against H_o for a number of N-methyl and N,N-dimethyl anilines gives a sigmoid type curve in each case (Fig. 43).

It is presumed that the value of H_o at which proton exchange becomes very slow is related to the pK_{BH^+} of the indicator. The point of inflection of these curves is taken as a measure of the acidity of the solution when exchange has become very slow. The results obtained for several bases in different media are given in Table XLVIII which lists the values of H_o at the point of inflection in the curve for each base.

TABLE XLVIII

H_o VALUES AT INFLECTION POINTS OF CURVES IN FIG. 43.

	Base	pK_{BH^+}	$-H_o$	Solvent
(1)	N,N-dimethyl-2,4-dinitroaniline	-1.00	7.2	CF_3COOH/H_2SO_4
(2)	N-methyl-4-chloro-2-nitroaniline	-1.49	7.85	"
(3)	"	"	7.97	H_2O/H_2SO_4
(4)	N-methyl-2-chloro-4-nitroaniline	-	8.2	CF_3COOH/H_2SO_4
(5)	"	-	8.25	H_2O/H_2SO_4
(6)	N,N-dimethyl-2,4,6-trinitroaniline	-4.81	9.3	$CF_3COOH/H_2SO_4/HSO_3F$
(7)	N-methyl-2,4-dinitroaniline	-	11.4	HSO_3F/H_2SO_4

In the cases where a base has been studied in both trifluoracetic acid/sulphuric acid and water/sulphuric acid, it is noticed that the point of inflection occurs at a slightly higher H_o in the water/sulphuric acid system. The H_o values used for the aqueous sulphuric acid system are the recently published values of Jorgenson and Hartter[106]. Those for the trifluoracetic acid/sulphuric acid system are due to Hyman and Garber[107] and the fluorosulphuric acid results are due to Barr[27]. The small differences found between the aqueous and trifluoracetic acid systems might be experimental error but could also be due to errors in the H_o values for the CF_3COOH/H_2SO_4 system. (The results for the aqueous system are very recent and appear to have been determined very carefully.)

Again it is found that as the pK_{BH^+} of the base becomes more negative a greater H_o value for the solvent is required in order to stop the exchange process. From the results in Fig. 43 and Table XLVIII it would appear that N-methyl-2-chloro-4-nitroaniline is a weaker base than N-methyl-4-chloro-2-nitroaniline and that N-methyl-2,4-dinitroaniline is a weaker base than N,N-2,4,6-trinitroaniline.

More quantitative results might be obtained if the actual rates of proton exchange were calculated from the collapse of the $N.CH_3$ peak with change in acidity. Reynolds and Schaefer[15] have measured exchange rates for N,N-dimethylaniline in trifluoracetic acid at various temperatures and state that they plan to study the variation of the exchange rate with change in pH. By using the bases mentioned above and others, a wide range of H_o could be covered.

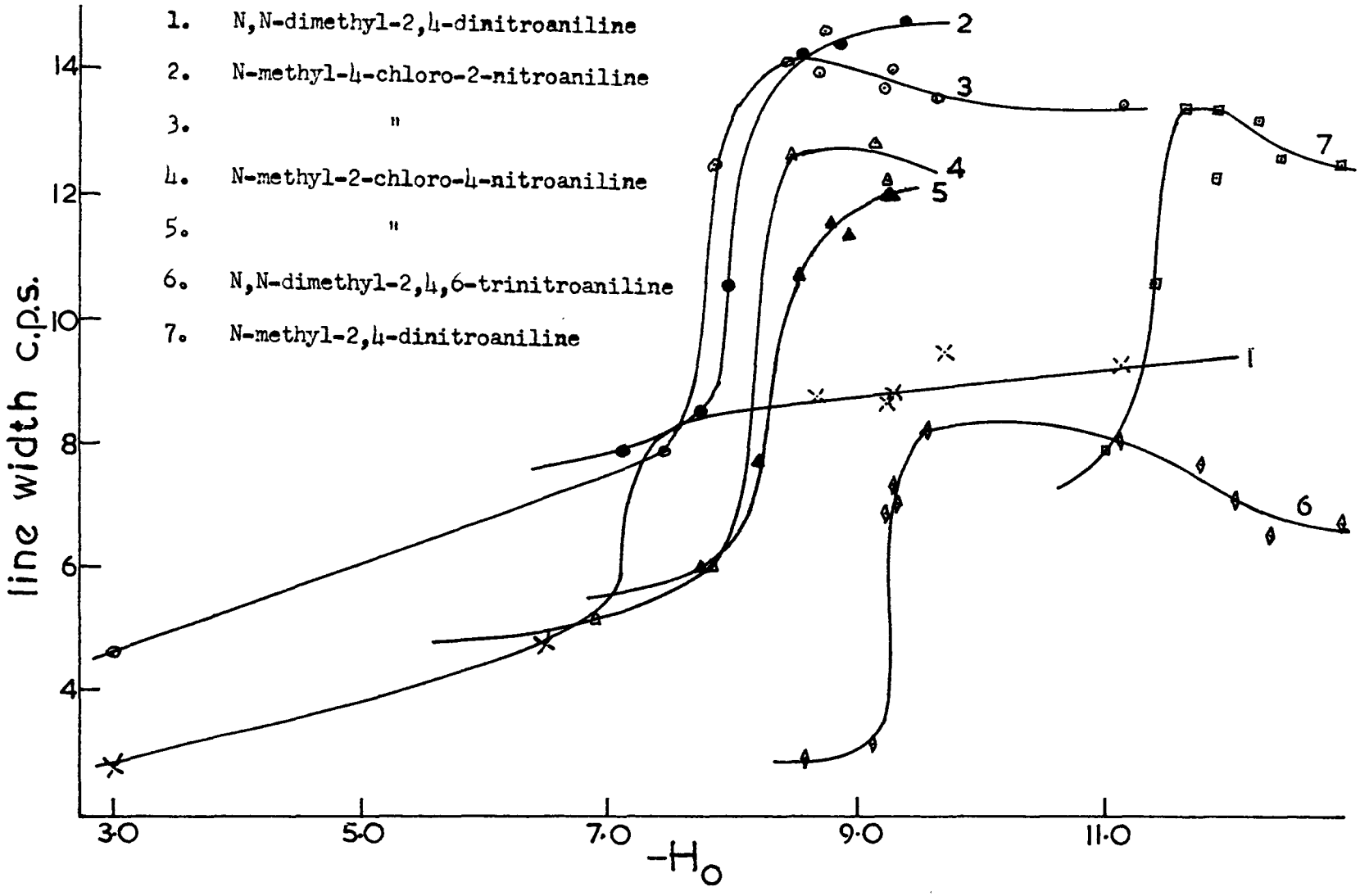


Fig. 43 SOLUTIONS OF N-METHYLANILINES: $N\text{-}CH_3$ LINE WIDTHS AGAINST H_o.

(4) APPLICATION OF F^{19} CHEMICAL SHIFTS TO THE MEASUREMENT OF H_o

Taft and Levins[30] have examined the F^{19} spectra of some para-substituted fluorobenzenes in acid solution and find that the F^{19} resonance undergoes a large chemical shift when the base is protonated. A plot of F^{19} chemical shift against H_o gives a sigmoid curve whose inflection point corresponded to the pK_{BH^+} of the base.

This method has been applied to strong acid solutions in this investigation. The ionisation of 1-fluoro-4-nitrobenzene and 1-fluoro-2,4-dinitrobenzene was studied in oleum and in fluorosulphuric acid solutions. The results are given in Tables XLIX-LI.

Fig. 44 shows the variation of the chemical shift for the two bases in oleum solutions and of 1-fluoro-4-nitrobenzene in H_2SO_4/HSO_3F solutions. The base 1-fluoro-4-nitrobenzene was examined at two different concentrations i.e. 5.31 and 1.40 mole % and the H_o values at the points of inflection are -12.27 and -11.70 respectively. It is evident that the chemical shift is affected by the concentration of the base. This must be due to the fact that as the base is protonated the concentrations of HSO_4^- and $HS_2O_7^-$ increase and as a result the acidity of the solution is decreased: the greater the concentration of base therefore, the more the acidity will be reduced and the more the curve will be shifted to higher acidity. This results in a high value for the pK_{BH^+} of the base. The value obtained at the lower concentration of base agrees quite well with the value of -11.62 given by Paul and Long[93]. A pK_{BH^+} of -11.6 was also obtained for this base in H_2SO_4/HSO_3F at a concentration of 1.45 mole % in excellent agreement with the value obtained in oleum solutions.

For 1-fluoro-2,4-dinitrobenzene in oleum solutions a value for the pK_{BH^+} of -13.45 was obtained. This is somewhat lower than the value of -13.84 obtained from the spectrophotometric method. This might be due, in part at least, to the fact that the H_o values used for the oleum solutions[105] are not very well established at the higher concentrations of SO_3.

When this base was studied in HSO_3F solutions it was found necessary to add SbF_5 to the solution in order to protonate it. The H_o of 100% HSO_3F was shown in section (2) to be -13.8 and since the pK_{BH^+} of this base was -13.84 [section (2)] , then this base dissolved in HSO_3F should be 50% protonated and there should be a corresponding large F^{19} chemical shift. That this is not observed must again be due to the reduction in acidity by the production of base, in this case SO_3F^-. Only upon the addition of SbF_5 does the F^{19} chemical shift change appreciably. In Fig. 45 the F^{19} chemical shifts for these solutions are plotted against mole % SbF_5. It can be seen from Fig. 45 and Table LI that the shift becomes appreciable only when the concentration of SbF_5 approaches that of the base i.e. about 1%, and the point of inflection occurs at a concentration of SbF_5 which would correspond to an H_o of -15.3 if the base was not present. This is a much higher value than was obtained for the pK_{BH^+} of this base by the spectrophotometric method. This difference is much greater than any error that could have been made either in the H_o determinations for these solutions or in the pK_{BH^+} value for this indicator.

When SbF_5 is dissolved in HSO_3F it has been shown that it

ionises according to (7.1),

$$SbF_5 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + SbF_5SO_3F^- \qquad (7.1)$$

i.e. it is a strong acid[44]. Thus as SbF_5 is added to a solution of 1.32 mole % of 1-fluoro-2,4-dinitrobenzene in HSO_3F the base is titrated by the SbF_5, producing the salt $BH^+.SbF_5SO_3F^-$ (7.2),

$$B + HSO_3F + SbF_5 = BH^+.SbF_5SO_3F^- \qquad (7.2)$$

and it is this process which is being followed by the observation of the change in the F^{19} chemical shift. At the point of inflection of this titration curve i.e. when $C_{BH^+} = C_B$, the acidity of the solution must be equal to the pK_{BH^+} of the base -13.84. This inflection point should occur when 0.66 mole % SbF_5 has been added, but is actually found to occur at approximately 1 mole %. There are not sufficient data to locate this point precisely and the difference between the observed and expected values is possibly due solely to experimental error. A solution of HSO_3F containing 0.66 mole % SbF_5 would have an H_o of -15.26 (Fig. 42) so that the addition of 1.32 mole % of 1-fluoro-2,4-dinitrobenzene must reduce the acidity from -15.26 to -13.84. This solution contains an equivalent amount of base and its conjugate acid. The effects of electrolytes upon H_o has been discussed by Paul and Long[93] and can lead to a reduction in H_o. It is reasonable to assume that the presence of unprotonated base could also lead to a reduction in H_o. Further addition of SbF_5 to this solution would be expected to cause no further increase in acidity until the concentration of SbF_5 exceeds that of the base.

It is clear that this method is applicable only when the

concentration of the base is very much smaller than the concentration of any of the components of the solution, in this case the SbF_5.

