# 503. *Cryoscopic Measurements in Sulphuric Acid. Part VII. The Basicity of Nitro-compounds, Sulphonyl Compounds, and Sulphuryl Compounds in Sulphuric Acid.*

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It is shown, by measurement of the freezing points of solutions in sulphuric acid, that nitro-compounds ionise as bases in that solvent. The basicity constants are determined for nitromethane, nitrobenzene, the *p*-methyl and *m*-ammonium substitution products of nitrobenzene, and for 2 : 4 : 6-trinitrotoluene. The proportions in which these compounds are ionised in 0·1 molal solution in anhydrous sulphuric acid at its freezing point range from about 20% (*e.g.*, trinitrotoluene) to about 70% (*p*-nitrotoluene).

By the same method, it is shown that benzenesulphonic acid and *p*-toluenesulphonic acid, as well as diphenyl sulphone, are likewise considerably ionised as bases in sulphuric acid. The basicity constants of these solutes are determined. A similar study of the solute ethyl alcohol indicates that it is converted substantially quantitatively into ethylsulphuric acid (ethyl hydrogen sulphate), which is also appreciably ionised.

Constitutional effects on basicity are considered. Reference is made to the bearing of this form of ionisation on the kinetics of aromatic nitration in sulphuric acid, *e.g.*, of nitro-compounds.

## (1) *Basicity and Nitration Rate in Sulphuric Acid.*

IT was recently pointed out (Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277) that rates of nitration in a strongly acidic medium such as sulphuric acid cannot but be dependent on the condition of the aromatic compound in such solutions. The great majority of those organic compounds that are soluble in sulphuric acid behave as bases in that solvent, taking up a proton with conversion into a cation. In this ionisation, an intermediate hydrogen-bond complex is often produced in considerable proportion—just as when ammonia functions as a base in water (Moore and Winmill) :

$$B + H_2SO_4 \rightleftharpoons BHSO_4H \rightleftharpoons BH^+ + SO_4H^-$$

Having summarised the evidence, largely based on cryoscopic and solubility data, in favour of this picture of sulphuric acid solutions, Gillespie and Millen noted that, since the complex $BHSO_4H$, and still more, the cation $BH^+$, will certainly have a depressed nuclear reactivity towards electrophilic reagents, nitration rate would be expected often to depend on the surviving proportion of free base B, and on the degree of incompleteness of conversion into the cation $BH^+$. They pointed out, further, that this effect could constitute one contributory cause of the well-established result that rates of nitration in sulphuric acid are first increased, and then decreased, by the progressive addition of water. Although water is a moderately strong base in sulphuric acid, it is known that the first 30 mols. per cent. of water do not destroy much nitronium ion; and hence one of their main kinetic effects on a nitration might be to cause the replacement of a less reactive by a more reactive form of the aromatic compound. Illustrations will be given later which show that very small proportions of water can cause substantial replacements of this type. Larger amounts of water will have a solvent effect (Gillespie, Hughes, Ingold, Millen, and Reed, *Nature*, 1949, **163**, 599; Hughes, Ingold, and Reed, *J.*, 1950, 2400). Large proportions of water will destroy the nitronium ion.

A quantitative interpretation of the recorded results on the kinetics of nitration in sulphuric acid (Martinsen, *Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605; Klemenc and Schöller, *Z. anorg. Chem.*, 1924, **141**, 231; Lauer and Oda, *J. pr. Chem.*, 1936, **144**, 176; Oda and Ueda, *Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 335; Lantz, *Bull. Soc. chim.*, 1939, **6**, 280 *et seq.*; Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871; Bennett, Brand, James, Saunders, and Williams, *J.*, 1947, 474) would require more knowledge than we yet possess concerning the proportions in which undissociated salts and cations are formed from aromatic compounds. The acceleration of nitration by limited additions of water to the solvent sulphuric acid have been reported for nitro-compounds, sulphonic acids, anthraquinones, and benzoic acids. It is already established that ketones, including anthraquinone, and carboxylic acids, including benzoic acid, function as strong bases in sulphuric acid, undergoing practically complete conversion into cationic forms in the anhydrous acid. For one ketone, acetone, and one carboxylic acid, acetic acid, the substantial completeness of the ionisation was illustrated in Part I (*J.*, 1950, 2473). The experiments on anthraquinone and benzoic acid will be published later. It will be shown in this paper that nitro-compounds and sulphonic acids also behave as bases in sulphuric acid, but weaker ones, undergoing considerable, though only partial, conversion into cationic forms.

### (2) *Basicity of Nitro-compounds in Sulphuric Acid.*

(2.1) *Previous Investigations.*—Hantzsch was the first to show, by cryoscopic and conductometric methods, that many organic substances behave as bases when dissolved in sulphuric acid (*Z. physikal. Chem.*, 1907, **61**, 257; **62**, 626; 1908, **65**, 41. Cf. Oddo and Scandola, *Gazzetta*, 1908, **38**, 603; 1909, **39**, I, 569; 1909, **39**, II, 1; 1910, **40**, II, 163; Oddo and Casalino, *ibid.*, 1917, **47**, II, 200, 2321. Cf. also Hantzsch, *Ber.*, 1925, **58**, 941). He concluded, albeit on the basis of a somewhat qualitative investigation, that certain of the solutes he examined, *e.g.*, ethyl ether, acetophenone, benzoic acid, *p*-nitroaniline, and 2 : 4-dinitroaniline, underwent complete ionisation in the solvent:

$$B + H_2SO_4 = BH^+ + HSO_4^-$$

Other solutes, such as dichloroacetic acid and *p*-nitrotoluene, appeared to be partly ionised. Yet others, notably trichloroacetic acid, nitromethane, *m*-dinitrobenzene, 2 : 4-dinitromesitylene, 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene, and picric acid, were concluded to dissolve without any form of change. The last four of these compounds were employed by Hantzsch for his determination of the cryoscopic constant of sulphuric acid.

