752. *Aromatic Sulphonation. Part III.* Correlation of the Velocity of Sulphonation with the* J*-Function of Sulphuric Acid.*

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Velocity measurements are reported for sulphonation of $C_6H_5{\cdot}NO_2$ and p-Hal$\cdot C_6H_4{\cdot}NMe_3^+$ in fuming sulphuric acid. The rate increases sharply with rising concentration of sulphur trioxide in the medium, and it is shown that this behaviour is consistent with the mechanism

$$ArH + SO_2{\cdot}OH^+ = Ar{\cdot}SO_2{\cdot}OH + H^+$$

The concentration of $SO_2{\cdot}OH^+$ ions in sulphuric acid is evaluated in terms of the J-function, where $J = H_0 - \log p_{SO_3}$ (cf. Gold and Hawes, *J.*, 1951, 2102), H_0 being the acidity function and p_{SO_3} the partial pressure of sulphur trioxide of the medium in question. Sulphonation *ortho* to a chloro- or bromo-substituent is appreciably retarded by steric factors.

SULPHONATION in fuming sulphuric acid always follows a simple first-order law with respect to the aromatic compound, but the apparent first-order coefficients, k_1, rise steeply and continuously with increasing concentration of sulphur trioxide in the medium. This was noted earlier for comparatively dilute oleums (Part II, *J.*, 1950, 1004) and the measurements have now been extended by the investigation of less reactive molecules in more concentrated media. It will be shown that the experimental results are consistent with the mechanism

$$ArH + SO_2{\cdot}OH^+ = Ar{\cdot}SO_2{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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* Part II, *J.*, 1950, 1004.

and that the variation of k_1 is determined essentially by the variation with medium composition of the concentration of the $SO_2{\cdot}OH^+$ cation.

The concentration of $SO_2{\cdot}OH^+$ is deduced formally from equilibrium (2)

$$HO{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}OH + H^+ \overset{K_1}{\rightleftharpoons} HO{\cdot}SO_2{\cdot}OH + SO_2{\cdot}OH^+ \quad . \quad . \quad . \quad . \quad (2)$$

the equilibrium constant, K_1, being given by

$$K_1 = (\{SO_2{\cdot}OH^+\}\{H_2SO_4\})/(\{H_2S_2O_7\}\{H^+\}) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the braces { } refer to activities relating to the standard state of an infinitely dilute solution in sulphuric acid. $\{H^+\}$ in equation (3) is eliminated by introducing the definition of the acidity function

$$H_0 = A - \{H^+\} \log (f_B/f_{BH^+}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where BH^+ and B represent the acid–base pair used in the measurement of H_0 and the f's refer to the standard state in sulphuric acid. The term A is constant at constant temperature and takes care of the fact that H_0 is usually defined with reference to a standard state in water (Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1939); the circumstance that a single constant will transfer from one standard state to another is equivalent to the assumption that the ratio f_B/f_{BH^+} has the same value in a given medium for all bases, and the supporting evidence for this assumption is summarised by Hammett (*loc. cit.*). In addition, $\{H_2S_2O_7\}$ and $\{H_2SO_4\}$ appearing in equation (3) may be replaced by experimentally accessible quantities through the relations (5)

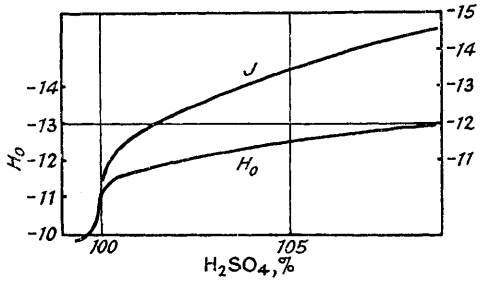

FIG. 1. H$_0$ *and* J-*functions of fuming sulphuric acid.*

$$\left.\begin{array}{l} H_2SO_4 + SO_3 \overset{K_2}{\rightleftharpoons} H_2S_2O_7 \\ K_2 = \{H_2S_2O_7\}/\{H_2SO_4\}\{SO_3\} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and substitution in equation (3) by means of (4) and (5) yields the expression (6) for the concentration of $SO_2{\cdot}OH^+$.

$$\log [SO_2OH^+] = \log \{SO_3\} - H_0 - \log (f_B/f_{BH^+}){\cdot}f_{SO_2{\cdot}OH^+} + A + \log (K_2K_1) \quad . \quad (6)$$