TABLE XLIX

F^{19} CHEMICAL SHIFTS OF 1-FLUORO-4-NITROBENZENE IN OLEUM SOLUTIONS

Conc. of base 5.31 mole %			Conc. of base 1.4 mole %		
δ (p.p.m.) from ext. CF_3COOH	mole % SO_3	$-H_o$	δ (p.p.m.) from ext. CF_3COOH	mole % SO_3	$-H_o$
17.10	0.00	11.3	15.77	0.00	11.30
11.70	5.30	12.16	14.79	0.32	11.45
9.31	7.97	12.33	10.99	1.78	11.70
9.33	8.02	12.35	10.16	2.34	11.82
4.95	15.14	12.66	7.22	4.14	12.03
1.92	23.81	12.92	5.61	6.18	12.20
1.05	32.79	13.17	3.45	8.34	12.35
			1.35	12.35	12.55
			0.34	15.68	12.67
			-4.16	34.12	13.22
			-4.54	38.50	13.33
				mole % H_2O	
			17.07	0.92	11.2
			17.97	6.64	10.8

H_o values are those of Gillespie et al.[105].

TABLE L

F^{19} CHEMICAL SHIFTS OF 1-FLUORO-2,4-DINITROBENZENE IN OLEUM SOLUTIONS

Conc. of base 1.06 mole %

δ (p.p.m.) from ext. CF_3COOH	mole % SO_3	$-H_o$
22.68	0.00	11.3
22.19	8.39	12.35
21.46	15.79	12.67
20.37	24.91	12.94
18.35	34.11	13.22
16.53	37.26	13.30
15.34	44.09	13.48
13.69	47.47	13.57
9.84	61.03	13.93
8.88	70.71	14.20

H_o values are those of Gillespie et al.[105].

TABLE LI

F^{19}CHEMICAL SHIFTS OF 1-FLUORO-4-NITROBENZENE AND 1-FLUORO-2,4-DINITROBENZENE IN FLUOROSULPHURIC ACID SOLUTIONS

1-Fluoro-4-nitrobenzene Conc. of base 1.45 mole %			1-Fluoro-2,4-dinitrobenzene Conc. of base 1.32 mole %		
δ (p.p.m.) from ext. CF_3COOH	mole % H_2SO_4	$-H_\delta$	δ (p.p.m.) from ext. CF_3COOH	mole % H_2SO_4	$-H_o$†
-0.70	0.00	13.8	22.91	67.30	11.80
0.30	12.28	12.86	22.99	58.45	12.06
1.32	17.18	12.74	22.72	30.70	12.47
4.35	45.99	12.24	22.40	17.93	12.70
5.70	62.58	11.99		mole % SbF_5	
7.19	66.78	11.90			
9.32	80.26	11.66	21.42	0.00	13.80
11.08	86.76	11.54	20.91	0.25	14.77
13.76	92.74	11.37	18.61	0.58	15.11
14.28	96.65	11.20	15.31	1.02	15.30
			10.68	1.19	15.32
			5.59	2.74	15.47
			0.00	8.21	15.75
			-1.39	12.75	-

* H_o values are those of Barr[27] and this work.

† H values are those of Gillespie et al.[105] and this work.

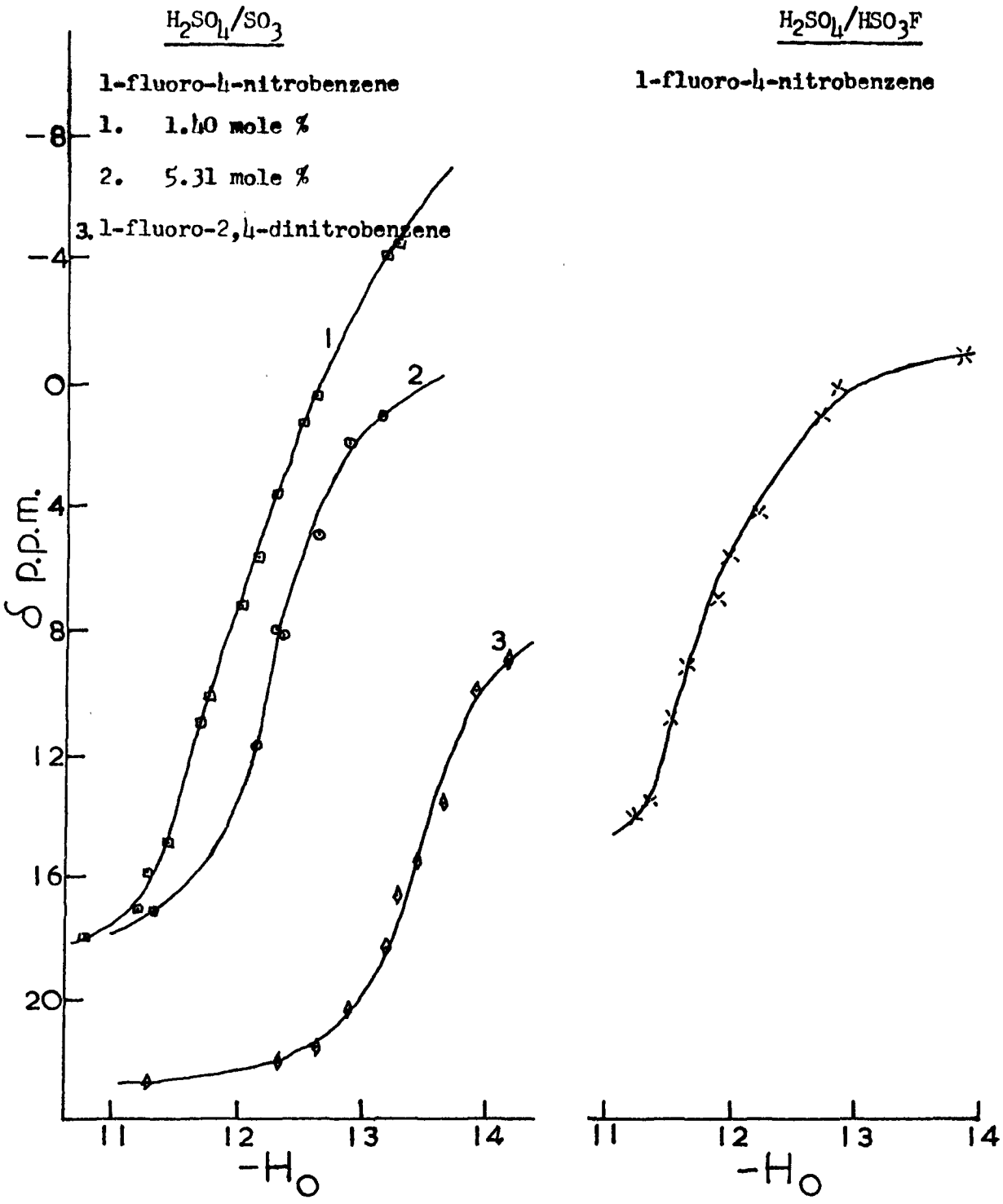


Fig. 44 SOLUTIONS OF FLUORONITROBENZENES IN H_2SO_4/SO_3 AND H_2SO_4/HSO_3F: F^{19} CHEMICAL SHIFTS AGAINST H_o.

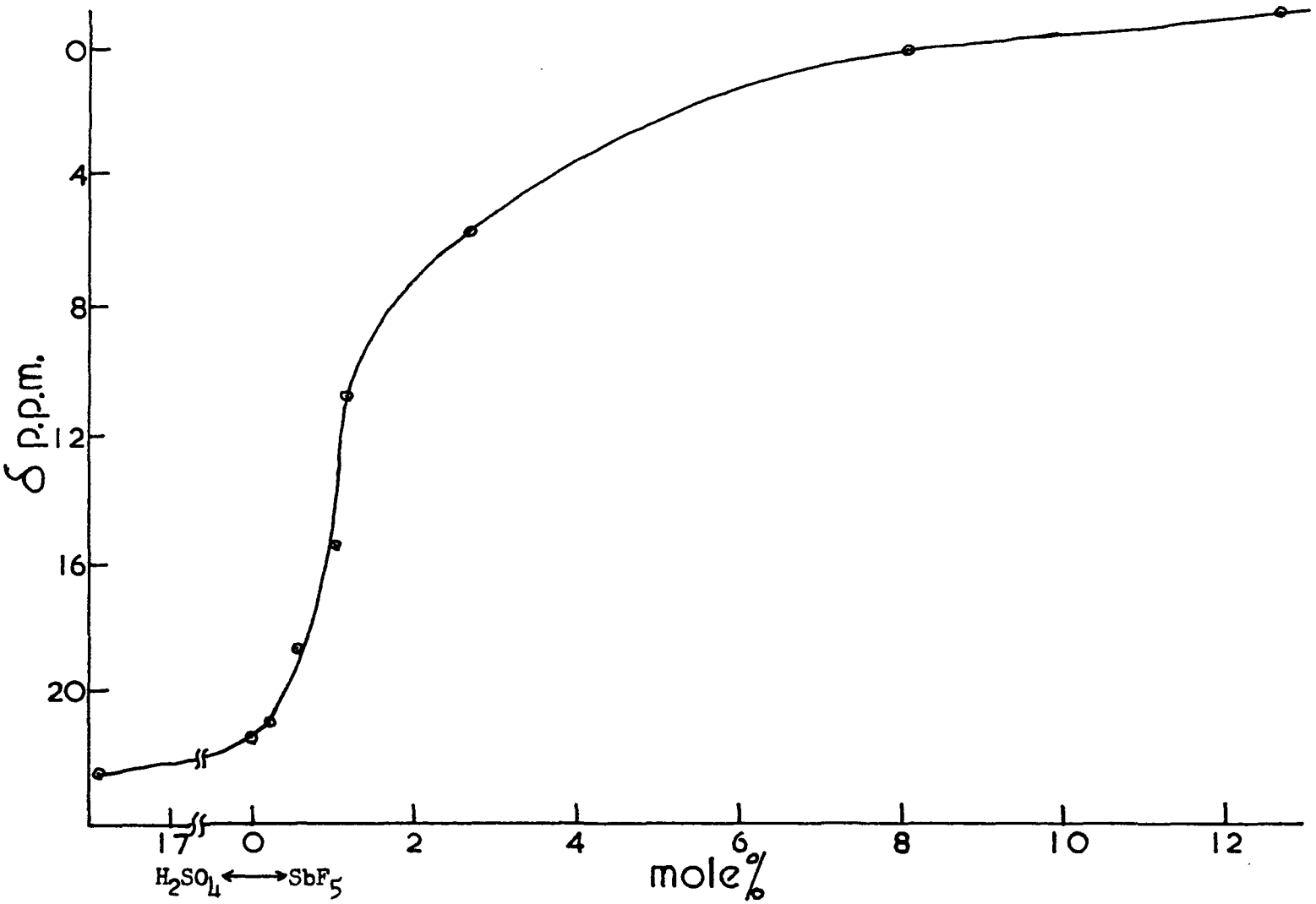


Fig. 45 SOLUTIONS OF 1-FLUORO-2,4-DINITROBENZENE IN HSO_3F/SbF_5: F^{19} CHEMICAL SHIFTS AGAINST MOLE % SbF_5.

(5) THE CORRELATION OF RATES OF PROTON EXCHANGE WITH H_0

The data given in Chapter V on the rates of proton exchange between the conjugate acids of acetophenones and the solvent suggested that there might be some correlation between these rates and the acidity of the solvent.

Acetone was chosen as the base for a more detailed investigation of this possible correlation because of its stability in flucrosulphuric acid and the fact that the rate of proton exchange can be measured over a wide range of SbF_5 concentrations in HSO_3F. The chemical shift data for a typical solution of acetone in HSO_3F containing SbF_5 has been given in Chapter V (Table XVI). Only two peaks are visible in the spectrum of the conjugate acid when exchange is very slow, one due to the CH_3 protons and the other to the proton captured by the carbonyl oxygen. Rates of proton exchange can be calculated for this system by the same method as used in Chapter V for acetophenones.