The conclusion that aromatic polynitro-compounds (except nitroanilines) dissolve as non-electrolytes in sulphuric acid has been accepted by all who have since studied the properties of that solvent: Oddo and Scandola (*Gazzetta*, 1918, **48**, II, 17), Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900), and Robles and Moles (*Anal. Fis. Quim.*, 1934, **32**, 474) all employed 1 : 3 : 5-trinitrobenzene and picric acid in their experimental determinations of the cryoscopic constant of sulphuric acid.

Hantzsch's conclusion that *p*-nitrotoluene is partly ionised in sulphuric acid was indirectly confirmed by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1708), who, in a more accurate study of the cryoscopic behaviour of nitrobenzene in sulphuric acid, found that nitrobenzene was partly ionised, having a $\nu$-factor of about 1·2.

In the course of their search for compounds which behave as simple bases in sulphuric acid, Hammett and Deyrup (*loc. cit.*) investigated the depressions of freezing point given by a number of nitroanilines. *o*-Nitroaniline, *p*-chloro-*o*-nitroaniline, 2 : 4-dichloro-6-nitroaniline, 2 : 4-dinitroaniline, 2 : 6-dinitro-4-methylaniline, 6-bromo-2 : 4-dinitroaniline, 2 : 4 : 6-trinitroaniline, and 2 : 4 : 6-trinitro-*NN*-dimethylaniline, all gave $\nu$-values of approximately 2·0. It was concluded that they all behaved as simple bases, ionising completely according to the general equation given above.

(2.2) *The Solute* 2 : 4 : 6-*Trinitrotoluene.*—For the present work, this substance was chosen as the representative polynitro-compound. The observed freezing points of its solutions in sulphuric acid, containing a small amount of added water, are recorded in Table I. For the calculation of $\nu$-factors it is a sufficient approximation to employ equation (5) of Part I (*J.*, 1950, 2473) with the substitution $s_2 = 1$ and $\nu_2 = 1$ in the nearly-unit correction factor. A value of unity is taken for $s_2$, because it is very likely that the non-ionised form of this and other nitro-compounds in sulphuric acid is not the free molecule but is a definite hydrogen-bonded compound with a molecule of sulphuric acid (cf. p. 2542, and Gillespie and Millen, *loc. cit.*). The values of the $\nu$-factor thus derived are given in Table I. They indicate approximately 9% of ionic dissociation in the range of concentration studied. From the figures one may compute the equilibrium constant

$$K_b(C_6H_2Me(NO_2)_3) = [C_6H_2Me(NO_2)_3H^+][HSO_4^-]/[C_6H_2Me(NO_2)_3]$$

representing the basic strength of 2 : 4 : 6-trinitrotoluene in sulphuric acid. The concentrations being expressed in molalities, this constant may be computed by means of the formula

$$K_b = \{(\nu - 1)^2 \Delta m_2 + (\nu - 1)m_4\}/(2 - \nu)$$

where $\Delta m_2$ is the molality of the nitro-compounds and $m_4$ that of the hydrogen sulphate ion formed from the water present. This latter quantity is easily calculated, as has already been outlined in Part I, from the concentration of water $m_3$ and its known ν-factor. The values of $K_b$ are shown in Table I.

TABLE I.

*Freezing points of solutions of* 2 : 4 : 6-*trinitrotoluene in sulphuric acid* (Expt. 39).

| Molality of | | | | |
|---|---|---|---|---|
| water ($m_3$). | $C_6H_2Me(NO_2)_3$ ($\Delta m_2$). | F. p. (° c.). | ν-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·074 | — | 9·691 | — | — |
| ,, | 0·0222 | 9·544 | 1·09 | 0·0068 |
| ,, | 0·0385 | 9·437 | 1·09 | 0·0069 |
| ,, | 0·0537 | 9·337 | 1·09 | 0·0071 |
| ,, | 0·0721 | 9·215 | 1·09 | 0·0072 |
| ,, | 0·0963 | 9·064 | 1·07 | 0·0057 |
| | | | Mean | 0·0067 |

2 : 4 : 6-Trinitrotoluene is thus a somewhat weak base with $K_b$ = 0·0067 g.-mol. kg.$^{-1}$ in sulphuric acid. Although the other polynitro-compounds, which have formerly been claimed to dissolve in sulphuric acid without ionisation, have not been re-examined, it cannot be doubted that they are all bases of appreciable strength. On theoretical grounds one might expect the least basic of them to be 1 : 3 : 5-trinitrobenzene and picric acid; and it happens that these compounds were studied by Hammett and Deyrup (*loc. cit.*). Their freezing-point depressions, together with our value of the cryoscopic constant of sulphuric acid, indicate several units per cent. of ionisation in the solutions investigated. The data of Hammett and Deyrup are not accurate enough to permit the calculation of basicity constants, but such constants could be determined by the cryoscopic method. Clearly, polynitro-compounds should not be used to determine the cryoscopic constant of sulphuric acid.

