

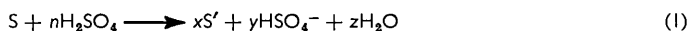
605. Cryoscopic Mixtures Based on Sulphuric Acid. Part II.¹
Seven Organic Solutes.

By J. A. LEISTEN and P. R. WALTON.

The reactions, in sulphuric acid, of skatole, xanthen, hexadecylamine, *t*-butyl alcohol, hexamethylbenzene, benzophenone, and acetonitrile have been studied by means of a cryoscopic method in which different sulphuric acid solutions are used as solvents. Salt-formation, oxidation, the solvolytic fission of carbon-carbon bonds, polymerisation, dehydration, sulphonation, and micelle-formation are among the types of behaviour identified.

Chemical differences between the cryoscopic mixtures are exploited in problems where fractional *i*-factors might be alternatively ascribed to non-ideality or to reversible chemical reactions.

SOLUTES in sulphuric acid are often protonated, with the concomitant formation of hydrogen sulphate ions, and frequently liberate water or extract water from the solvent; thus the chemical behaviour of a generalised solute, S, in sulphuric acid solutions can be usefully represented by the equation:



(S' refers to foreign particles, other than hydrogen sulphate ions and water molecules: *x* of these particles must carry a total of *y* positive charges.) Knowledge of *x*, *y*, and *z*, which is often sufficient to reveal the exact nature of the reaction, can be obtained from cryoscopic measurements. Each term on the right-hand side of eqn. (1) will contribute to the depression of freezing point associated with the solute S; thus the van't Hoff *i*-factor is given by the equation

$$x + yi' + zi'' = i \quad (2)$$

where *i'* is the *i*-factor for a single hydrogen sulphate ion, *i''* is that for a water molecule, and every particle S' is assumed to produce a unit depression of freezing point. The quantities *i'* and *i''* have different values in different solvent mixtures, and by measuring the *i*-factor of the solute in three such mixtures, three specific forms of eqn. (2) are obtained from which *x*, *y*, and *z*, can be evaluated. This technique is here applied to seven organic solutes.

Values of *i'* and *i''* for the solvent mixtures used are given in Table 1. The theory which leads to these values, and the ranges of composition over which the theory holds with sufficient accuracy, have been considered in Part I.¹ Table 1 does not include pure sulphuric acid, but equivalent values (in column 2) obtain for sulphuric acid containing a little water; this solvent has an advantage, in that water represses the self-dissociation of sulphuric acid and thereby eliminates the need to correct subsequent freezing-point measurements for this effect.²

TABLE 1.

i-Factors for the addition of hydrogen sulphate ion (*i'*) and water (*i''*) to sulphuric acid containing various solutes.

Principal solute species	H ₃ O ⁺ , HSO ₄ ⁻	H ₂ S ₂ O ₇ , HS ₂ O ₇ ⁻	HS ₂ O ₇ ⁻ , HSO ₄ ⁻	H ₃ SO ₄ ⁺ , H ₂ S ₂ O ₇	H ₃ SO ₄ ⁺ , H ₃ O ⁺
<i>i'</i>	1	0	1	-1	-1
<i>i''</i>	2	-1	0	-1	0

Skatole (3-Methylindole).—As shown in Table 2, the *i*-factor of 3-methylindole in slightly aqueous sulphuric acid varies from 2.57, immediately after dissolution, to 6.74, after 16 hours at 25°, which suggests greater complexity of behaviour than that of any

¹ Part I, preceding Paper.

² Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

TABLE 2.
Cryoscopic measurements in slightly aqueous sulphuric acid.

Solute (molality)	Molality of water	Time of storage at 25° (min.)		<i>i</i> -Factor	
Skatole (0.025)	0.093	{	0	2.57	
			60	3.61	
			120	4.62	
			960	6.74	
Xanthen (0.04)	0.112	{	0	5.23	
			30	6.18	
Hexadecylamine {	0.16	{	0	1.93	
			0	1.71	
			0	1.39	
			0	1.21	
			0	1.08	
t-Butyl alcohol (0.04)	0.068	{	0	2.24	
			10	2.49	
			20	2.80	
			60	3.53	
			240	5.05	
			480	5.34	
			960	5.34	
Hexamethylbenzene (0.03)	0.052	{	0	2.89	
			10	3.56	
			20	4.23	
			30	4.96	
			960	11.25	
Benzophenone (0.05)	0.052	{	0	2.20	
Acetonitrile (0.10)	{	{	0.10	0	1.28
			0.32	0	1.19
			0.32	0	1.23

TABLE 3.
Cryoscopic measurements in the sulphuric acid–disulphuric acid–disulphate solvent.