The rate of proton exchange has been calculated for solutions in HSO_3F containing fixed amounts of acetone, but varying concentrations of SbF_5 and also in solutions containing a fixed amount of SbF_5 but with different concentrations of acetone. Plots of log k against 1/T are shown in Figs. 46 and 47 and the results are summarised in Tables LII and LIII.

It is seen from Table LII that an increase in the concentration of acetone produces an increase in the rate of proton exchange. A plot of log k_o against mole % acetone gives a smooth curve (Fig. 47), the increase in rate being greatest when the acetone concentration approaches that of the SbF_5. Table LIII shows the variation of rate

with change in SbF_5 concentration (constant amount of acetone) and a plot of log k_o against mole % SbF_5 (Fig. 47) indicates that the rate varies almost linearly until the concentration of SbF_5 becomes less than the concentration of acetone when the rate increases enormously. This increase in rate can be accounted for as explained in the previous section by the titration of $H_2SO_3F^+$ by the acetone which reduces the acidity of the solution to that of 100% HSO_3F in which the rate of proton exchange between the conjugate acid of acetone and the solvent is much more rapid.

It appears that at a sufficiently low concentration of acetone the rate of exchange would become independent of the acetone concentration, and for solutions containing an excess of SbF_5 over acetone the rate is a linear function of H_o. If this behaviour is general for other bases, then if a sufficient number of overlapping plots of rate against H_o could be obtained a new method for determining H_o could be developed.

TABLE LII

RATE DATA FOR SOLUTIONS OF ACETONE IN FLUOROSULPHURIC ACID CONTAINING 6 MOLE % SbF_5.

Mole %		Act. Energy	log k_o	log k
Acetone	SbF_5	Kcal./mole		(0°)
2.95	6.29	11.26	10.19	1.18
3.05	6.29	12.15	10.65	0.93
4.91	6.15	12.70	12.03	1.86
5.96	6.08	12.81	13.44	3.19
6.30	6.06	10.25	12.06	3.86

TABLE LIII

RATE DATA FOR SOLUTIONS OF ACETONE (2.4 - 3.05 MOLE %) IN FLUOROSULPHURIC ACID CONTAINING VARYING AMOUNTS OF SbF_5.

Mole %		Act. Energy	log k_o	log k	$-H_o$
Acetone	SbF_5	Kcal./mole		(0°)	
2.64	7.37	12.12	10.49	0.76	15.72
2.82	8.34	12.44	10.74	0.79	15.77
3.04	6.29	12.15	10.65	0.93	15.66
2.95	6.29	11.26	10.19	1.18	15.65
2.95	5.55	11.96	10.95	1.38	15.63
2.44	4.52	13.05	11.84	1.40	15.57
2.73	3.73	13.13	12.10	1.59	15.53
2.92	2.83	9.95	13.76	5.80	15.48
2.79	1.94	exchange too rapid			15.43

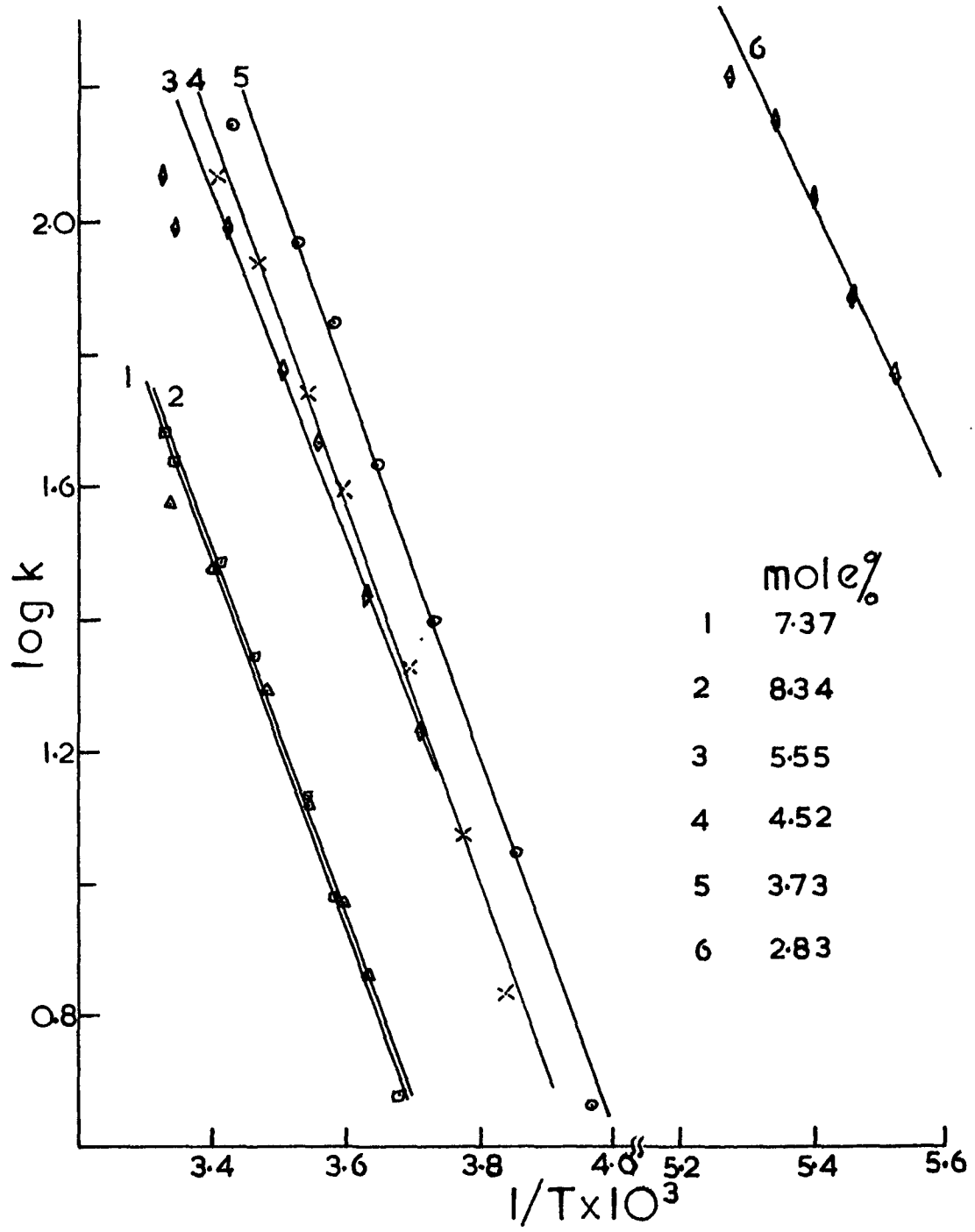


Fig. 46 SOLUTIONS OF ACETONE IN SbF_5/HSO_3F (VARYING SbF_5 CONC. 2.4-3.05 MOLE % ACETONE): LOG k AGAINST 1/T.

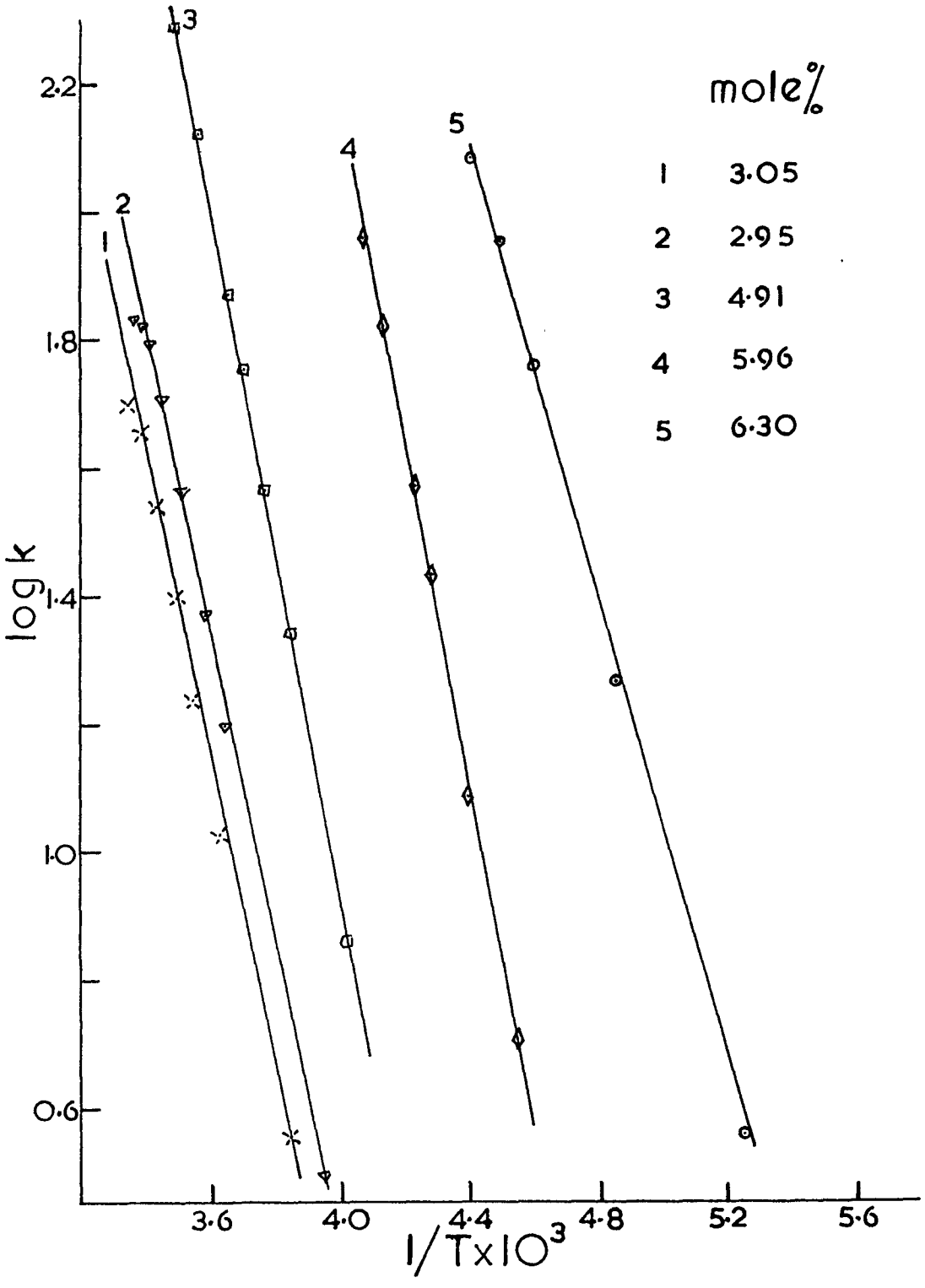


Fig. 47 SOLUTIONS OF ACETONE IN SbF_5/HSO_3F (VARYING ACETONE CONC. 6 MOLE % SbF_5): LOG k AGAINST 1/T.