(2.3) *The Solute* m-*Nitroaniline.*—Since two nitro-groups, both *m*-situated with respect to a given nitro-group, do not attract electrons from the latter sufficiently strongly to suppress completely its measurably basic behaviour in sulphuric acid, it was to be expected that a single *m*-situated ammonium pole would also be unable fully to suppress similarly manifested basic character in the nitro-group. The point has been tested by means of the cryoscopic study, recorded in Table II, of *m*-nitroaniline in solvent sulphuric acid. The observed freezing-point depressions are given under the heading ($\Delta\theta_1$). They have to be corrected, in the manner outlined in Part I, for the repression of the ionisation of the water present, and for repression of the autoprotolysis of the solvent, by the hydrogen sulphate ion which is formed in the first ionisation of the *m*-nitroaniline. The corrected freezing-point depressions are given in the table under the heading ($\Delta\theta_2$). From these corrected depressions ν-factors have been calculated by means of the usual equation (Part I) after substitution of $s_2 = 2$ and $\nu_2 = 2$. This substitution assumes that the *m*-nitroanilinium ion, like other nitro-compounds, forms a hydrogen-bonded compound with one molecule of sulphuric acid. The resulting ν-factors show that *m*-nitroaniline is acting to an appreciable extent as a di-acid base. Values of its second-stage ionisation constant, defined by

$$K_b(\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2) = [\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}\overset{+}{N}O_2H][HSO_4^-]/[\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2]$$

with the concentrations in molalities, and therefore calculated by means of the formula

$$K_b^+ = \{(\nu - 1)(\nu - 2)\Delta m_2 + (\nu - 2)m_4\}/(3 - \nu)$$

are given in the table. The basic strength of the cation *m*-$\overset{+}{N}H_3{\cdot}C_6H_4{\cdot}NO_2$, evidently exerted through its nitro-group, is represented by the basicity constant 0·014 g.-mol. kg.$^{-1}$.

No *o*- or *p*-nitro-substituted anilines have been investigated in the present work; but Hammett and Deyrup concluded (*loc. cit.*) that *o*-nitroaniline and 2 : 4-dinitroaniline, as well as several of their substitution products, behave as mono-acid bases in sulphuric acid. This interpretation would mean that they are completely converted into anilinium ions, and then, having acquired an ammonium pole, become quite incapable of a second stage of ionisation involving proton-uptake by an *o*- or *p*-situated nitro-group. Whether or not the separation of the stages of ionisation is quite as sharp as this, we should, on theoretical grounds, expect it to be substantially sharper for these *o*- and *p*-nitro-compounds than for the *m*-nitro-compound. A comparison of Hammett and Deyrup's results for the *o*- and *p*-nitro-compounds with the present results for *m*-nitroaniline suggests that in fact the *o*- and *p*-nitro-substituted anilinium ions are less basic than is the *m*-nitroanilinium ion, though the data for the *o*- and *p*-compounds are not quite precise enough to permit a quantitative assessment of the differences.

TABLE II.

*Freezing points of solutions of* m-*nitroaniline in sulphuric acid* (Expt. 91).

| Molality of | | | Depressions | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $m$-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | $\nu$-Factor. | $K_b^+$ (g.-mol. kg.$^{-1}$). |
| 0·052 | — | 9·959 | — | — | — | — |
| ,, | 0·01045 | 9·834 | 0·125° | 0·131° | 2·08 | 0·010 |
| ,, | 0·02536 | 9·654 | 0·305 | 0·317 | 2·11 | 0·016 |
| ,, | 0·03191 | 9·569 | 0·390 | 0·405 | 2·10 | 0·015 |
| ,, | 0·03712 | 9·504 | 0·455 | 0·473 | 2·10 | 0·016 |
| | | | | | Mean | 0·014 |

The reciprocal effect of nitro-groups on an amino-group can be observed: three *o*- and *p*-situated nitro-groups appreciably impede even the first stage of ionisation of an aniline in sulphuric acid. 2 : 4 : 6-Trinitroaniline provides the illustration: for the data which Hammett and Deyrup record (*loc. cit.*) prove that this base is by no means fully converted into the anilinium ion when dissolved in sulphuric acid. This can be shown in two ways.

First, the ν-factor given by Hammett and Deyrup for 2 : 4 : 6-trinitroaniline, *viz.*, 1·83, is notably lower than those which they obtained for *o*-nitroaniline, 2 : 4-dinitroaniline, and the other nitro-anilines, which were concluded to dissolve as binary electrolytes. It is true that the ν-factors recorded by these authors are only approximate; but when allowance is made for this, it would appear that the real ν-factor for 2 : 4 : 6-trinitroaniline cannot lie higher than about 1·90. That is, the sulphuric acid solutions must contain an amount of the order of 10% of the free base.

A second method of estimating the incompleteness of the ionisation can be based on the use of Hammett's acidity function $H_0$. Its value for anhydrous sulphuric acid is $-10{\cdot}60$. The extent to which a base B is converted into its conjugate acid $BH^+$ depends only on the strength of the base and the acidity function of the solvent, the relation being

$$H_0 = \mathrm{p}K_a + \log\{[\mathrm{B}]/[\mathrm{BH}^+]\}$$

where the strength of the base is represented by the acidity constant $K_a$ of the conjugate acid:

$$\mathrm{p}K_a = -\log\{(\mathrm{H}^+)(\mathrm{B})/(\mathrm{BH}^+)\}$$

(the parentheses denote activities). The basic strength of 2 : 4 : 6-trinitroaniline, as determined by the indicator method (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827), is given by the value $\mathrm{p}K_a = -9{\cdot}29$. From these figures it can be computed that in fully anhydrous sulphuric acid 2 : 4 : 6-trinitroaniline should remain non-ionised to the extent of 5%. For the very slightly aqueous sulphuric acid employed in cryoscopic measurements on bases, the proportion of non-ionised amine would be greater. For instance, in a solution 0·05 molal with respect to water, and 0·05 molal with respect to 2 : 4 : 6-trinitroaniline the proportion of the latter remaining un-ionised would be 10%. The two estimates of the incompleteness of the ionisation are thus in satisfactory agreement.