If we define the activity of sulphur trioxide in sulphuric acid solution to be equal to its vapour pressure, and write $J = H_0 - \log (P_{SO_3})$, by analogy with the J_0 function for aqueous sulphuric acid introduced by Gold and Hawes (*J.*, 1951, 2102), equation (6) becomes simply

$$\log [SO_2OH^+] = -J - \log (f_B/f_{BH^+}){\cdot}f_{SO_2{\cdot}OH^+} + A + \log (K_1K_2) \quad . \quad . \quad (7)$$

On the basis of equation (1), the velocity of sulphonation is given by

$$-\,d[ArH]/dt = k[ArH][SO_2OH^+]{\cdot}f_{ArH}{\cdot}f_{SO_2{\cdot}OH^+}/f^{\ddagger}$$

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

$$-\,d[ArH]/dt = k_1[ArH]; \; k_1 = k[SO_2{\cdot}OH^+](f_{ArH}{\cdot}f_{SO_2{\cdot}OH^+}/f^{\ddagger}) \quad . \quad . \quad (8)$$

Combination of the equations (7) and (8) yields equation (9)

$$\log k_1 = -J + \log (f_{ArH}/f^{\ddagger})/(f_{BH^+}/f_B) + [\log k + \log (K_1K_2) + A] \quad . \quad . \quad (9)$$

which expresses the variation of the experimental velocity coefficient, k_1, with medium composition in terms of the J-function (Fig. 1) and an activity coefficient term of approximately symmetrical form. The final term in equation (9), in square brackets, is constant at constant temperature because k, K_1, and K_2 are thermodynamic constants.

Equation (9) is applied to the experimental results (Tables 2 and 3, and Part II) in Fig. 2. If the mechanism represented by (1) is correct, and if the activity coefficient term in equation (9) is zero, the points should fall on a straight line of unit slope. In practice, straight lines through the experimental points have slopes varying from 1·03 for nitrobenzene (curve *c*) to 1·16 for the trimethylphenylammonium ion (curve *b*). The results cover an effective variation of velocities of several powers of ten and provide a reasonably comprehensive test; in fact, it is not certain that the deviation from unit slope exceeds the experimental error in J. However, although there are excellent reasons for believing that the activity-coefficient term in (9) is small, it is probably too simple, in view of the large alteration of medium composition, to assume that it is actually zero; but if the term is non-zero it is more difficult to decide whether it is positive or negative. An immediate argument is that, in the case of nitration in fuming sulphuric acid, the term $f_{\mathrm{ArH}} \cdot f_{\mathrm{NO_2^+}}/f^{\ddagger}$ is known experimentally to increase with rising sulphur trioxide concentration,* *i.e.*, its logarithm is positive. The analogy is not complete, but it does not seem unreasonable that $\log (f_{\mathrm{ArH}}/f^{\ddagger})/(f_{\mathrm{BH^+}}/f_{\mathrm{B}})$ should also be positive, and the slopes of the lines in Fig. 2 therefore slightly greater than unity.

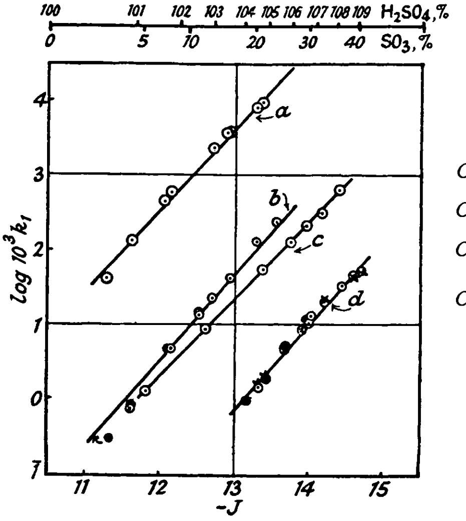

FIG. 2. *Velocity of sulphonation as a function of* J.

	Reactant		Ordinate	Slope
Curve a.	p-Me·C_6H_4·NO_2		$\log 10^3 k_1$	1·07
Curve b.	p-Me·C_6H_4·NMe_3^+	●	$\log 10^3 k_1 - 2{\cdot}56$	1·16
	C_6H_5·NMe_3^+	⊙	$\log 10^3 k_1$	
Curve c.	C_6H_5·NO_2		$\log 10^3 k_1$	1·03
Curve d.	p-F·C_6H_4·NMe_3^+	×	$\log 10^3 k_1$	1·14
	p-Cl·C_6H_4·NMe_3^+	⊙	$\log 10^3 k_1$	
	p-Br·C_6H_4·NMe_3^+	●	$\log 10^3 k_1 - 0{\cdot}11$	