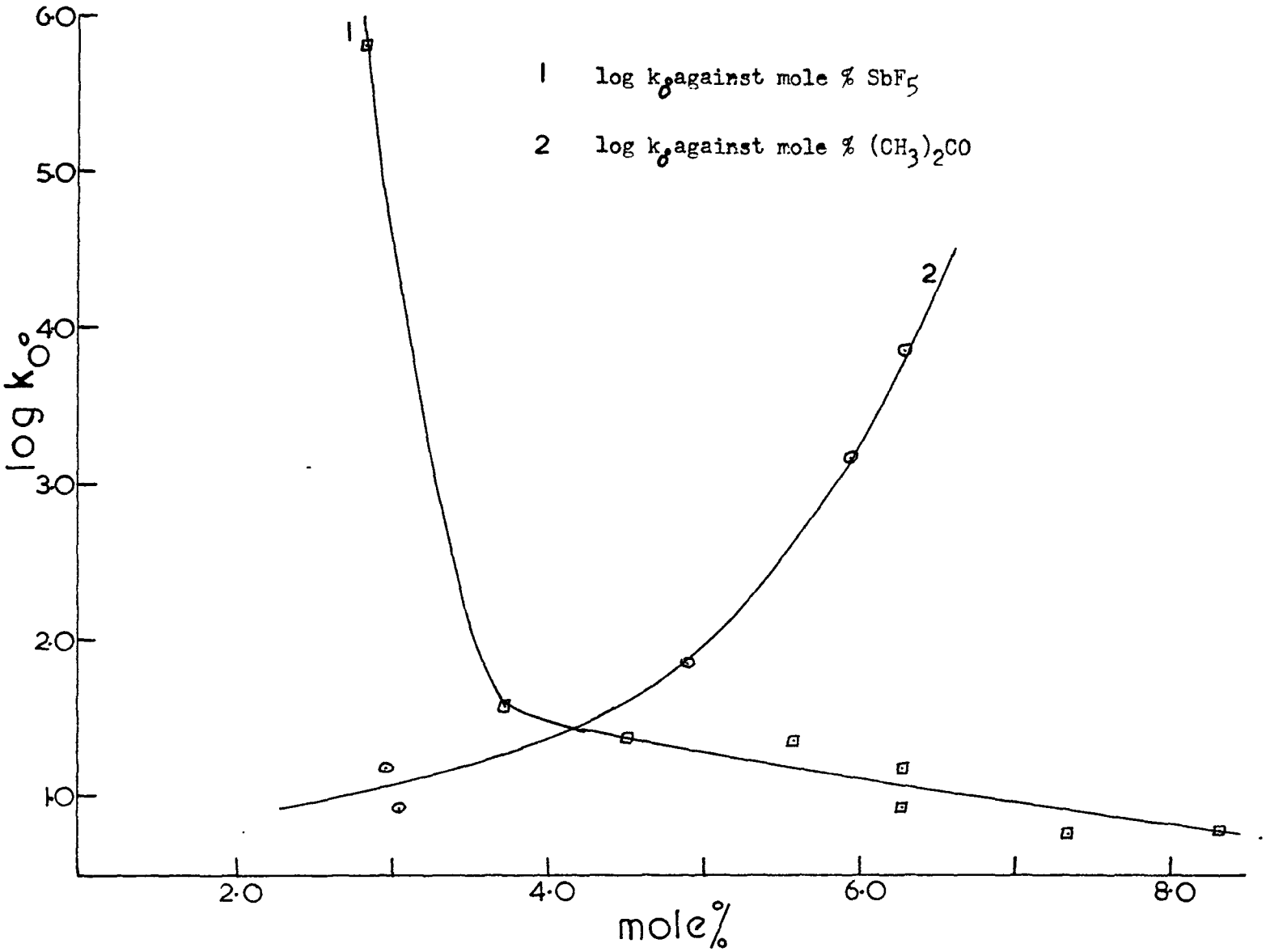


Fig. 48 SOLUTIONS OF ACETONE IN SbF_5/HSO_3F: LOG k_{0° AGAINST MOLE % ACETONE AND MOLE % SbF_5.

(6) DISCUSSION

All of the methods described suffer from the disadvantage that relatively large concentrations of base are required in contrast to the spectrophotometric method where the concentrations are of the order of 10^{-5} molar. The method due to Taft and Levins[30] is certainly the simplest since it only involves the measurement of chemical shifts and in addition the pK_{BH^+} is obtained directly. Measurement of the rates of proton exchange and their correlation with H_o is more complicated and suffers from the disadvantage that pK_{BH^+} is not obtained directly. However in the case of the bases N-methyl and N,N-dimethylanilines their concentration can be reduced to about 0.2 mole %, since one is observing an n.m.r. signal due to three, or six protons and not just one proton as in the case of acetone. In this case it might be possible to obtain a useful correlation of rate with H_o.

CHAPTER VIII

EFFECTS OF ELECTROLYTES ON THE CHEMICAL SHIFTS OF H_2SO_4 AND HSO_3F

(1) INTRODUCTION

The effect of electrolytes upon the proton resonance of hydrogen-bonded solutions has been the subject of many papers published in recent years. Shoolery and Alder[108] were the first to observe that the chemical shift produced by dissolving electrolyes in water varied with the electrolyte. They were able to separate the contributions of the cation and anion by assuming a value for the chemical shift of ClO_4^- of 0.085 p.p.m./mole. The shifts obtained were interpreted in terms of a low-field shift for the protons of water molecules of hydration, together with a shift to high field due to the breaking up of the hydrogen-bonded structure of the water by the ions. No correction for differences in the bulk diamagnetic susceptibilities of the solution and reference were made. A similar study by Hertz and Spalthoff[109] arrived at essentially the same conclusions, though there are some discrepancies between the two sets of results. Shcherbakov[39], who has reviewed the literature up to 1961, concludes that the results of Hertz and Spalthoff[109] are probably the more accurate since they do make susceptibility corrections. These workers, however, find that Na^+ gives the same molar shift as K^+ although Na^+ is generally recognised as being more solvated than K^+[110].

Axtmann[111] has recorded the chemical shifts for solutions of nitrates in water and obtained some correlation between the molar shift and pK_a for the reaction (9.1).

$$M(H_2O)_6^{x+} + H_2O \rightleftharpoons H_3O^+ + M(H_2O)_5(OH)^{+(x-1)} \qquad (9.1)$$

Fabricand and Goldberg[112] have studied the proton resonance shifts of alkali halide solutions and have correlated these shifts with ionic charge, ionic radii and electrolyte concentration. By assuming the value for the molar shift due to Cl^- to be zero, the molar shifts for the other ions were obtained. These authors[112] point out that there is a limitation upon the accuracy of their results as a consequence of the fact that the susceptibility corrections are of the same order, and often greater than the measured chemical shifts. Larger shifts to high field were found the greater the size of the cation.

Hindman[40] has also examined the effects of 1-1 electrolytes on the proton resonance of aqueous solutions and has calculated contributions due to the separate ions assuming the chemical shift due to the ammonium ion to be zero. Hindman[40] interprets his results in terms of bond-breaking, structural, polarisation, and non-electrostatic effects and calculates effective hydration numbers for the individual ions. As with the work of Fabricand and Goldberg[112], the corrections for bulk susceptibility are of the same order as the measured shifts. The agreement between the values obtained by these two groups[40,112] for the actual measured, uncorrected, molar chemical shifts for a particular salt is, in some cases, not particularly good.

Gillespie and White[36] have carried out a study of $MHSO_4$ salts in H_2SO_4 solutions and interpreted their results in terms of the

breaking-up of the hydrogen-bonded structure by the ions and solvation effects. For a particular nucleus the value at which the n.m.r. frequency actually occurs depends upon the chemical environment for that nucleus. A proton which is involved in a hydrogen bond is less shielded from the applied magnetic field than one which is not involved in a hydrogen bond with the result that the hydrogen-bonded proton gives a resonance at a lower applied field. Thus the breaking of a hydrogen bond results in an increase in the shielding of the proton and a shift of the n.m.r. signal to higher field. This phenomenon is used to interpret the changes in chemical shift which occur when electrolyes are dissolved in sulphuric and fluorosulphuric acids. Other workers have used the chemical shifts of other nuclei to investigate the effects of electrolytes upon the structure of the solvent: Carrington and Hines[113], and Connick and Poulson[114] studied F^{19} spectra, Jackson et al.[115] studied O^{17} spectra, and Gutowsky and McGarvey[116] studied Tl^{203} spectra.

(2) SOLUTIONS OF $MHSO_4$ IN H_2SO_4

The chemical shift produced when a metal hydrogen sulphate is dissolved in sulphuric acid is known to vary with the cation and its concentration[36]. The investigation begun by Gillespie and White[36] has been extended to include Li^+, Rb^+, Cs^+, Ag^+, $Et\ N^+$, $(C_6H_5)\ As^+$, $(C_6H_5)_2COH^+$, Ca^{++} and Ba^{++} and in addition some more results have been obtained for the electrolytes studied by these workers. In this previous work no correction was made for differences in the bulk diamagnetic susceptibilities of the solution and the external reference.

In the present work the solutions were referenced with respect to external 100% sulphuric acid and susceptibility corrections were made where possible. The results obtained are shown in Table LIV and Figs. 49-51. It can be seen (Table LIV) that although the susceptibility corrections are small they are not negligible, however they are much smaller than the corresponding corrections for aqueous solution[40,111].

The chemical shift (δ p.p.m.) when plotted against the proton fraction p (the proton fraction is that fraction of the total number of protons that is associated with a particular species) gives plots which are in general linear over a considerable concentration range. The slopes of the linear portions of the curves are given in Table LV. Deviations from linearity are sometimes observed at high concentrations, particularly for ions that are generally accepted as being highly solvated in solution; this phenomenon will be explained later. At very low concentrations a slight curvature is observed and the linear portion

does not pass through the origin. This can be explained by the fact that small amounts of $MHSO_4$ suppress the autoprotolysis of the sulphuric acid and thus remove $H_3SO_4^+$ from the solution. The sulphuric acidium ion, as a result of its positive charge, would be expected to reduce the shielding at the protons and so cause the proton resonance to shift to lower field. Therefore removal of $H_3SO_4^+$ has the effect of producing a shift to high field which counteracts the low field shift due to the addition of $MHSO_4$. The net effect is a smaller shift to low field than expected.

It has been concluded[36] that the effect of a cation on the proton resonance is largely a result of its structure-breaking effect on the solvent. Thus the greater the extent of solvation the greater will be the number of hydrogen bonds broken and the more the resonance will shift to higher fields. For the alkali metal cations except for Li^+ the order of the proton resonance shift to high field, compared to Cs^+, is in the order expected from their known solvation numbers in sulphuric acid[117]. The lithium ion gives a smaller shift to high than expected. It has been suggested by Gurney[118] that in aqueous solution cations smaller than potassium are net structure forming, while potassium and larger ions tend to be structure breaking. If this is so in sulphuric acid then the smaller shift to high field than expected for Li^+ is accounted for; the ordering producing a low field shift. The fact that Na^+ gives a shift consistent with its solvation number indicates that in sulphuric acid Na^+ is net structure breaking in contrast to its behaviour in aqueous solution. The deviation from linearity which occurs at $p = 0.08$ for Li^+ must arise from the fact

that at high concentrations there is competition for the limited number of solvent molecules and hence the average solvation number of a Li^+ ion decreases giving a corresponding shift to high field.

In the case of the alkaline earths the same effects are observed. The smaller the cation the greater the solvation, with the result that more structure breaking occurs and the resonance is shifted to higher field. It is found that the relative shift to higher field is in the order $Ca^{++} > Sr^{++} > Ba^{++}$. Deviations from a straight line are also noted in these cases presumably for the same reason as the Li^+ case. The increased shift to lower field of these ions over those of the alkali metals is to be expected in view of the large low field attributed to the HSO_4^- ion[36] since at a given concentration of cation there is twice the concentration of HSO_4^- for an alkaline earth hydrogen sulphate than for an alkali metal hydrogen sulphate. In addition it has been suggested that the dipositive ions will give rise to a larger polarisation effect which would shift the resonance to lower fields[36].