(2.4) *The Solute Nitrobenzene.*—As is noted above, the cryoscopic work of Hantzsch, and especially of Hammett, leaves no doubt of the fact that nitrobenzene behaves as a base in sulphuric acid. Some new cryoscopic measurements, which are recorded in Table III, were carried out with the object of determining, for this parent aromatic nitro-compound, the basic strength as defined by the equilibrium constant

$$K_b(C_6H_5{\cdot}NO_2) = [C_6H_5{\cdot}NO_2H^+][HSO_4^-]/[C_6H_5{\cdot}NO_2]$$

the concentrations being as usual in molalities. The observed depressions ($\Delta\theta_1$) have to be corrected for the repression of the ionisation of water, and of the autoprotolysis of sulphuric acid, by the hydrogen sulphate ion formed by the ionisation of the nitrobenzene. These corrected depressions ($\Delta\theta_2$) were used in order to calculate the ν-factors by means of the usual equation with the substitution $s_2 = 1$ and $\nu_2 = 1{\cdot}3$ in the correction factor. The basicity constant $K_b$ was calculated by using the equation

$$K_b(C_6H_5{\cdot}NO_2) = \{(\nu - 1)^2\Delta m_2 + (\nu - 1)m_3\}/(2 - \nu)$$

and the values obtained are in the table. It appears that 27% of nitrobenzene is ionised in a 0·1 molal solution in the slightly aqueous sulphuric acid used. From the basicity constant $K_b = 0{\cdot}29$ g.-mol. kg.$^{-1}$ it can be computed that about 41% of the nitrobenzene would be ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE III.

*Freezing points of solutions of nitrobenzene in sulphuric acid* (Expt. 41).

| Molality of | | | Depression. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $C_6H_5{\cdot}NO_2$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | $\nu$-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·059 | — | 9·871 | — | — | — | — |
| ,, | 0·0426 | 9·558 | 0·313° | 0·318° | 1·23 | 0·019 |
| ,, | 0·0844 | 9·230 | 0·641 | 0·651 | 1·27 | 0·028 |
| ,, | 0·1121 | 9·031 | 0·840 | 0·853 | 1·28 | 0·033 |
| ,, | 0·1383 | 8·823 | 1·048 | 1·063 | 1·27 | 0·033 |
| ,, | 0·1585 | 8·688 | 1·183 | 1·200 | 1·25 | 0·031 |
| | | | | | Mean | 0·029 |

Hammett and Chapman have noted (*J. Amer. Chem. Soc.*, 1934, **56**, 1282) that the solubility of nitrobenzene in aqueous sulphuric acid becomes suddenly great at sulphuric acid concentrations at which the acidity of the medium is still much too small to allow any significant amount of conversion of the nitrobenzene into its conjugate acid. They point out that, in order to account for the solubility increase, some form of interaction between nitrobenzene and sulphuric acid must be assumed, other than an ionising proton-transfer.

A compound, $C_6H_5{\cdot}NO_2,H_2SO_4$, having considerable stability, has been described by Cherbuliez (*Helv. Chim. Acta*, 1923, **6**, 281) and by Masson (*J.*, 1931, 3200). Its melting point, 11·6°, is higher than that of either of its components. Masson regarded it as an ionised salt. However, the cryoscopic data show that, in solution in excess of sulphuric acid, most of it remains un-ionised, except at *very* low concentrations. On these grounds, Gillespie and Millen (*loc. cit.*) have assumed it to be the hydrogen-bonded precursor of the ionised salt, and to be the compound whose formation is responsible for the solubility effects studied by Hammett and Chapman.

(2.5) *The Solute* p-*Nitrotoluene*.—The introduction of a methyl group in the *para*-position to the nitro-group in nitrobenzene would be expected appreciably to enhance the basicity of this nitro-group. *p*-Nitrotoluene had been investigated by Hantzsch, who concluded that it was partly ionised. Some new cryoscopic measurements, which are recorded in Table IV, have now been carried out in order to determine the value of its basicity constant, defined by the equation

$$K_b(CH_3{\cdot}C_6H_4{\cdot}NO_2) = [CH_3{\cdot}C_6H_4{\cdot}NO_2H^+][HSO_4^-]/[CH_3{\cdot}C_6H_4{\cdot}NO_2]$$

concentrations being as usual in molalities. Calculations of the ν-factors, and of $K_b$, were made exactly as for nitrobenzene, and the results are in Table IV. In the nearly-unit correction factor of the usual freezing-point equation, the substitutions $s_2 = 1$ and $\nu_2 = 1{\cdot}6$ were made. It appears that about 60% of the *p*-nitrotoluene is ionised in a 0·1 molal solution in the slightly aqueous sulphuric acid used. From the basicity constant, $K_b = 0{\cdot}20$ g.-mol. kg.$^{-1}$, it can be calculated that about 73% of the *p*-nitrotoluene is ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE IV.

*Freezing points of solutions of* p-*nitrotoluene in sulphuric acid* (Expt. 108).

| Molality of | | | Depressions. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $p$-$CH_3{\cdot}C_6H_4{\cdot}NO_2$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | $\nu$-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·061 | — | 9·883 | — | — | — | — |
| ,, | 0·03106 | 9·577 | 0·306° | 0·314° | 1·69 | 0·17 |
| ,, | 0·07341 | 9·165 | 0·718 | 0·735 | 1·66 | 0·20 |
| ,, | 0·1167 | 8·769 | 1·114 | 1·137 | 1·62 | 0·20 |
| ,, | 0·1506 | 8·464 | 1·419 | 1·444 | 1·59 | 0·20 |
| ,, | 0·1828 | 8·175 | 1·708 | 1·736 | 1·58 | 0·22 |
| | | | | | Mean | 0·20 |

(2.6) *The Solute Nitromethane.*—This parent nitro-compound has been examined in order to ascertain whether aliphatic as well as aromatic nitro-compounds display basic properties in sulphuric acid. No study of the cryoscopic behaviour of any aliphatic nitro-compound in sulphuric acid seems to have been recorded, apart from the original investigation of nitromethane by Hantzsch, who concluded that it dissolved without essential change.