Two points of detail may be mentioned here. First, in the substitution of derivatives of C_6H_5·NMe_3^+, ArH in equation (9) stands for an ion of unit charge and the transition state is a doubly-charged dipolar ion, so that the symmetry of the activity coefficient term is not immediately apparent. But there are experimental reasons for believing that the ratios $f_{\mathrm{^+B}}/f_{\mathrm{^+BH^+}}$ and $f_{\mathrm{B}}/f_{\mathrm{BH^+}}$ (where $^+$B and B represent a charged and an uncharged base respectively) vary in a similar way in solvents of high dielectric constant (Brand, Horning, and Thornley, *J.*, 1952, 1374) and it can be argued, therefore, that $f_{\mathrm{ArH}}/f^{\ddagger}$ will be approximately the same for a charged and an uncharged reactant. Supporting evidence is provided by the fact that the relative velocity of nitration of C_6H_5·NMe_3^+ and C_6H_5·NO_2 in sulphuric acid is independent of medium (Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955), because this must mean that the ratios $f_{\mathrm{Ph \cdot NMe_3^+}}/f^{\ddagger (2+)}$ and $f_{\mathrm{Ph \cdot NO_2}}/f^{\ddagger (+)}$ vary with medium composition in the same way. Secondly, it is obvious from Fig. 2 that the nitro-compounds furnish slopes nearer unity than do the quaternary ammonium systems. This may be due partly to the greater symmetry of the activity coefficient quotient, but it is more probably explained by the fact that the H_0 scale, which is the least certain of the experimental quantities, enters twice into the correlation of $\log k_1$ with J, so that the errors

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* It is interesting that the most rapid rise occurs in 101—102% media, because it is in the same region of composition that the points in Fig. 2 tend to deviate from linearity.

in H_0 tend to balance out. The nitro-compounds are extensively ionised in the sulphuric acid medium, and the H_0 scale is used to evaluate the degree of ionisation, so that the velocity of sulphonation can be referred to the un-ionised molecules only (Parts I and II). The quaternary ammonium systems, of course, are not involved in an acid–base equilibrium of this kind.

The correlation in Fig. 2 shows that the velocities are consistent with the mechanism represented by (1), but the argument is too general to be regarded as an unequivocal proof of mechanism. Some alternatives can be eliminated: *e.g.*, neither monomolecular SO_3 (velocities correlated with partial pressure) nor $H_3SO_4^+$ (correlation with H_0) is possible. However, because H_0 and log (p_{SO_3}) are almost parallel functions of the medium composition (cf. Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1144), log k_1 could be correlated successfully with $2H_0$ or with 2 log (p_{SO_3}) instead of *J*, all three functions having similar relative values. The first possibility corresponds to sulphonation by $H_4SO_4^{++}$ (too improbable to be considered further), the second to S_2O_6. An argument for preferring $SO_2{\cdot}OH^+$ to S_2O_6 in oleum is that it explains the exceptional power of sulphuric acid as a sulphonating medium, in terms of the high proton-activity of the solution; this is particularly striking if it is remembered that the presence of sulphuric acid is in other respects unfavourable, because the equilibrium $SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7$ causes a large proportion of the sulphur trioxide to be stored unprofitably as disulphuric acid. In aprotic solvents however, there is kinetic evidence in favour of S_2O_6 (Hinshelwood and his co-workers, *J.*, 1939, 1372; 1944, 469, 649), and S_2O_6 is even analogous to $SO_2{\cdot}OH^+$ in the general system of acids and bases.

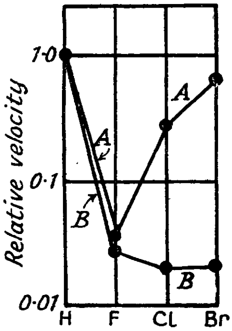

FIG. 3. *Relative velocities of substitution of* p-Hal·C_6H_4·NMe_3^+.

Curve A. Nitration in H_2SO_4.
Curve B. Sulphonation in H_2SO_4.