Solute (molality)	Molality of H ₂ S ₂ O ₇	Molality HS ₂ O ₇ ⁻	Time of storage at 25° (min.)	<i>i</i> -Factor	
Skatole (0.025)	0.179	0.104	{	0	-0.57
			60	-1.37	
			960	-1.84	
Xanthen (0.04)	0.172	0.110	{	0	-1.76
			20	-1.82	
			240	-1.93	
Hexadecylamine (0.06)	0.183	0.098	{	0	-0.06
Benzophenone (0.05)	0.140	0.140	{	0	1.09
			960	1.10	

TABLE 4.
Cryoscopic measurements in the sulphuric acid–disulphate–hydrogen sulphate solvent.

Solute (molality)	Molality of HS ₂ O ₇ ⁻	Molality of HSO ₄ ⁻	Time of storage at 25° (min.)	<i>i</i> -Factor	
Skatole (0.025)	0.103	0.111	{	0	2.16
			60	2.26	
			960	2.47	
Xanthen (0.04)	0.126	0.098	{	0	1.43
			240	1.55	
t-Butyl alcohol (0.04)	0.097	0.121	{	0	0.52
			15	0.66	
			30	0.72	
			110	1.21	
			190	1.21	
Hexamethylbenzene (0.03)	0.100	0.134	{	0	2.19
			10	2.87	
			960	5.28	
Benzophenone (0.05)	0.100	0.138	{	0	2.09

solute studied in Part I. It was noticed, however, that the solution remained perfectly clear, and that its colour, bright yellow at first, changed in a qualitatively parallel way with the *i*-factor, attaining a stable violet as the freezing point of the solution approached constancy. The cryoscopic behaviour in three other solutions is summarised in Tables 3—5. The violet colour appeared immediately as the solute dissolved in either the two mixtures containing disulphuric acid, and it seemed clear that in order to determine the nature of the violet product, the final *i*-factors in Tables 2 and 4 would have to be compared with the initial values in Tables 3 and 5. For simple reactions, the terms on the left-

TABLE 5.

Cryoscopic measurements in the sulphuric acid–disulphuric acid–sulphuric acidium solvent.

Solute (molality)	Molality of H ₂ S ₂ O ₇	Molality of H ₃ SO ₄ ⁺	Time of storage at 25° (min.)	<i>i</i> -Factor
Skatole (0.025)	0.10	0.07	0	–1.30
			960	–2.12
Acetonitrile (0.05)	0.04	0.21	0	–0.10

TABLE 6.

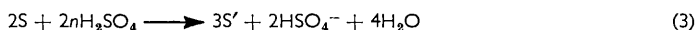
Cryoscopic measurements in the sulphuric acid–hydroxonium–sulphuric acidium solvent.

Solute (molality)	Molality of H ₃ O ⁺	Molality of H ₃ SO ₄ ⁺	Time of storage at 25° (min.)	<i>i</i> -Factor
Xanthen (0.04)	0.10	0.13	0	1.19
			240	1.19
Hexadecylamine (0.06)	0.10	0.13	0	–0.87
Hexamethylbenzene (0.03)	0.10	0.13	0	0.45
			960	3.14
Acetonitrile (0.05)	0.014	0.054	0	0.19
	0.020	0.058	0	0.13

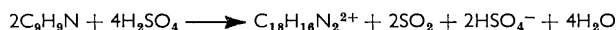
hand side of eqn. (2) will be integral, and it is reasonable to express *i* to the nearest integer; but it is noticeable, in the present case, that the four *i*-factors to be compared (6.74, –0.57, 2.47, and –1.30) are all closer to half-integers, and specialised forms of eqn. (2) are therefore written as follows:

$$x + y + 2z = 6.5 \quad x - z = -0.5 \quad x + y = 2.5 \quad x - y - z = -1.5$$

Solving any three of these equations, $x = 1.5$, $y = 1$, and $z = 2$; thus the reaction with the violet product is probably