Some measurements for nitromethane are recorded in Table V. From them, ν-factors and the basicity constant

$$K_b(CH_3{\cdot}NO_2) = [CH_3{\cdot}NO_2H^+][HSO_4^-]/[CH_3{\cdot}NO_2]$$

are calculated, in the same way as for 2 : 4 : 6-trinitrotoluene. It is obvious from the ν-factors that, in 0·1—0·2 molal concentration in the slightly aqueous sulphuric acid employed as solvent, about 8% of the nitromethane is ionised. From the basicity constant, $K_b = 0{\cdot}0055$, it can be computed that, in 0·1 molal concentration in anhydrous sulphuric acid, about 21% would be ionised.

TABLE V.

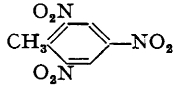
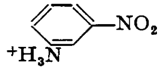
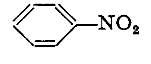
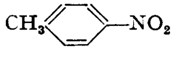
*Freezing points of solutions of nitromethane in sulphuric acid* (Expt. 33).

| Molality of | | | Depressions. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $CH_3{\cdot}NO_2$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | ν-Factors. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·060 | — | 9·866 | — | — | — | — |
| ,, | 0·0380 | 9·625 | 0·249° | 0·250° | 1·09 | 0·0059 |
| ,, | 0·0764 | 9·371 | 0·495 | 0·498 | 1·08 | 0·0055 |
| ,, | 0·1043 | 9·192 | 0·674 | 0·678 | 1·07 | 0·0049 |
| ,, | 0·1352 | 8·992 | 0·874 | 0·879 | 1·07 | 0·0051 |
| ,, | 0·1519 | 8·879 | 0·987 | 0·992 | 1·07 | 0·0051 |
| ,, | 0·1844 | 8·668 | 1·198 | 1·204 | 1·08 | 0·0062 |
| | | | | | | Mean 0·0055 |

(2.7) *Relative Basicities of Nitro-compounds.*—The information that we have obtained concerning the basicities of the nitro-compounds studied is summarised in Table VI.

TABLE VI.

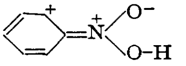
*Basicities of nitro-compounds in sulphuric acid.*

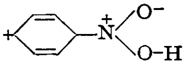
| Compound. | $K_b$ (g.-mol. kg.$^{-1}$). | Approx. % ionisation (0·1 molal in anhyd. $H_2SO_4$). |
|---|---|---|
| $CH_3$-$NO_2$ | $5{\cdot}5 \times 10^{-3}$ | 21 |
|  | $6{\cdot}7 \times 10^{-3}$ | 23 |
|  | $1{\cdot}4 \times 10^{-2}$ | 31 |
|  | $2{\cdot}9 \times 10^{-2}$ | 41 |
|  | $2{\cdot}0 \times 10^{-1}$ | 73 |

It will be noted that nitrobenzene is a stronger base than nitromethane in solvent sulphuric acid, although aniline is a weaker base than methylamine in water. The inversion, as between aliphatic and aromatic analogues, may plausibly be referred to the theory that the mesomeric effect in the aromatic series displaces the electron distribution oppositely for nitro-compounds and for amines, *viz.*, towards the nitro-group in nitrobenzene and away from the amino-group in aniline.

The present work establishes conclusively that the nitro-group possesses a definite, although small, basicity in sulphuric acid; this, as would be expected, is increased when the attached residue is electron-repelling, and decreased when it is electron-attracting. The relatively small basicity of the nitro-group, despite its two negatively charged oxygen atoms, is, no doubt, to be attributed to the large amount of resonance energy which must be lost on the addition of the proton.

It is of some interest that the pale yellow colour of nitrobenzene and of *p*-nitrotoluene is considerably intensified on dissolution in sulphuric acid, whereas solutions of nitromethane in sulphuric acid, and the pure substance, are colourless. The enhanced colour of the aromatic compounds in sulphuric acid is presumably to be associated with the increased importance, in their ions, of structures with a positive charge situated in the aromatic nucleus, *e.g.*,





### (3) *Basicity of Sulphonyl Compounds in Sulphuric Acid.*

(3.1) *Previous Investigations.*—The original object of the experiments reported below was to discover whether sulphonic acids, which have been extensively employed in the study of effects due to the medium on rates of nitration in sulphuric acid solvents, behave as bases towards sulphuric acid. The enquiry was extended to include sulphones for a reason which will appear in Section 4.

The only previous cryoscopic investigation of sulphonic acids in solvent sulphuric acid is that of Hantzsch (*Z. physikal. Chem.*, 1908, **65**, 41), who examined benzenesulphonic acid, *m*-nitrobenzenesulphonic acid, and *p*-toluenesulphonic acid. In each case he employed the sodium salt of the sulphonic acid as the added solute, but made allowance for that part of the freezing-point depression which was attributable to the formed sodium hydrogen sulphate. He found that the depressions due to benzenesulphonic acid, and to *m*-nitrobenzenesulphonic acid, were approximately those to be expected of the non-ionised molecule in either case. On the other hand, the depression given by *p*-toluenesulphonic acid was considerably greater than that of the non-ionised molecule. The experiments were not sufficiently precise to detect with certainty a limited amount of ionisation of the free sulphonic acid, and therefore the question of the reality of such ionisation has been reinvestigated in the examples of sodium benzenesulphonate and sodium *p*-toluenesulphonate. There is no previous record of cryoscopic experiments on sulphones in sulphuric acid.