Other simple univalent hydrogen sulphates studied were NH_4^+, Ag^+, and Tl^+. The ammonium ion gives a shift to low field which is of the same order as that produced by K^+ in agreement with the degree of solvation of these ions[117]. The resonance of the protons of the ammonium ion are found to shift very slightly to low field as the concentration of the ion is increased[36]. It has been suggested that this is due to an increase in the strength of the hydrogen bonds between the ammonium ion and the solvent due to the increasing basicity of the solvent. However this increase in hydrogen-bond strength must be very small as the shift is only 0.033 p.p.m. for an increase in p

from 0.0091 to 0.1317. Both Ag^+ and Tl^+ give bigger low field shifts than expected from their cationic radii. This would seem to suggest that these ions are similar to Li^+ in that they are so solvated that they actually are structure forming thus producing a low field shift, which is not very likely for Tl^+ since it has been shown to be very little solvated in sulphuric acid [117], or that there is ion-pair formation which would withdraw electron density from the hydrogens and give a low field shift. Thallous salts are generally recognised as being associated in aqueous solution [110] and Gutowsky and McGarvey [116] have used the n.m.r. of Tl^{203} to study the nature of the ion pairs formed in solution. Silver ions may behave in the same way.

The ions $(CH_3)_2COH^+$, $(C_6H_5)_2COH^+$, $(C_2H_5)_4N^+$ and $(C_6H_5)_4As^+$ were studied in order to investigate the chemical shift produced by very large ions. The shift produced by these cations is greater than that produced by any of the alkali metals except Cs^+. However it has been shown (Chapter V) that the $=OH^+$ resonances of the conjugate acids of acetone and benzophenone occur at lower field than that due to the HSO_3F or H_2SO_4, and since these conjugate acids are exchanging rapidly with the solvent then part of the low field shift produced by dissolving these bases in H_2SO_4 is the result of exchange between $=OH^+$ and the acid. It is seen (Fig. 50) that at a given proton fraction the shift produced by the conjugate acid of acetone is greater than that produced by the conjugate acid of benzophenone: this is in agreement with the positions of the $=OH^+$ resonances of the two ions, $=OH^+$ for acetone being at lower field by $\sim$ 1.5 p.p.m. than that for

benzophenone. The tetraethylammonium and tetraphenylarsonium ions both give extremely large low field shifts. Since the larger ion, tetraphenylarsonium ion, gives a smaller low field shift than the smaller tetraethylammonium ion, it must be concluded that this ion is acting as a structure breaker thus causing a shift to high field compared to tetraethylammonium ion: presumably the arsonium ion does not fit too well into the structure of the solution. It should be pointed out that no susceptibility corrections have been applied in the case of the arsonium ion solutions but these are not expected to be very different to those applied to the other solutions and hence would not be large enough to affect the above explanation. One must then assume that the tetraethylammonium ion is neither net structure forming nor structure breaking and so does not affect the chemical shift due to the solvent protons: no appreciable shift is observed for the proton resonance of the ethyl groups of this ion with increase in concentration so that this assumption is perhaps not unreasonable. The whole of the shift to low field must then be attributed to the added hydrogen sulphate ion. If this is so then the chemical shift of the hydrogen sulphate ion can be calculated from (8.1).

$$\delta = \delta_{H_2SO_4} + p(\delta_{HSO_4^-} - \delta_{H_2SO_4}) \qquad (8.1)$$

Since all the chemical shifts are measured relative to 100% H_2SO_4 $\delta_{HSO_4^-}$ is found to be -10.54 p.p.m. This negative value is rather unexpected as one would expect the resonance due to HSO_4^- to be at higher field than H_2SO_4 since the single proton in hydrogen sulphate ion would be expected to have more electron density around it than

the protons in H_2SO_4. The large low field shift found must be the result of strong hydrogen-bond formation with the solvent.

If the value obtained by Gillespie and White[36] for $\delta_{H_2SO_4}$ from water is added to the above value for $\delta_{HSO_4^-}$ the chemical shift of the hydrogensulphate ion from water is found to be -16.44 p.p.m. By using this value and the value for $\delta_{H_3O.HSO_4}$ of -7.4 found by Gillespie and White[36] a value for $\delta_{H_3O^+}$ can be calculated using (8.2).

$$\delta_{H_3O.HSO_4} = \frac{\delta_{HSO_4^-}}{4} + \frac{3\,\delta_{H_3O^+}}{4} \qquad (8.2)$$

The value found is -4.39 p.p.m. from an external water reference, or +1.51 p.p.m. from external H_2SO_4. From an external T.M.S. reference the chemical shift would be -9.59 p.p.m. (δ_{H_2O} -5.2[1]) which is in quite good agreement with the value for $\delta_{H_3O^+}$ postulated in Chapter V (-10.5).

TABLE LIV

PROTON CHEMICAL SHIFTS FOR SOLUTIONS OF $MHSO_4$ IN H_2SO_4

Hydrogen sulphate	p	Bulk suscept. corrn.(p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	corrected $-\delta_{H_2SO_4}$
$LiHSO_4$	0.0159	0.006	0.074	0.068
	0.0348	0.012	0.189	0.177
	0.0434	0.015	0.197	0.182
	0.0629	0.022	0.300	0.278
	0.0664	0.024	0.321	0.297
	0.1006	0.036	0.438	0.402
	0.1254	0.045	0.507	0.462
	0.1532	0.057	0.573	0.516
$NaHSO_4$	0.0094	0.005	0.010	0.005
	0.0198	0.011	0.030*	0.019
	0.0407	0.023	0.145	0.122
	0.0645	0.037	0.230*	0.193
	0.0951	0.054	0.360*	0.306
	0.1125	0.065	0.440*	0.375
$KHSO_4$	0.0045	0.003	0.012	0.009
	0.0260	0.021	0.090*	0.069
	0.0278	0.023	0.137	0.114
	0.0536	0.044	0.268	0.224
	0.0598	0.049	0.270*	0.221

* Data of Gillespie and White[36]

TABLE LIV (Contd.)

Hydrogen sulphate	p	Bulk suscept. corrn. (p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	corrected $-\delta_{H_2SO_4}$
$KHSO_4$	0.0899	0.074	0.449	0.375
	0.0907	0.075	0.460*	0.385
	0.1405	0.117	0.720*	0.603
$RbHSO_4$	0.0091	0.009	0.021	0.012
	0.0129	0.017	0.058	0.041
	0.0261	0.036	0.119	0.083
	0.0610	0.087	0.338	0.251
	0.1168	0.165	0.703	0.538
$CsHSO_4$	0.0080	0.010	0.030	0.020
	0.0313	0.052	0.206	0.154
	0.0645	0.111	0.429	0.318
	0.1069	0.190	0.745	0.555
$AgHSO_4$	0.0047	0.002	0.041	0.039
	0.0131	0.023	0.093	0.070
	0.0166	0.032	0.103	0.071
	0.0172	0.033	0.109	0.076
	0.0190	0.038	0.125	0.087
	0.0208	0.042	0.182	0.140
	0.0229	0.047	0.159	0.112
	0.0290	0.062	0.214	0.152
	0.0314	0.069	0.224	0.155
	0.0522	0.118	0.351	0.233

[36]

* Data of Gillespie and White

TABLE LIV (Contd.)

Hydrogen sulphate	p	Bulk suscept. corrn.(p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	corrected $-\delta_{H_2SO_4}$
$TlHSO_4$	0.0083	0.011	0.09*	0.079
	0.0325	0.065	0.26*	0.195
	0.0444	0.090	0.39*	0.300
	0.0775	0.159	0.62*	0.461

Hydrogen sulphate	p	Bulk suscept. corrn.(p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	measured $\delta_{NH_4^+}$	corrected $-\delta_{H_2SO_4}$	corrected $\delta_{NH_4^+}$
NH_4HSO_4	0.0091	-0.002	0.025	4.845	0.027	4.843
	0.0209	0.005	0.07*	-	0.065	-
	0.0211	0.005	0.088	4.792	0.083	4.797
	0.0573	0.025	0.26*	4.82*	0.235	4.845
	0.0655	0.030	0.30*	4.81*	0.270	4.840
	0.0760	0.036	0.36*	4.80*	0.324	4.836
	0.1317	0.065	0.67*	4.72*	0.605	4.785
				$\delta_{C_2H_5}$		$\delta_{C_2H_5}$
$(C_2H_5)_4N\ HSO_4$	0.0065	-0.001	0.035	9.515	0.036	9.514
	0.0108	-0.002	0.078	9.532	0.080	9.530
	0.0172	-0.003	0.156	9.514	0.159	9.511
	0.0257	-0.004	0.258	9.522	0.262	9.518
	0.0293	-0.004	0.305	9.515	0.309	9.511

* Data of Gillespie and White

TABLE LIV (Contd.)

Hydrogen sulphate	p	Bulk suscept. corrn.(p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	$\delta_{C_6H_5}$	corrected $-\delta_{H_2SO_4}$	
$(C_6H_5)_4AsHSO_4$	0.0026	-	-0.008	3.090		
	0.0067	-	0.002	3.123		
	0.0083	-	0.010	3.152		
	0.0124	-	0.060	3.112		
	0.0224	-	0.122	3.147		
	0.0352	-	0.202	3.196		
				δ_{CH_3}		δ_{CH_3}
$(CH_3)_2COH.HSO_4$	0.0113	-0.010	0.042	7.733	0.053	7.722
	0.0169	-0.011	0.061	7.723	0.072	7.712
	0.0362	-0.019	0.171	7.785	0.190	7.766
	0.0547	-0.027	0.279	7.758	0.306	7.731
	0.1246	-0.055	0.676	7.774	0.731	7.719
				$\delta_{C_6H_5}$		$\delta_{C_6H_5}$
$(C_6H_5)_2COH.HSO_4$	0.0115	-0.013	0.010	-	0.023	-
	0.0219	-0.020	0.052	2.576	0.072	2.556
	0.0269	-0.023	0.064	2.571	0.087	2.548
	0.0587	-0.044	0.186	2.516	0.230	2.472
	0.0703	-0.052	0.252	2.464	0.304	2.412
	0.0711	-0.052	0.254	2.446	0.306	2.394
	0.1174	-0.083	0.447	2.333	0.530	2.250
	0.1434	-0.101	0.543	2.301	0.644	2.200

36

* Data of Gillespie and White

TABLE LIV (Contd.)

Hydrogen sulphate	p	Bulk suscept. corrn.(p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	corrected $-\delta_{H_2SO_4}$
$Ca(HSO_4)_2$	0.0066	-0.004	0.027	0.031
	0.0136	0.007	0.076	0.069
	0.0229	0.018	0.146	0.128
	0.0367	0.034	0.229	0.195
	0.0539	0.054	0.329	0.275
	0.0668	0.069	0.403	0.334
$Sr(HSO_4)_2$	0.0063	0.002	0.022	0.020
	0.0117	0.011	0.054	0.043
	0.0164	0.019	0.148	0.129
	0.0207	0.025	0.134	0.109
	0.0238	0.029	0.180	0.151
	0.0350	0.046	0.239	0.193
	0.0554	0.077	0.359	0.282
	0.0667	0.094	0.434	0.340
	0.0992	0.143	0.585	0.442
$Ba(HSO_4)_2$	0.0071	0.006	0.029	0.023
	0.0134	0.019	0.06*	0.041
	0.0238	0.036	0.152	0.116
	0.0296	0.046	0.191	0.145

36

* Data of Gillespie and White

TABLE LIV (Contd.)