It is obvious, in this case, that S' must refer to more than one chemical species and that the cryoscopic technique alone does not yield enough information. One product was identified by means of its odour, and it was subsequently shown by volumetric analysis that one mole of sulphur dioxide is produced per mole of skatole. Eqn. (3) can now be written more precisely:



The conjugate base, C₁₈H₁₄N₂, has not been described, but structure (I) has been suggested to us by Professor T. S. Stevens. It is analogous to that of the dipyrromethenes.³ Structure (II) for the di-protonated molecule places one of the positive charges in a highly conjugated system, and is therefore consistent with the bathochromic shift which accompanies the reaction. The results given in Tables 2 and 4 suggest that a mono-protonated skatole is formed initially, the structure of which has been determined by

³ See, e.g., Piloty, Krannick, and Will, *Ber.*, 1914, **47**, 2531.

nuclear magnetic resonance measurements in less-concentrated sulphuric acid.⁴ The yellow colour is due to this species.

Hinman and Whipple⁴ have studied a reaction of skatole in 96% sulphuric acid (18M)

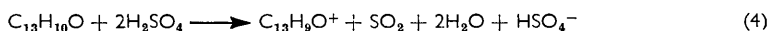


which gives an unidentified product apparently related to di-skatole. The reaction proceeds faster in more-aqueous solutions, unlike our oxidative condensation which is inhibited by water, and from this it seems that the reactions of skatole and similar compounds in acid solutions provide further problems.

Xanthen.—It is reported that xanthen is oxidised to the xanthylium cation in aqueous sulphuric acid.⁵ The rate, which is unaffected by degassing, increases with the concentration of the acid and becomes immeasurably fast in 85% sulphuric acid. Expressing the initial *i*-factors in Tables 2, 4, and 6 to the nearest integers, and solving the appropriate equations, we find the values $x = 1$, $y = 0$, and $z = 2$, which are best explained by the equation



The product is presumably xanthen-2,7-disulphonic acid. The cryoscopic results cannot be reconciled with oxidation according to eqn. (4) and the production of sulphur dioxide



was shown to be negligible by means of volumetric analysis. This conclusion is surprising, but not necessarily inconsistent with the reported behaviour in 85% sulphuric acid. Sulphonation occurs very much more readily in anhydrous than in aqueous sulphuric acid,⁶ and sulphonic acid groups should hinder the electronic shifts required to form the xanthylium cation. In some range between 85 and 100% sulphuric acid, oxidation presumably gives way to sulphonation.

The changing *i*-factor in slightly aqueous sulphuric acid suggests further sulphonation. This explanation is confirmed by the results in the sulphuric acid–disulphuric acid–disulphate mixture, an oleum solvent in which sulphonation should be very rapid (Table 3); the initial *i*-factor indicates the appreciable formation of a trisulphonic acid, and the steady *i*-factor of -1.93 , after four hours at 25°, is consistent with the completion of this reaction.

Hexadecylamine.—The freezing points of solutions of hexadecylamine in sulphuric acid change with time, but the change is so slow that *i*-factors measured immediately after dissolution can be used confidently for determining the initial behaviour of the solute. The *i*-factors in Tables 2, 3, and 6, for solute concentrations between 0.06 and 0.08M, lead to the unusual values $x = 0$, $y = 1$, and $z = 0$; each molecule of solute appears to produce a hydrogen sulphate ion and no other particle. The interpretation is that hexadecylamine forms micelles which are so large as to make no appreciable contribution to the freezing-point depression. Each amino-group is protonated, and all the hydrogen sulphate ions so produced are kinetically free, unlike the situation in water where a significant proportion would be adsorbed on the surface of the micelles. (This difference is credible since the dielectric constant of sulphuric acid is considerably greater than that of water.⁷)

The variation of *i*-factor with solute concentration in aqueous sulphuric acid is shown in the Figure. Each point was determined by means of a separate experiment, so as to

⁴ Hinman and Whipple, *J. Amer. Chem. Soc.*, 1962, **84**, 2534.

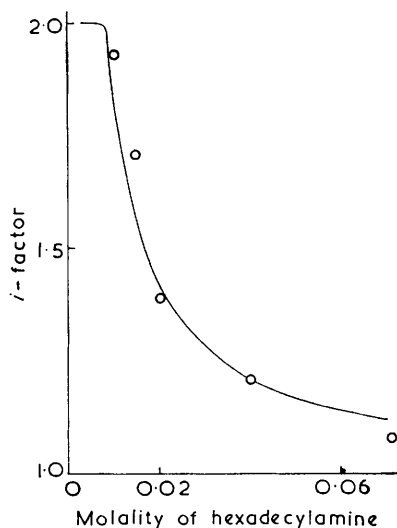
⁵ Deno, Saines, and Spangler, *J. Amer. Chem. Soc.*, 1962, **84**, 3295.