(3.2) *The Solute Sodium Benzenesulphonate* (*Basicity of Benzenesulphonic Acid*).—Some measurements of the depression, produced by sodium benzenesulphonate, of the freezing point of sulphuric acid are given in Table VII. It is necessary to correct the observed freezing-point depressions ($\Delta\theta_1$) for the repression of ionisation of the water, and of autoprotolysis in the solvent, by the hydrogen sulphate ions which are formed in the solvolysis of the sodium benzenesulphonate. This has been done by the method outlined in Part I. From the corrected depressions ($\Delta\theta_2$), $\nu$-factors have been calculated from the general formula (equation 5 in Part I), with the substitutions $s_2 = 4$ and $\nu_2 = 3$ in the correction factor. The value of $s_2$ is based on the reasonable assumptions that sodium hydrogen sulphate, like potassium hydrogen sulphate, has a solvation number of 2 (cf. Part I), and that a non-ionised benzenesulphonic acid molecule forms a hydrogen-bonded compound with one molecule of sulphuric acid, *i.e.*, has the solvation number 1, like nitrobenzene. It appears that under the conditions of these experiments, which involve the presence of an excess of hydrogen sulphate ion, the benzenesulphonic acid is ionised as a base * to the extent of about 13%.

TABLE VII.

*Freezing points of solutions of sodium benzenesulphonate in sulphuric acid* (Expt. 61).

| Molality of | | | Depressions. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $C_6H_5 \cdot SO_3Na$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | $\nu$-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·048 | — | 9·999 | — | — | — | — |
| ,, | 0·00667 | 9·876 | 0·123° | 0·126° | 3·10 | 0·007 |
| ,, | 0·01441 | 9·727 | 0·272 | 0·280 | 3·20 | 0·016 |
| ,, | 0·02570 | 9·522 | 0·477 | 0·490 | 3·14 | 0·012 |
| ,, | 0·03946 | 9·268 | 0·731 | 0·747 | 3·11 | 0·011 |
| ,, | 0·04789 | 9·108 | 0·891 | 0·909 | 3·10 | 0·011 |
| | | | | | Mean | 0·011 |

The basicity constant of benzenesulphonic acid, as defined by the expression

$$K_b(\mathrm{Ph{\cdot}SO_3H}) = [\mathrm{Ph{\cdot}SO_3H_2}^+][\mathrm{HSO_4}^-]/[\mathrm{Ph{\cdot}SO_3H}]$$

with the concentrations in molalities, has been calculated from the formula

$$K_b = \{(\nu - 2)(\nu - 3)\Delta m_2 + (\nu - 3)m_4\}/(4 - \nu)$$

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* The idea that it might be ionised as an acid is excluded by comparisons with other acids (even perchloric acid is very weak—cf. Part VI), and by the consideration that a *p*-methyl substituent increases the ionisation (Section 2.3), as it should increase basic ionisation, but contrary to the way in which it should influence acidic ionisation.

The values are in the Table. From the mean value of $K_b$ it can be calculated that benzenesulphonic acid would be ionised to the extent of about 28% in a 0·1 molal solution in anhydrous sulphuric acid.

(3.3) *The Solute Sodium* p-*Toluenesulphonate* (*Basicity of* p-*Toluenesulphonic Acid.*)—Some new measurements have been made of the freezing-point depression produced by sodium *p*-toluenesulphonate in sulphuric acid. The results are given in Table VIII. Values of the ν-factor and of $K_b$ have been calculated in exactly the same way as for sodium benzenesulphonate. The results show that *p*-toluenesulphonic acid is appreciably more basic than benzenesulphonic acid. It is ionised to the extent of about 22% under the conditions of the experiment, and, as can be calculated from the mean $K_b$ value, about 40% of the acid would be ionised in a 0·1 molal solution in anhydrous sulphuric acid.

TABLE VIII.

*Freezing points of solutions of sodium* p-*toluenesulphonate in sulphuric acid* (Expt. 109).

| Molality of | | | Depressions. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | *p*-$CH_3 \cdot C_6H_4 \cdot SO_3Na$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | ν-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·053 | — | 9·943 | — | — | — | — |
| ,, | 0·05150 | 9·654 | 0·289° | 0·296° | 3·23 | 0·021 |
| ,, | 0·02844 | 9·396 | 0·547 | 0·559 | 3·24 | 0·027 |
| ,, | 0·04036 | 9·174 | 0·769 | 0·784 | 3·19 | 0·023 |
| ,, | 0·05208 | 8·936 | 1·007 | 1·024 | 3·22 | 0·032 |
| ,, | 0·06973 | 8·598 | 1·345 | 1·367 | 3·20 | 0·025 |
| | | | | | Mean | 0·026 |

(3.4) *The Solute Diphenyl Sulphone.*—For the purpose of comparison with the compounds discussed in the two preceding sections, some measurements have been made on diphenyl sulphone, and the results are given in Table IX. Freezing-point depressions have been corrected as in the preceding examples. The ν-factors in the Table have been calculated from the general formula (equation 5 in Part I) with $s_2 = 1$ and $\nu_2 = 1$ substituted in the nearly-unit correction factor. We have assumed, as we have for benzene- and toluene-sulphonic acids, that the non-ionised molecule of the solute diphenyl sulphone has a solvation number of unity. The basicity constant of diphenyl sulphone, as defined by the expression

$$K_b(Ph_2SO_2) = [Ph_2SO_2H^+][HSO_4^-]/[Ph_2SO_2]$$

with the concentrations in molalities, has been calculated from the formula

$$K_b = \{(\nu - 1)^2\Delta m_2 + (\nu - 1)m_4\}/(2 - \nu)$$

The values obtained are recorded in the Table. It can be seen that, in the slightly aqueous sulphuric acid employed in the experiment, about 19% of the diphenyl sulphone is ionised. From the mean value of $K_b$ it can be calculated that about 33% of it would be ionised in anhydrous sulphuric acid.