Hydrogen sulphate	p	Bulk suscept. corrn. (p.p.m.)	Chemical shifts (p.p.m.) measured $-\delta_{H_2SO_4}$	corrected $-\delta_{H_2SO_4}$
$Ba(HSO_4)_2$	0.0298	0.046	0.191	0.145
	0.0323	0.051	0.204	0.153
	0.0386	0.061	0.25*	0.189
	0.0434	0.070	0.287	0.217
	0.0509	0.083	0.39*	0.307
	0.0521	0.085	0.316	0.231
	0.0714	0.119	0.413	0.294

* Data of Gillespie and White[36]

TABLE LV

RATIO OF δ/p FOR SOLUTIONS OF $MHSO_4$ IN H_2SO_4

$MHSO_4$	$\frac{-\delta_{H^1}}{p}$	Cationic radii
$LiHSO_4$	4.36	0.60
$NaHSO_4$	3.52	0.95
$KHSO_4$	4.34	1.33
$RbHSO_4$	4.64	1.48
$CsHSO_4$	5.36	1.69
NH_4HSO_4	4.46	1.48
$AgHSO_4$	5.25	1.26
$TlHSO_4$	6.12	1.49
$(C_2H_5)_4NHSO_4$	11.71	4.00
$Ca(HSO_4)_2$	5.17	0.99
$Sr(HSO_4)_2$	5.45	1.13
$Ba(HSO_4)_2$	5.72	1.35

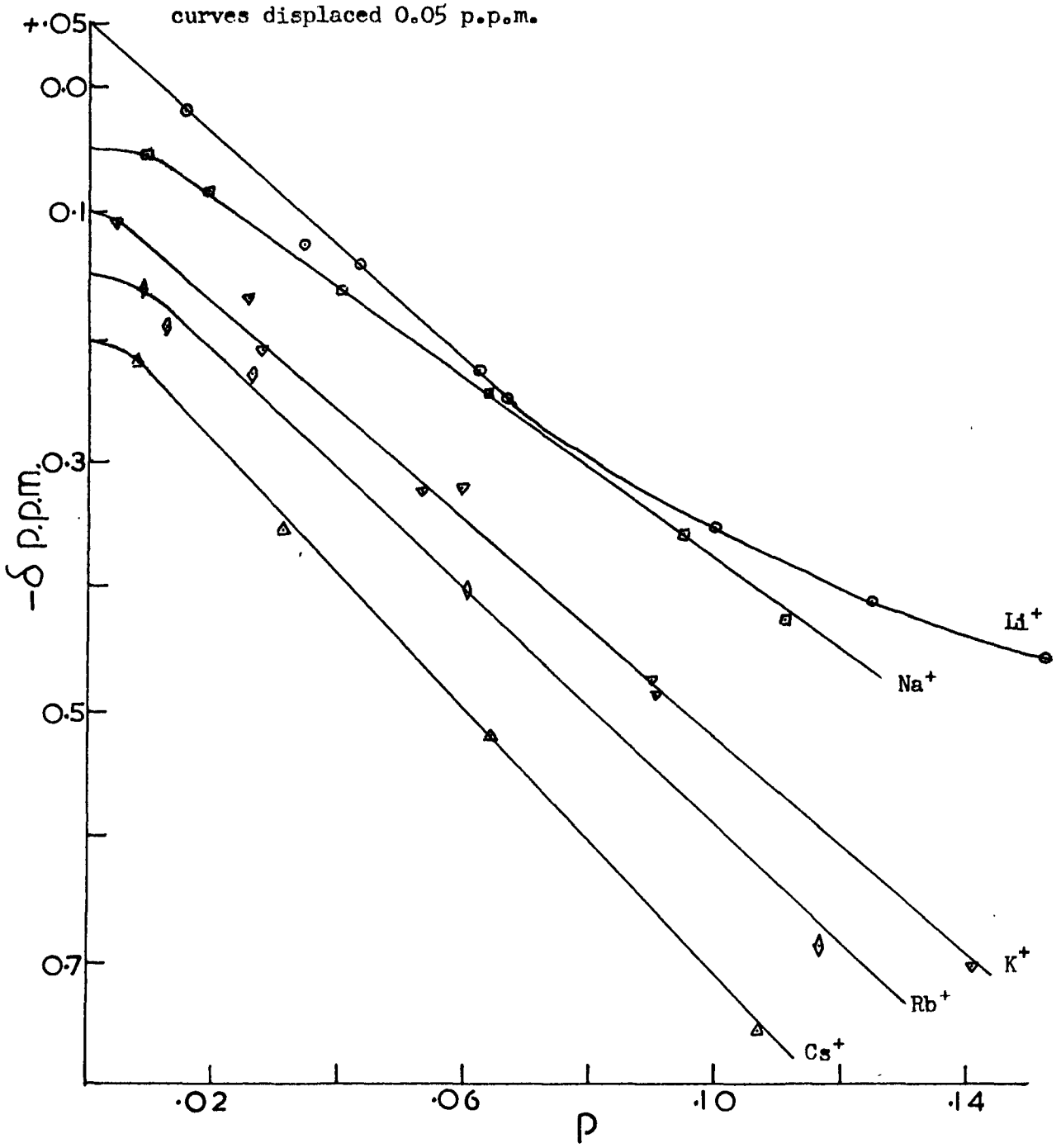


Fig. 49 SOLUTIONS OF $MHSO_4$ IN H_2SO_4: PROTON CHEMICAL SHIFTS.

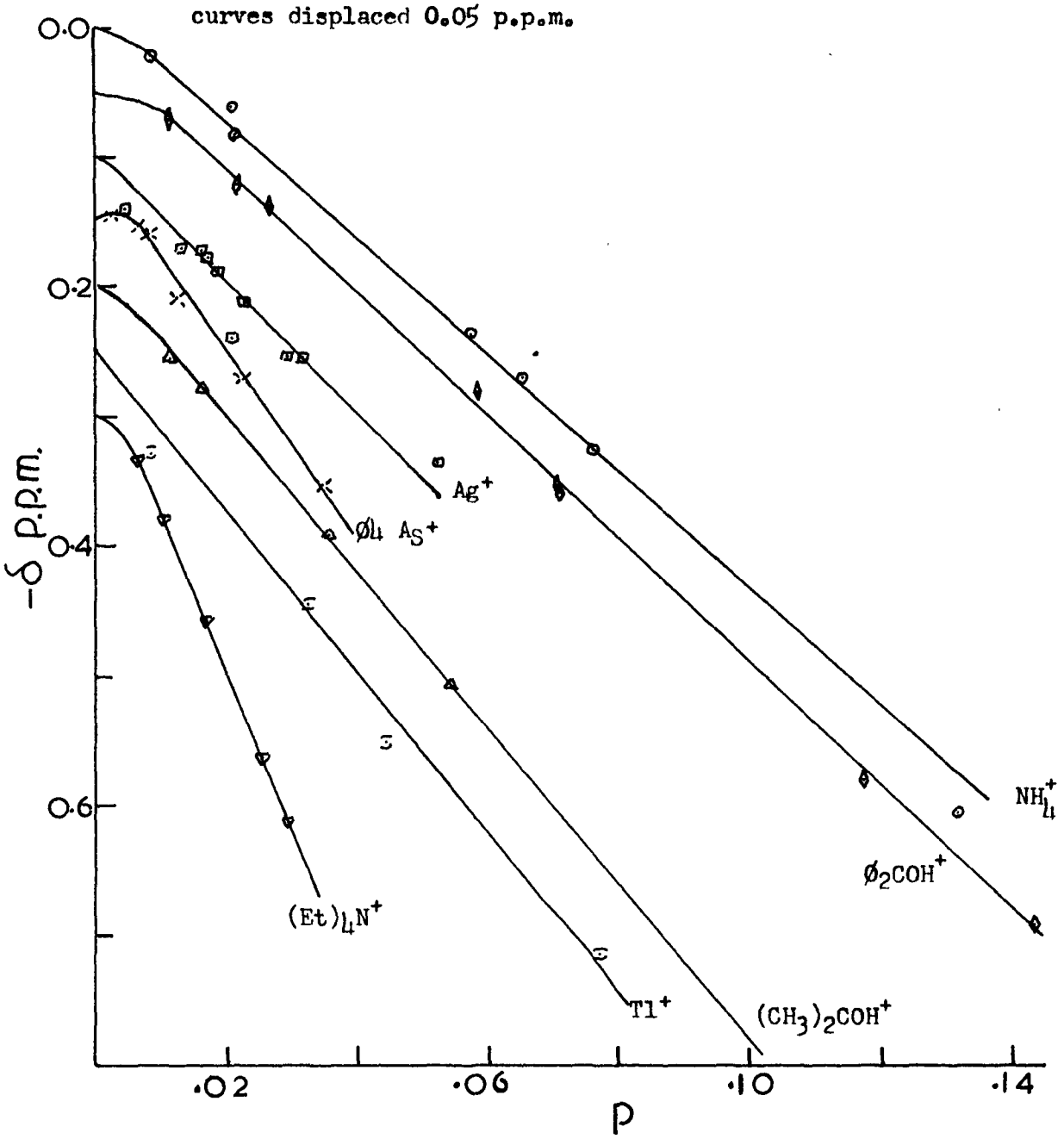


Fig. 50 SOLUTIONS OF $MHSO_4$ IN H_2SO_4: PROTON CHEMICAL SHIFTS.

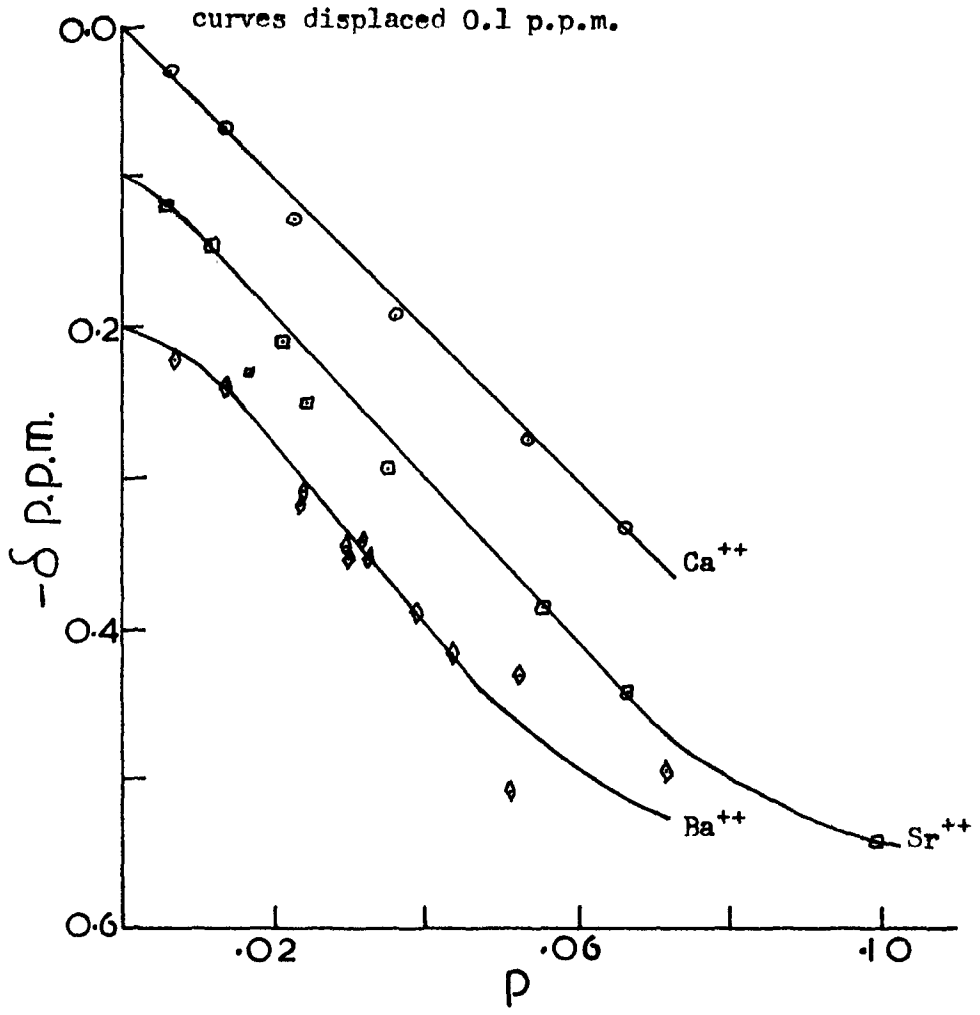


Fig. 51 SOLUTIONS OF $M(HSO_4)_2$ IN H_2SO_4: PROTON CHEMICAL SHIFTS.