Steric Retardation of Sulphonation.—The relative velocity of sulphonation of derivatives of $C_6H_5{\cdot}NMe_3^+$ is practically independent of the medium composition, and this condition is also satisfied for nitration in sulphuric acid (Bonner, James, Lowen, and Williams, *loc. cit.*); the effect of the greater size of the sulphonating agent can therefore be seen by comparing directly the relative velocities of nitration and sulphonation (Table 1). It seems reasonable to suppose that, apart from the size factor, the influence of the halogens should be qualitatively in the same order for both sulphonation and nitration. In the examples given in Table 1, with the exception of the parent compound, the point of attack is *ortho* to the halogen substituent; and, sulphonation being compared with nitration, the results give a clear indication of steric compression in the transition state of sulphonation of the chloro- and bromo-derivatives (Fig. 3). A fluoro-substituent does not impede sulphonation appreciably. The iodo-compound does not react smoothly in sulphuric acid solution, and velocity measurements are not available.

TABLE 1. *Relative velocities of substitution of* p-Hal·C_6H_4·NMe_3^+ *in sulphuric acid* (*at* 25°).

	H	F	Cl	Br
Nitration *	1·0	0·030	0·165	0·32
Sulphonation	1·0	0·026	0·020	0·022

* Brand and Paton, *J.*, 1952, **281**.

EXPERIMENTAL

Materials.—p-*Fluorophenyltrimethylammonium methyl sulphate,* prepared from *p*-fluorodimethylaniline and methyl sulphate in acetone, had m. p. 104·5° (Found : C, 45·1; H, 5·9; N, 5·4. $C_{10}H_{16}O_4NFS$ requires C, 45·3; H, 6·1; N, 5·3%). p-*Iodophenyltrimethylammonium methyl sulphate,* prepared similarly, had m. p. 185° (decomp.) (Found : C, 32·4; H, 4·3; N, 3·9. $C_{10}H_{16}O_4NIS$ requires C, 32·2; H, 4·3; N, 3·75%), but decomposed too readily in sulphuric acid solution for velocity measurements to be undertaken.

Velocity Measurements.—The velocity of sulphonation of nitrobenzene was determined directly from the change of transmission at 3650 Å (Table 2). Owing to the fact that the nitrobenzene is present in the solution as phenylnitracidium cation the reaction is attended by a large, approximately 20-fold, decrease in ε at this wave-length, corresponding to the replacement of $C_6H_5{\cdot}NO{\cdot}OH^+$ by $NO_2{\cdot}C_6H_4{\cdot}SO_3H$. Protonisation of the nitrobenzenesulphonic acid only occurred to an appreciable extent in the most powerfully acidic media (>35% oleum). The reaction was conducted in optical cells (depth, 1 cm.), fitted with side-arms and stoppers, immersed in a small tank through which water circulated at 25°. The tank was provided with glass windows and was placed in the cell-compartment of a Hilger " Spekker " absorptiometer. The apparent velocity coefficients, k_a, were evaluated by plotting log {log $(I_0/I)_t$ − log $(I_0/I)_\infty$} (where the I's are intensities and the subscripts refer to time) against time (Fig. 4). The true velocity coefficients, k_1 (Table 2, col. 6), are referred to the concentration of *un-ionised* nitrobenzene only and are evaluated by using the ionisation data of Brand, Horning, and Thornley (*loc. cit.*). The overall rate of sulphonation of nitrobenzene (k_a) in concentrated oleum is actually lower than that of the quaternary systems p-Hal$\cdot C_6H_4{\cdot}NMe_3^+$, owing to the immobilisation of a high proportion of the nitrobenzene as an unreactive cation (Fig. 4).

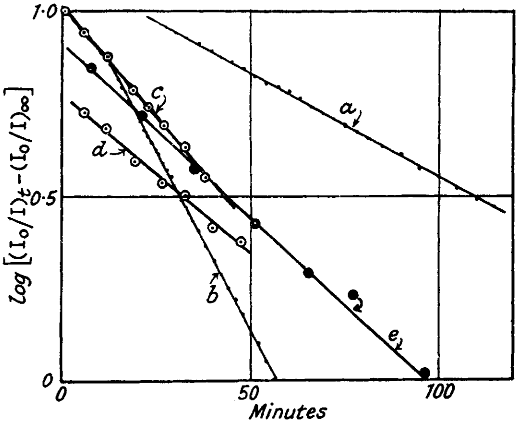

FIG. 4. *Spectrophotometric velocity coefficients for sulphonation in fuming sulphuric acid.*

Curve a, $C_6H_5{\cdot}NO_2$ (108·22% H_2SO_4), k_a = 0·0129 min.$^{-1}$.

Curve b, p-$CH_3{\cdot}C_6H_4{\cdot}NO_2$ (103·43% H_2SO_4), k_a = 0·0438 min.$^{-1}$.

Curve c, p-$F{\cdot}C_6H_4{\cdot}NMe_3^+$ (107·45% H_2SO_4), k_1 = 0·0282 min.$^{-1}$.