TABLE IX.

*Freezing points of solutions of diphenyl sulphone in sulphuric acid* (Expt. 107).

| Molality of | | | Depressions. | | | |
|---|---|---|---|---|---|---|
| water ($m_3$). | $Ph_2SO_2$ ($\Delta m_2$). | F. p. (° c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | ν-Factor. | $K_b$ (g.-mol. kg.$^{-1}$). |
| 0·060 | — | 9·897 | — | — | — | — |
| ,, | 0·01050 | 9·822 | 0·075° | 0·076° | 1·21 | 0·015 |
| ,, | 0·03045 | 9·682 | 0·215 | 0·218 | 1·20 | 0·015 |
| ,, | 0·05330 | 9·525 | 0·372 | 0·377 | 1·18 | 0·014 |
| ,, | 0·07990 | 9·324 | 0·573 | 0·580 | 1·21 | 0·019 |
| ,, | 0·1139 | 9·110 | 0·787 | 0·796 | 1·16 | 0·014 |
| ,, | 0·1383 | 8·932 | 0·965 | 0·976 | 1·17 | 0·016 |
| | | | | | Mean | 0·016 |

## (4) *Basicity of Sulphuryl Compounds in Sulphuric Acid.*

(4.1) *Previous Investigations.*—The contrast between the cryoscopic properties in solvent sulphuric acid of the non-basic halogen-sulphuryl compounds, which were used for the determination of the cryoscopic constant of sulphuric acid, as described in Part I (*J.*, 1950, **2473**), and those of the definitely basic aryl-sulphonyl compounds, treated in the preceding Section, suggested that some examination ought to be made of the esters of sulphuric acid, which, on general electrostatic grounds, would be expected to exhibit an intermediate degree of basic character. The normal esters of sulphuric acid appear, however, to be unsuitable solutes for cryoscopic study in sulphuric acid, dimethyl sulphate having given evidence of partial decomposition in that solvent (cf. Part I). On the other hand, the alkyl-sulphuric acids (alkyl hydrogen sulphates) are well known to be stable in sulphuric acid, in excess of which they are rapidly and completely formed from the simpler alcohols. Accordingly ethylsulphuric acid ($EtHSO_4$) was considered a suitable subject for the present study.

Advantage was taken of the reaction by which ethyl alcohol is converted into ethylsulphuric acid for the convenience of being able to introduce the latter through the medium of a weighed solute of easily controlled purity. So far as is known, the conversion of ethyl alcohol into ethylsulphuric acid by a large excess of sulphuric acid is quantitative. Even if it were not quite quantitative, no advantage would be gained by adding weighed ethylsulphuric acid, or one of its salts, since a similar solution would result from the setting up of an esterification equilibrium, whether the initially added substance were the ester or the alcohol. Actually, the cryoscopic results themselves indicate that the formation of the ester is quantitative.

The cryoscopic behaviour of a number of aliphatic and aromatic alcohols has been investigated by Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257; 1908, **65**, 41) and by Oddo and Scandola (*Gazzetta*, 1909, **39**, II, 1). They showed that methyl and ethyl alcohols gave an approximately three-fold depression of the freezing point of sulphuric acid; and this is consistent with an extensive, or possibly a complete, conversion of the alcohol into the corresponding alkylsulphuric acid and water, *e.g.*,

$$C_2H_5{\cdot}OH + 2H_2SO_4 = C_2H_5{\cdot}SO_4H + H_3O^+ + HSO_4$$

Oddo and Scandola obtained this result for these two, and some other, primary alcohols; but with a number of secondary and tertiary alcohols they obtained depressions which varied, according to the compound, from two to three times that of a non-electrolyte. These secondary and tertiary alcohols, unlike methyl and ethyl alcohol, give yellow solutions in sulphuric acid, and, on pouring them into ice-water, unsaturated hydrocarbons are obtained. In disagreement with Hantzsch, these authors found that triphenylcarbinol gave a four-fold, and not a three-fold, freezing-point depression, a result which has since been confirmed by Hammett and Deyrup (*loc. cit.*). This indicates that triphenylmethylsulphuric acid is completely ionised in sulphuric acid into the triphenylmethyl cation and the hydrogen sulphate ion, or in other words, that triphenylcarbinol is fully ionised according to the equation

$$Ph_3C{\cdot}OH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

Hantzsch also investigated methyl- and ethyl-sulphuric acids by measuring the depression produced by their sodium salts, and allowing for the depression caused by the sodium hydrogen sulphate. His results showed that these two alkylsulphuric acids are little, if at all, ionised in sulphuric acid.

(4.2) *The Solute Ethyl Alcohol* (*Basicity of Ethylsulphuric Acid*).—The observed freezing points of solutions of ethyl alcohol in sulphuric acid are given in Table X. The freezing-point depressions $\Delta\theta_2$ are corrected for the repression of autoprotolysis by the formed water. The $\nu$-factors are calculated by means of the general equation, with the substitutions $s_2 = 2$ and $\nu_2 = 3$ in the correction factor. These substitutions take care of a previous conclusion that the solvation number of hydroxonium hydrogen sulphate is unity.

TABLE X.