(3) SOLUTIONS OF MSO_3F IN HSO_3F

Solutions of metal fluorosulphates in 100% fluorosulphuric acid produce large low field shifts in the proton resonance of the solvent as has been found for metal sulphates in sulphuric acid. This large low-field shift is presumably the result of a large low-field shift due to the SO_3F^- which increases the hydrogen bonding in the solution and so decreases the shielding of the protons. Each cation then produces its own effect which changes the shift produced by SO_3F^- to give the observed shift. The chemical shifts, measured from an external reference of 100% HSO_3F, are given in Table LVI and are plotted against mole fraction (x) in Figs 52 and 53. It can be seen that the shifts produced are much larger than those obtained in the sulphuric acid system. This has been explained[36] on the basis that the intrinsic shift of HSO_4^- must be to higher field than H_2SO_4 and this counteracts the shift to low field produced by interaction with the solvent; whereas the fluorosulphate ion has no proton shift and so the full effect of the increased hydrogen bonding due to the SO_3F^- ion is obtained.

As with the sulphates each cation produces its own effect on the proton resonance depending upon its solvating power. Thus it is found that, as before, ions which are the most solvated produce the largest shifts to high field and the order found is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ in agreement with the relative degrees of solvation found for these ions in fluorosulphuric acid[72]. The alkaline earth cations likewise produce shifts which are in the order expected for

their degree of solvation i.e. $Ca^{++} > Sr^{++} > Ba^{++}$ and as with the corresponding sulphates the alkaline earths produce greater chemical shifts. As all the data necessary for the calculation of the susceptibility corrections was not available the results plotted in Figs. 52 and 53 are uncorrected values. The slopes of these plots are given in Table LVII. However where these corrections have been calculated (Table LVI) they are found to be smaller than those for the corresponding sulphates and as the shifts are larger in the HSO_3F system the interpretation of the results would not be appreciably affected by the application of the correction. As in the sulphuric acid system Tl^+ gives a bigger shift to low field than expected for its size which can again be explained by postulating ion-pair formation.

It is found that the F^{19} chemical shift of HSO_3F is also affected by the addition of metal fluorosulphate and like the proton shift is dependent upon the cation. The F^{19} chemical shifts were measured with respect to external HSO_3F and are given in Table LVI and Figs. 54 and 55.

Since the F^{19} chemical shifts are generally an order of magnitude greater than the proton shifts, they are more sensitive to the solvation and hydrogen-bonding effects occurring in these solutions, and marked differences between the different cations are noted. All of the shifts can be accounted for by the explanations already given for the proton shifts. One would expect the fluorine nucleus to be more shielded in the SO_3F^- ion than in HSO_3F, but

hydrogen bonding will have the effect of moving it to lower field. However this does not completely overcome the intrinsic high field shift of the SO_3F^- ion as all the chemical shifts but one are to high field. It is still found that the most solvated ions produce the greatest shift to high field due to the breaking of hydrogen bonds, and the dipositive ions produce the largest shifts. Since no larger ions have been studied, it is not possible to know whether the F^{19} shift is due solely to the SO_3F^- ion in the case of $CsSO_3F$ solutions. Until some larger ions have been examined in HSO_3F no value can therefore be obtained for the chemical shift of SO_3F^-.

Thallous fluorosulphate is the only salt which gives a F^{19} shift to low field. This is explained if ion-pair formation occurs since this would produce a large low field shift which in this case must completely counteract the intrinsic high field shift of the fluorosulphate ion.

TABLE LVI

H^1 AND F^{19} CHEMICAL SHIFTS FOR SOLUTIONS OF MSO_3F IN HSO_3F

MSO_3F	x	Chemical shifts (p.p.m.) $-\sigma_{H^1}$	$\sigma_{F^{19}}$	Suscept. corn. (p.p.m.)
$LiSO_3F$	0.0188	0.225	0.099	-
	0.0357	0.410	0.227	-
	0.0789	0.830	0.528	-
	0.1428	1.583	1.067	-
$NaSO_3F$	0.0286	0.320	0.172	-
	0.0586	0.670	0.395	-
	0.0987	1.143	0.671	-
KSO_3F	0.0126	0.155	0.066	-0.001
	0.0445	0.515	0.227	-0.005
	0.0674	0.787	0.385	-0.007
	0.0794	0.913	0.431	-0.008
	0.0955	1.099	0.515	-0.010
$RbSO_3F$	0.0089	0.123	-	-0.003
	0.0160	0.208	0.126	-0.005
	0.0283	0.332	0.124	-0.009
	0.0320	0.355	0.146	-0.011
	0.0449	0.518	0.176	-0.015
	0.0803	0.925	0.335	-0.027
$CsSO_3F$	0.0115	0.135	-	-
	0.0157	0.198	-	-
	0.0268	0.327	0.057	-
	0.0428	0.515	0.092	-
	0.0697	0.822	0.155	-

TABLE LVI (Contd.)

MSO_3F	x	Chemical shift (p.p.m.)			Suscept. corn.
		$-\delta_{H^1}$	$\delta_{NH_4^+}$	$\delta_{F^{19}}$	(p.p.m.)
NH_4SO_3F	0.0205	0.220	4.624	-	0.002
	0.0772	0.845	4.605	0.318	0.008
	0.0912	0.997	-	0.369	0.010
	0.1364	1.487	-	0.537	0.014
$TlSO_3F$	0.0209	0.250		-0.057	
	0.0266	0.322		-0.069	
	0.0354	0.425		-0.106	
	0.0509	0.613		-0.163	
$Ca(SO_3F)_2$	0.0125	0.262		0.110	
	0.0173	0.383		0.177	
	0.0236	0.501		0.249	
	0.0337	0.685		0.367	
	0.0377	0.689		0.367	
$Sr(SO_3F)_2$	0.0060	0.148		0.062	
	0.0198	0.468		0.208	
	0.0348	0.768		0.360	
	0.0645	1.345		0.665	
$Ba(SO_3F)_2$	0.00[illegible]	0.232		-	
	0.0161	0.394		0.082	
	0.0263	0.625		0.207	
	0.0268	0.639		0.202	
	0.0414	0.957		0.349	

TABLE LVII

RATIO OF δ/x FOR SOLUTIONS OF MSO_3F IN HSO_3F

MSO_3F	$\frac{-\delta_{H^1}}{x}$	$\frac{\delta_{F^{19}}}{x}$	Cationic radii A°
$LiSO_3F$	10.43	6.7	0.60
$NaSO_3F$	11.4	6.8	0.95
KSO_3F	11.5	5.4	1.33
$RbSO_3F$	11.5	4.17	1.48
$CsSO_3F$	11.8	2.23	1.69
NH_4SO_3F	10.9	3.93	1.48
$TlSO_3F$	12.02	-2.99	1.49
$Ca(SO_3F)_2$	21.2	10.12	0.99
$Sr(SO_3F)_2$	21.7	10.3	1.13
$Ba(SO_3F)_2$	24.0	10.35	1.35

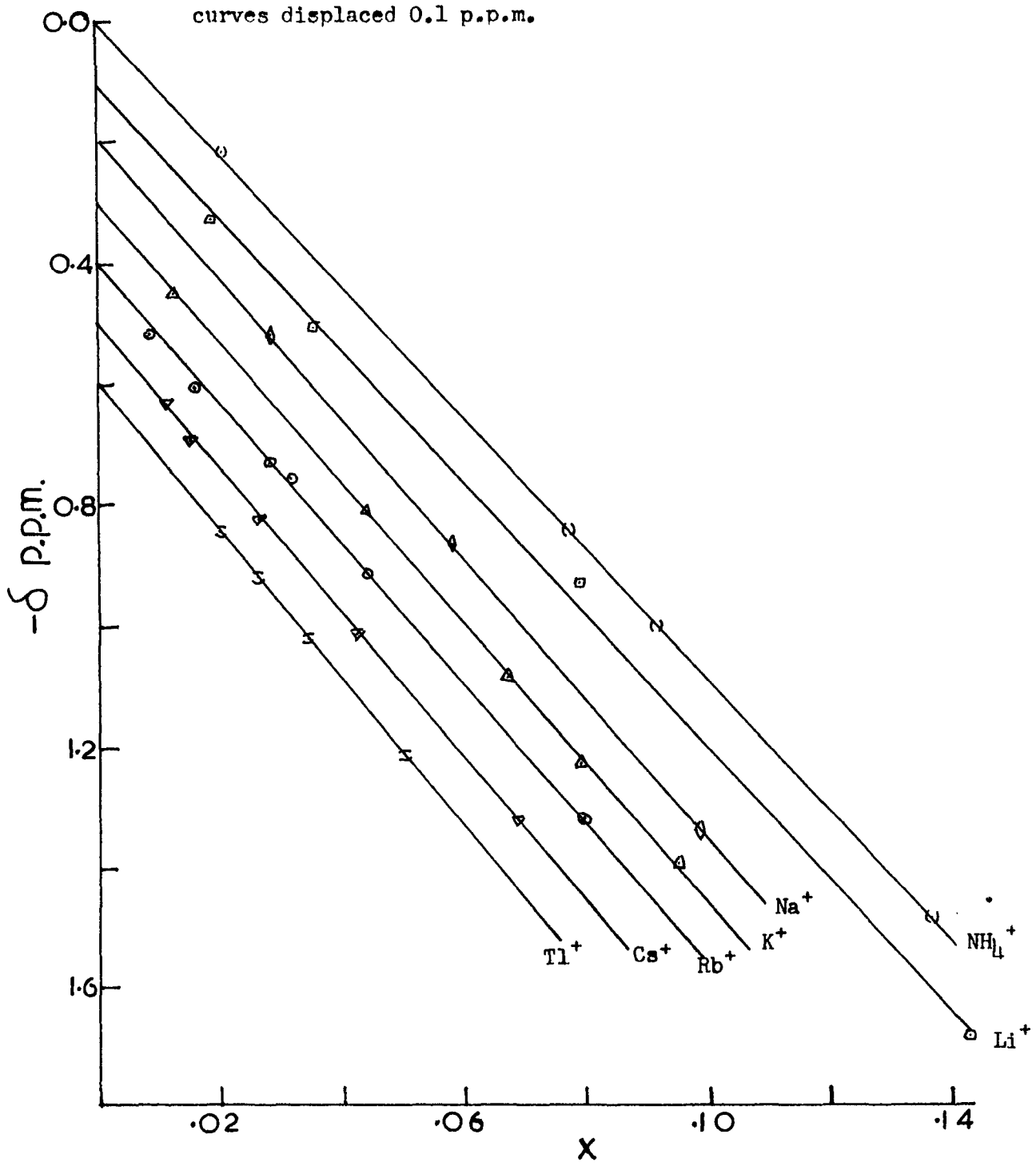


Fig. 52 SOLUTIONS OF MSO_3F IN HSO_3F: PROTON CHEMICAL SHIFTS.