Curve d, p-$Cl{\cdot}C_6H_4{\cdot}NMe_3^+$ (107·45% H_2SO_4), k_1 = 0·0198 min.$^{-1}$.

Curve e, p-$Br{\cdot}C_6H_4{\cdot}NMe_3^+$ (107·45% H_2SO_4), k_1 = 0·0212 min.$^{-1}$.

TABLE 2. *Influence of medium on the rate of sulphonation* (*at* 25°).

Medium						
H_2SO_4, %	SO_3, %	10^3k_a (min.$^{-1}$)	$-H_0$	Fraction of un-ionised nitrobenzene	10^3k_1 (min.$^{-1}$)	$-J$
		Nitrobenzene, pK_a = − 11·26.*				
101·27	5·66	0·305	11·77	0·236	1·29	11·83
102·77	12·3	1·07	12·11	0·123	8·69	12·60
104·77	21·2	3·16	12·46	0·059	53·3	13·36
106·07	27·0	5·29	12·58	0·042	126	13·75
106·75	30·0	7·25	12·71	0·034	212	13·96
107·33	32·6	8·60	12·80	0·028	308	14·16
108·22	36·6	12·8	12·95	0·020	640	14·40
		p-*Nitrotoluene,* pK_a = − 10·34.*				
103·43	15·2	43·9	12·25	0·0121	3630	12·88
104·70	20·9	70·6	12·46	0·0075	9420	13·36

* Brand, Horning, and Thornley, *loc. cit.*

The values of the velocity coefficient, k_1, for un-ionised nitrobenzene are slightly *lower* than the results for the trimethylphenylammonium cation in the same medium, instead of being slightly higher as reported in Part II. This is due to a revision of the H_0 scale; it is important to emphasise that H_0 is much more uncertain experimentally than the velocity coefficients.

The quaternary ammonium ions were added as crystalline methyl sulphates to the sulphonating medium, and the progress of the reaction was followed by an indirect method. Aliquot portions of the reaction mixture were withdrawn by pipette, and the sulphonation arrested by running the mixtures into solutions of potassium nitrate in *ca.* 85% sulphuric acid. The unsulphonated quaternary ammonium ions were nitrated slowly but quantitatively, the sulphonic acid being unattacked under these conditions, and the nitro-compound was then estimated from the transmission of the solution in a spectral region (3200—3400 Å) where the nitro-group absorbed strongly but where the other constituents of the solution were transparent. The optical density at these wave-lengths was proportional to the concentration of unsulphonated material, and k_1 could be evaluated directly. The mean results are collected in Table 3.

TABLE 3. *Influence of medium on the rate of sulphonation of* p-Hal·C_6H_4·NMe_3^+ (*at* 25°).

Medium		10^3k_1 (min.$^{-1}$) for			
H_2SO_4, %	SO_3, %	F	Cl	Br	$-J$
104·18	18·6	—	—	0·959	13·16
104·70	20·9	2·1	1·45	—	13·33
105·00	22·2	2·66	—	1·92	13·44
105·81	25·9	6·10	4·59	4·63	13·68
106·54	29·1	11·1	8·60	—	13·91
106·76	30·1	—	10·5	11·6	13·99
106·89	30·6	—	13·2	—	14·02
107·45	33·1	28·3	19·9	21·2	14·21
108·88	39·5	50	45·1	50·7	14·60
109·23	41·0	65	52	—	14·71

Initial concentrations were 10^{-3}—10^{-4}M, depending on the intensity of absorption. Under these conditions individual experiments always yielded first-order coefficients. A low reactant concentration was desirable because quite small concentrations of methosulphate ions exert a pronounced retardation (Part II), but in the present case the effect was within the limits of experimental error.

J-Function of Fuming Sulphuric Acid (Fig. 1).—The J-function is defined by the equation $J = H_0 - \log (p_{SO_3})$ (cf. Gold and Hawes, *loc. cit.*). Because the vapour pressure of sulphur trioxide in dilute oleum is too small for accurate measurement at 25°, J has been evaluated from vapour-pressure measurements at 50° (Brand and Rutherford, *J.*, 1952, 3916). This treatment is justified because the gradient of the log (p_{SO_3}) plot is independent of the composition of the medium, and the ***relative*** values of J are therefore independent of the temperature to which the vapour-pressure measurements refer, provided they always refer to the same temperature. The J-function in this paper is purely relative, in the sense that the definition attaches no significance to the absolute values.

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