*Freezing points of solutions of ethyl alcohol in sulphuric acid.*

| Molality of EtOH | | F. p. | Depression. | | $\nu$- | Molality of EtOH | | F. p. | Depression. | | $\nu$- |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ($m_2$). | ($\Delta m_2$). | (°c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | Factor. | ($m_2$). | ($\Delta m_2$). | (°c.). | $\Delta\theta_1$. | $\Delta\theta_2$. | Factor. |
| Expt. No. 58. Molality of water ($m_3$) = 0·027. | | | | | | Expt. No. 59. Molality of water ($m_3$) = 0·046. | | | | | |
| — | — | 10·207 | — | — | — | — | — | 10·024 | — | — | — |
| 0·0100 | — | 10·028 | — | — | — | 0·0127 | — | 9·815 | — | — | — |
| 0·0213 | — | 9·839 | — | — | — | 0·0244 | 0·0117 | 9·610 | 0·205° | 0·210° | 2·96 |
| 0·0326 | 0·0113 | 9·640 | 0·199° | 0·205° | 3·00 | 0·0333 | 0·0206 | 9·449 | 0·366 | 0·373 | 2·99 |
| 0·0414 | 0·0201 | 9·483 | 0·356 | 0·365 | 2·99 | 0·0421 | 0·0294 | 9·295 | 0·520 | 0·529 | 2·97 |
| 0·0572 | 0·0359 | 9·207 | 0·632 | 0·645 | 2·96 | 0·0507 | 0·0380 | 9·145 | 0·670 | 0·682 | 2·95 |
| | | | | Mean | 2·98 | | | | | Mean | 2·97 |

A completed single-stage esterification of the alcohol, according to the reaction

$$C_2H_5{\cdot}OH + 2H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_3O^+ + HSO_4^-$$

would require $\nu = 3$. A completed two-stage esterification, according to the equation

$$2C_2H_5{\cdot}OH + 3H_2SO_4 = (C_2H_5)_2SO_4 + 2H_3O^+ + 2HSO_4^-$$

would require $\nu = 2{\cdot}5$. These equations require correction, since, as is shown in Part II (*J.*, 1950, 2493), the ions of water will partly reassociate, setting up the equilibrium

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

It was established in Part II that, owing to this balanced reaction, the $\nu$-factor for water is not 2, but has a mean value of 1·89 over the range of concentrations which it has been found convenient to use in the present cryoscopic work. Thus the theoretical $\nu$-factor for no esterification is 1·00, for a quantitative one-stage esterification it has the mean value 2·89, and for a complete two-stage esterification it has the smaller value 2·39. Thus, when the conversion into ethylsulphuric acid is quantitative, the $\nu$-factor should reach a maximum of 2·89, or, more accurately, 2·92, allowance here being made for the repression or solvent autoprotolysis by the formed water. The difference between the expected maximum of 2·92 and the observed value of 2·97 means that, over the range of concentrations employed, ethylsulphuric acid has a $\nu$-factor of 1·05. There are two possible interpretations * of this result: either ethylsulphuric acid behaves as a simple but fairly weak base, ionising according to the equation

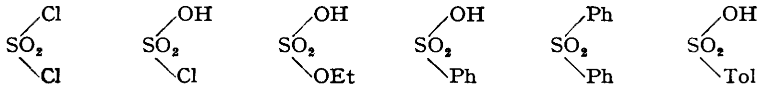
$$C_2H_5{\cdot}SO_4H + H_2SO_4 = C_2H_5{\cdot}SO_4H_2^+ + HSO_4^-,$$

or it dissociates to a limited extent into the ethyl cation and a hydrogen sulphate ion, thus

$$C_2H_5{\cdot}SO_4H = C_2H_5^+ + HSO_4^-$$

The known formation of the triphenylmethyl cation from triphenylcarbinol, and the indication of the existence of carbon cations in solutions of secondary and tertiary alcohols in sulphuric acid, provide some support for the formation of the ethyl cation in small amounts in solutions of ethyl alcohol in sulphuric acid. However, if this latter reaction does not occur, and ethylsulphuric acid behaves simply as a base, then we must conclude that it is a weak base, somewhat weaker than benzenesulphonic acid.

(4.3) *Relative Basicities of Sulphonyl and Sulphuryl Compounds.*—Having regard to data recorded in Part I of this series, and in Section 2 of this paper, the above measurements can be considered to complete a constitutionally graded series, in which the group $-SO_2-$ is bonded, in $R'R''SO_2$, to various groups R, satisfying the conditions that they do not contain atoms intrinsically more basic than the oxygen atoms of the sulphone group itself. In practice this condition limits the groups R to hydrocarbon radicals, hydroxyl or alkoxyl groups, and halogen atoms. The following series (Tol = *p*-tolyl) appears to represent an order of increasing basicity:



$Cl{-}SO_2{-}Cl$ $\quad$ $HO{-}SO_2{-}Cl$ $\quad$ $HO{-}SO_2{-}OEt$ $\quad$ $HO{-}SO_2{-}Ph$ $\quad$ $Ph{-}SO_2{-}Ph$ $\quad$ $HO{-}SO_2{-}Tol$

It appears, as seems reasonable, that increasing basicity is observed when either variable group becomes less electronegative, *i.e.*, when there is a substitution of any group by another standing to its right in the following electropolar series: Cl, OR, Ph, Tol.

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[*Received, December* 17*th*, 1949.]

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* It is considered extremely unlikely that ethylsulphuric acid could be ionised as an acid: such an explanation would require it to be a much stronger acid than sulphuric acid, comparable in strength, indeed, to perchloric acid (though this is still a weak acid in solvent sulphuric acid). This would seem to be improbable on electrostatic grounds, and it would be contrary to the general regularities, discussed in Part VI, concerning the strengths of oxy-acids.