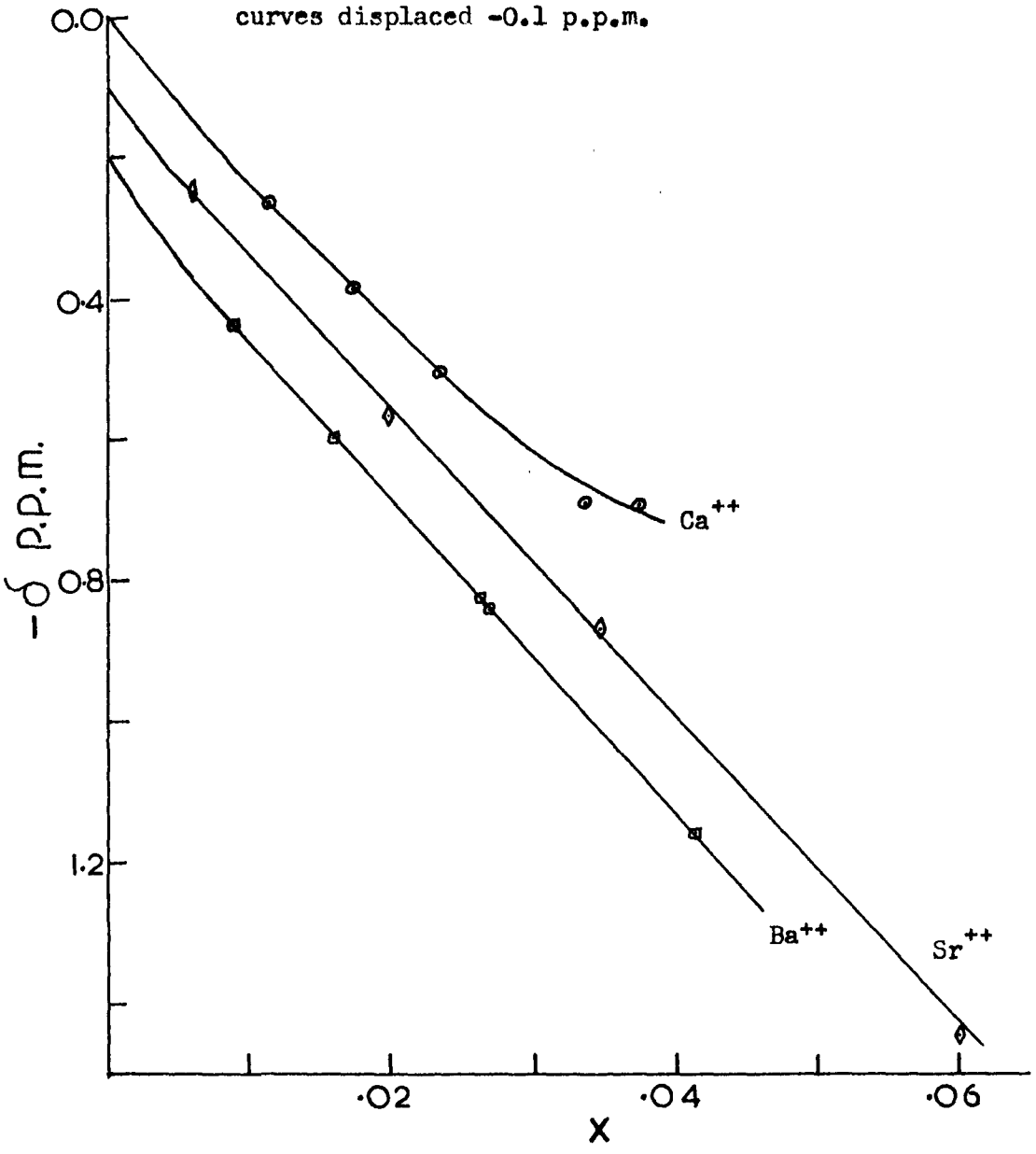


Fig. 53 SOLUTIONS OF $M(SO_3F)_2$ IN HSO_3F: PROTON CHEMICAL SHIFTS.

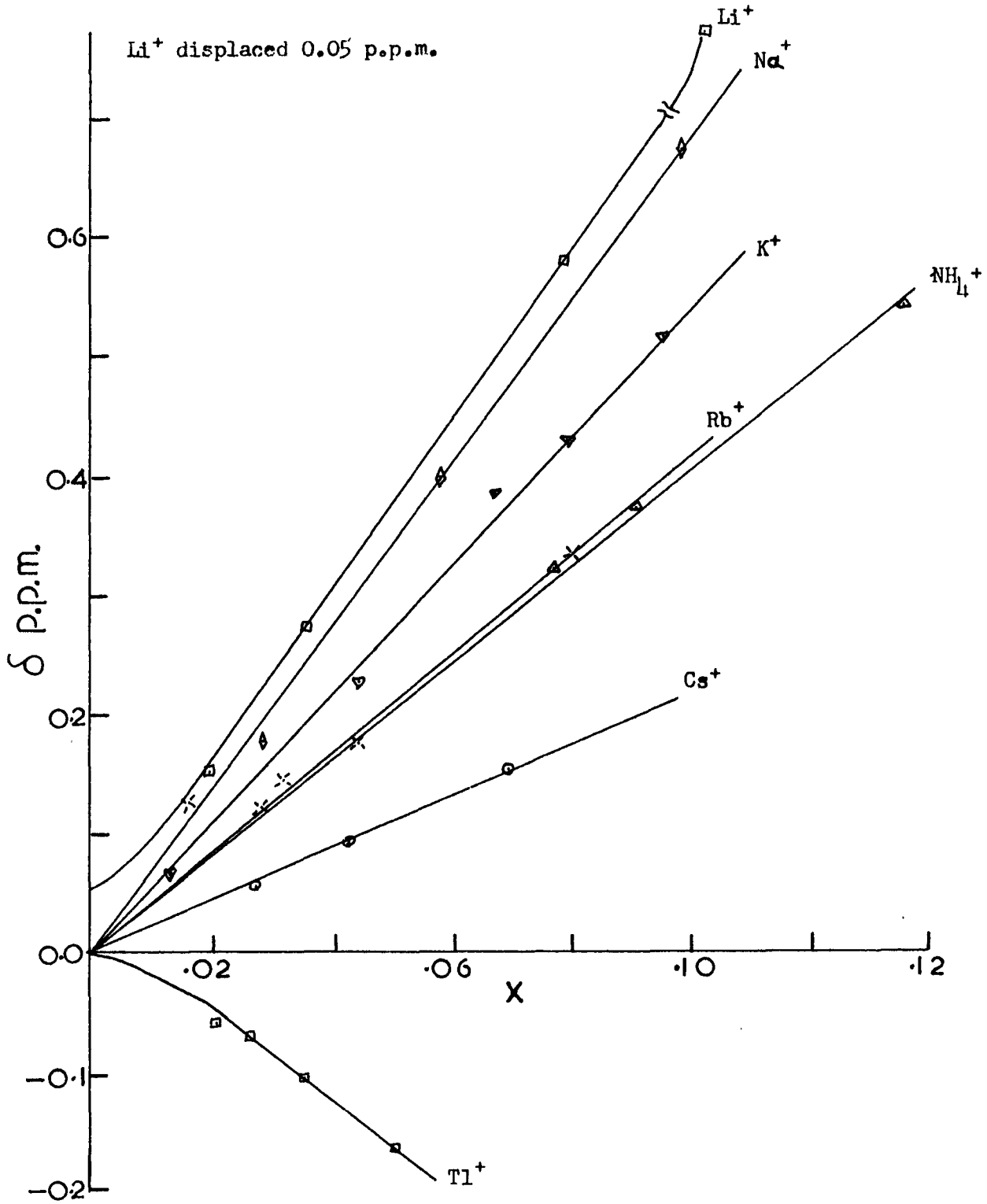


Fig. 54 SOLUTIONS OF MSO_3F IN HSO_3F: F^{19} CHEMICAL SHIFTS.

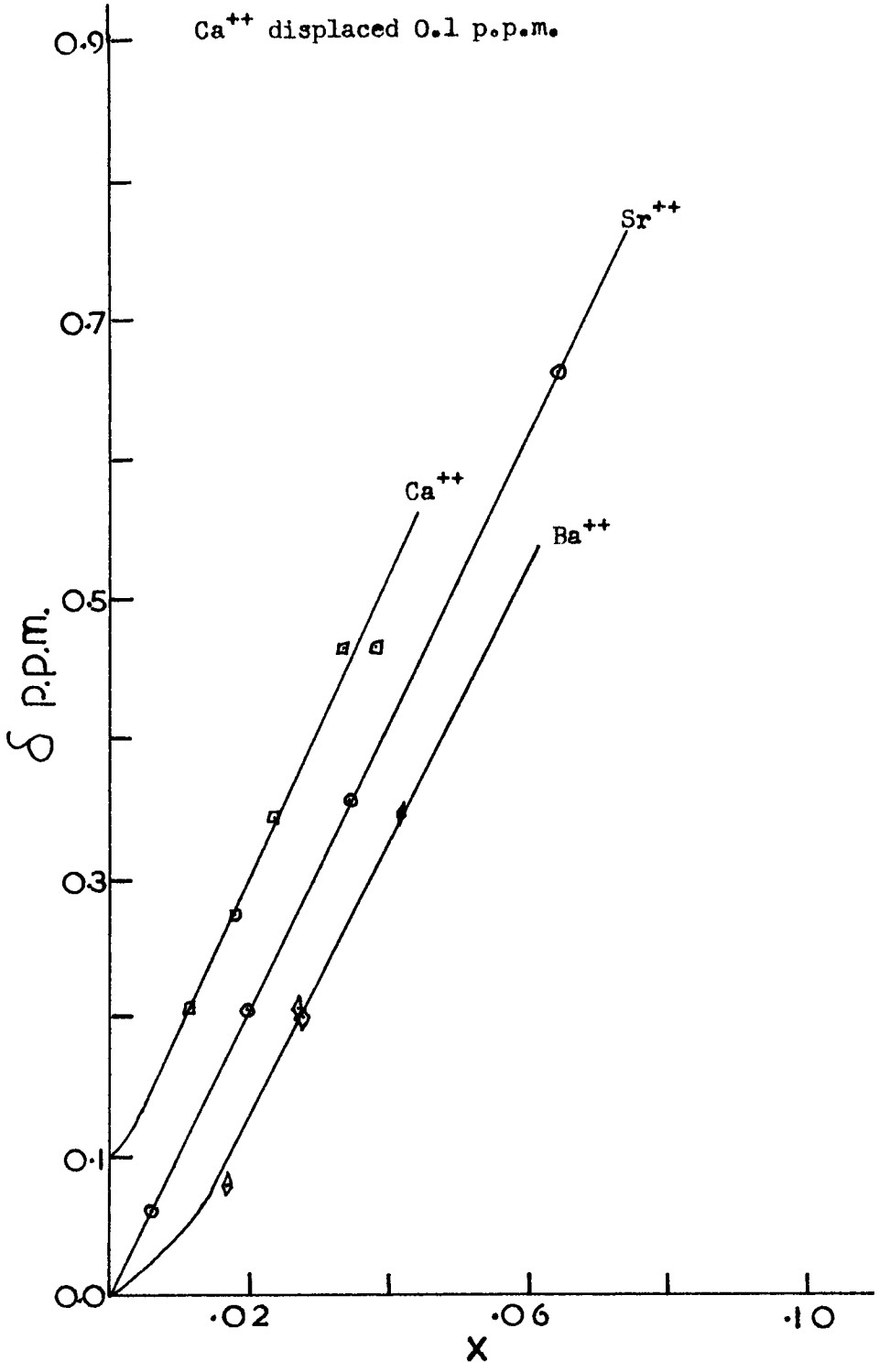


Fig. 55 SOLUTIONS OF $M(SO_3F)_2$ IN HSO_3F: F^{19} CHEMICAL SHIFTS.

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