⁶ Cowdrey and Davies, *J.*, 1949, 1872.

⁷ Brand, James, and Rutherford, *J.*, 1953, 2447; Gillespie and Cole, *Trans. Faraday Soc.*, 1956, **52**, 1325.

avoid cumulative changes in *i*-factor due to subsequent reactions. It is clear that at low concentrations, where the *i*-factor approaches two, the protonated hexadecylamine is mainly present as simple ions. The variation of *i*-factor shown by the line is that predicted on the assumption that the critical micelle concentration is 0.0085m, that the dissociated salt exerts a two-fold freezing-point depression, and that the micellised salt exerts a unit depression. This appears to be the first demonstration that long-chain amines form micelles in sulphuric acid, but similar behaviour for stearic acid has been suspected for many years following the observation that this solute causes sulphuric acid to foam.⁸ Further work is in progress.

t-Butyl Alcohol.—This case shows the ease with which cryoscopic results from a single sulphuric acid solvent may be misinterpreted. The two-fold depression observed immediately after dissolution of *t*-butyl alcohol in aqueous sulphuric acid has been generally



Variation of *i*-factor with concentration of hexadecylamine in aqueous sulphuric acid. The circles are experimental values; the line shows the variation calculated on the assumption that the critical micelle concentration is 0.0085 m. (see p. 3181).

thought to show oxonium salt formation, because this correctly explains the similar observations that have been made on ethers, esters, ketones, and other oxygen-containing compounds.⁹ In fact, our results confirm a different interpretation (suggested by work on another solvent, methanesulphonic acid), *viz.*, that *t*-butyl alcohol is immediately dehydrated and polymerised.¹⁰ If the initial *i*-factor in aqueous sulphuric acid (Table 2) is two, and that in the disulphate–hydrogen sulphate mixture (Table 4) is zero:

$$x + y + 2z = 2 \quad \text{and} \quad x + y = 0$$

it is impossible that *x*, and almost inconceivable that *y*, should be less than zero. It follows from these equations that *x* and *y* must both be zero, and *z* unity. Physical restrictions in this case enable the three values to be determined from measurements in only two solvents. (The *i*-factors of two and zero are rather low by comparison with the experimental results. This suggests that the polyisobutene produced is a low polymer which contributes significantly to the freezing-point depression. The value of *x* is fractional rather than zero.)

Although the freezing points change on standing, it is noticeable that, in both the solvents studied, quite stable and low *i*-factors are attained after a few hours at 25°. It

⁸ Dr. A. S. C. Lawrence, personal communication.

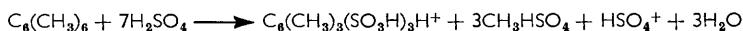
⁹ Hantzsch, *Z. phys. Chem.*, 1908, **65**, 41; Newman, Craig, and Garrett, *J. Amer. Chem. Soc.*, 1949, **71**, 869; Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

¹⁰ Craig, Garrett, and Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 163.

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appears from this that the subsequent reactions which occur may be simpler and more amenable to study than has been supposed.⁹

Hexamethylbenzene.—Hexamethylbenzene is reported to behave as a Brønsted base,¹¹ and in common with other polyalkylbenzenes undergoes interesting reactions in sulphuric acid involving the displacement of alkyl groups.^{12,13} The freezing points of the solutions change rapidly with time, but the initial *i*-factors are consistent with simple protonation as a first step. Steady *i*-factors are attained in all the solutions after a few hours at 25°, and these values, recorded in Tables 2, 4, and 6, require that $x = 4$, $y = 1$, and $z = 3$. The chemical interpretation was suggested to us by Professor C. Eaborn:



It is not clear whether the displacement of methyl groups and sulphonation occur synchronously or whether solvolysis of the carbon-carbon bonds occurs first, but in either case it appears that the replacement of three methyl groups by sulphonic acid groups deactivates the nucleus sufficiently to prevent further reaction.

Benzophenone.—Although cryoscopy is qualitatively a very certain technique, it is relatively imprecise. *i*-Factors vary with concentration, and those observed for a simple base, for example, may be several tenths of a unit from the theoretical value of 2.0. It is therefore difficult to relate a fractional *i*-factor to the partial formation of products in a reversible reaction. One attempt to meet this difficulty has been the introduction of the ν -factor (a thermodynamic refinement of the van't Hoff *i*-factor) which correlates rather better with the number of foreign particles per molecule of solute.¹⁴ The present work provides an alternative approach, which utilises the chemical differences between the cryoscopic mixtures.

Both *i*- and ν -factors for benzophenone in aqueous sulphuric acid are higher than expected for a simple base,¹⁵ and although the discrepancies can be attributed to non-ideality, they could also indicate that a sulphonic acid is formed in fractional amounts. Chalcone and similar ketones are known to readily undergo sulphonation at room temperature.¹⁶ Suppose that benzophenone is sulphonated sufficiently in aqueous sulphuric acid to affect the *i*-factor. (The value of 2.20, given in Table 2, was obtained with a solvent in which the water concentration was 0.052m.) In that case, sulphonation should be complete in the disulphuric acid-disulphate mixture specified in Table 3, where the concentration of sulphonating agent (disulphuric acid^{13,17}) is about 700 times as great as it is in the aqueous acid.¹⁸ The observed *i*-factor, however, is 1.09, which is consistent with simple protonation. A similar value is obtained after storage for 16 hours at 25°, and so sulphonation is imperceptible under these conditions.

Acetonitrile.—This solute produces a slightly greater than unit freezing-point depression in aqueous sulphuric acid, as shown in Table 2, and it appeared from conductimetric measurements that this could be due to weakly basic ionisation.¹⁹ The possibility can be tested by determining the *i*-factor in a cryoscopic mixture of greater acidity. The acidity of sulphuric acid solutions is determined by the concentration of sulphuric acidium ions, just as the acidity in water depends upon hydroxonium ions, although the ionic product is much smaller than that for water:

$$[\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 1.7 \times 10^{-2} \text{ mole}^2 \text{ kg.}^{-2}$$

¹¹ Kilpatrick and Hyman, *J. Amer. Chem. Soc.*, 1958, **80**, 77.

¹² Jacobson, *Ber.*, 1886, **19**, 1209.

¹³ Kilpatrick, Meyer, and Kilpatrick, *J. Phys. Chem.*, 1960, **64**, 1433.

¹⁴ Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

¹⁵ Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1758; Gillespie and Leisten, unpublished work.

¹⁶ Gillespie and Leisten, *J.*, 1954, **1**, 7.

¹⁷ Leisten and Walton, unpublished work.

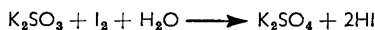
¹⁸ Bass, Gillespie, and Robinson, *J.*, 1960, 821.

¹⁹ Liler and Kosanovic, *J.*, 1958, 1084.

According to this value,¹⁸ a solution in water having a molality of 0.17 (*i.e.*, 0.17m in hydrogen sulphate ion) contains 10^{-3} mole kg^{-1} of sulphuric acidium ion. The solutions specified in Tables 5 and 6 contain *ca.* one hundred times this concentration, and the fact that the *i*-factors in these mixtures are all close to zero, shows that virtually complete conversion of acetonitrile to its conjugate acid occurs in them.

EXPERIMENTAL

The preparation of solvent mixtures and the cryoscopic technique are described in Part I.¹ Sulphur dioxide was estimated by bubbling air through the sulphuric acid solutions and then through 15% solutions of potassium hydroxide, the latter being subsequently added to excess of 0.1N-iodine in aqueous acid:



The residual iodine was titrated with sodium thiosulphate. Skatole was prepared by rearrangement of propionaldehyde phenylhydrazone,²⁰ and was distilled twice under reduced pressure. Xanthen was prepared by reduction of xanthone,²¹ and was recrystallised from ethanol. *t*-Butyl alcohol was redistilled. The remaining solutes were commercial materials recrystallised from suitable solvents.

We thank Dr. K. L. Wright for carrying out the experiments with acetonitrile.

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²⁰ Arbusow and Tichwinsky, *Ber.*, 1910, **43**, 2302.

²¹ Heller and Kostanecki, *Ber.*, 1908, **41**, 1325.
