399. *The Kinetics and Mechanism of Sulphonation in Sulphuric Acid.*

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The kinetics of the sulphonation of *p*-nitrotoluene have been measured over the range 92% sulphuric acid to 10% oleum, where there is no significant reverse reaction. The rate is proportional to the concentrations of nitrotoluene and of sulphur trioxide [which in 92—99% acid is proportional to $1/w(w + c)$, where w and c are the respective analytical contents of water and added sodium hydrogen sulphate].

The true activation energy is 7·4 kcals. in sulphuric acid and 18·0 kcals. in oleum.

These facts suggest that the reaction is a simple bimolecular attack of sulphur trioxide on nitrotoluene, the disposal of the displaced proton being more difficult in oleum, and this is discussed in terms of the assumption that sulphuric acid is a hydrogen-bonded liquid like water.

This mechanism provides a semi-quantitative explanation for previously recorded rates of sulphonation and desulphonation.

Aromatic sulphonation is almost certainly brought about by an electron-seeking or "kationoid" reagent (cf. Robinson, "Outline of an electrochemical theory of organic reactions," Inst. of Chem., 1932; Ingold, *Chem. Reviews*, 1934, **15**, 225); the precise nature of the attacking species, and the mode of disposal of the displaced proton, are, however, unknown. Recent investigations on nitration in sulphuric acid (Kharasch and Westheimer, *J. Amer. Chem. Soc.*, 1946, **68**, 1871; Ingold, Hughes, *et al.*, *Nature*, 1946, **158**, 448, 480, 514; Bennett *et al.*, *J.*, 1946, 869, 875; 1947, 474) have shown that here the reaction is brought about by the ion NO_2^+ and that the proton is removed by HSO_4^-, H_2SO_4, or $HS_2O_7^-$. The present paper describes a parallel investigation designed to establish which of the species SO_3, SO_3H^+, H_2SO_4, or $(SO_3)_n$ is the sulphonating agent in sulphuric acid, and to discover the fate of the hydrogen ion.

Previous experimental work on the kinetics of sulphonation in sulphuric acid is sketchy. Martinsen (*Z. physikal. Chem.*, 1908, **62**, 713) followed the sulphonation of *p*-nitrotoluene in 99·4% and 100% sulphuric acid and in 2·4% oleum by a method depending on the differing ease of nitration of reactant and product, but neither he nor Joffe (*J. Gen. Chem. U.S.S.R.*, 1933, **3**, 437) could adequately explain the results. The results obtained in oleum can approximately be represented by an equation for a reaction of first order; Martinsen interpreted the reaction as being of the first order with respect to nitrotoluene and of zero order with respect to sulphur trioxide, whilst Joffe preferred to regard it as of the first order with respect to both; the experimental results barely permit a decision between the two. Neither author could explain the results in sulphuric acid, where the reaction was very much slower and retarded by the water produced, so that the order could not be determined. Pinnow (*Z. Elektrochem.*, 1915, **21**, 380; 1917, **23**, 243) measured the rate of the reversible sulphonation of quinol in 40—70% sulphuric acid. The forward reaction was of the first order with respect to quinol, and the back reaction was of the first order with respect to the sulphonic acid. Both rates increased with the concentration of sulphuric acid, the former more sharply than the latter. No satisfactory conclusions about the mechanism were drawn. Lauer and Oda (*J. pr. Chem.*, 1935, **144**, 32) studied the kinetics of anthraquinone sulphonation in oleum, but they worked always at equimolecular concentrations of anthraquinone and sulphur trioxide. The ratio (initial rate/anthraquinone concentration) increased with the sulphur trioxide concentration over the range 1—6% and then dropped almost to zero, finally increasing again between 10% and 20%, and they postulated that sulphur trioxide in 5—10% oleum was in an " inactive " form.

A study of sulphonation, in nitrobenzene, by sulphur trioxide and sulphuric acid was made by Hinshelwood and his collaborators (*J.*, 1939, 1372; 1944, 469, 649). The reaction is first-order with respect to the aromatic compound and second-order with respect to sulphur trioxide, and the latter dependence was interpreted as meaning either that S_2O_6, present in small concentration, is the sulphonating agent, or that one molecule of SO_3 is required as sulphonating agent and another to remove the displaced proton. The activation energies in the sulphonation of a series of substituted benzene derivatives are linearly related to the dipole moments (or algebraic sum of the group moments.)

In the present investigation, the kinetics of sulphonation of *p*-nitrotoluene (chosen for analytical convenience) have been measured in 92—99% sulphuric acid and 1—8% oleum at a series of temperatures.

EXPERIMENTAL.

Oleum solutions were prepared by drawing dry air through warm 65% oleum and into 98% AnalaR sulphuric acid, and standardised by the method of Brand (*J.*, 1946, 585). The end-point of each titration was checked by determining the final freezing point of the acid, and, if necessary, a small correction was made.

100% Sulphuric acid was prepared by mixing pure oleum with 98% AnalaR sulphuric acid in proportions such that the m. p. was 10·4°, it being assumed (cf. Brand, *loc. cit.*) that acid of maximum m. p. is 100% in concentration.

Kinetics of Nitrotoluene Sulphonation in 92—99% *Sulphuric Acid.*—These were measured by making up solutions of weighed quantities of nitro-compound, water, and dried anhydrous sodium sulphate in 100% sulphuric acid, and heating aliquot samples in sealed tubes immersed in constant-temperature baths for known times. Reaction was stopped by cooling, and the samples were diluted with water and extracted with benzene to remove unchanged nitrotoluene. The nitrotoluenesulphonic acid was determined by adding an excess of standard titanous sulphate, boiling under carbon dioxide, and back-titrating with standard ferric alum.

Kinetics of Sulphonation in Oleum.—These were determined by making up, by weight, a solution of nitrotoluene in 100% sulphuric acid in a vessel provided with a side-arm, connected through a ground joint, and containing a weighed quantity of oleum of known strength. The apparatus was immersed in a thermostat, and the two solutions were mixed by rotating the side-arm in the ground joint. At intervals samples were removed with a pipette, and the reaction was stopped by drowning into water. Analysis was carried out as before. " Blank " experiments showed that no significant absorption of water occurred during these operations. No attempt to maintain a constant ionic strength was made, for two reasons. First, the use of perchlorates (the only salts which could be used) in reactions in sulphuric acid at *ca.* 100° does not seem desirable; secondly, sulphuric acid is a solvent in which salt effects are likely to be small (cf. Hammett, " Physical Organic Chemistry," McGraw Hill, 1940, p. 278).

Results in 92—99% *Sulphuric Acid.*—The reaction is a simple first-order process as long as the water produced does not seriously change the total water concentration. The apparent rate constant is depressed by increasing the analytical water content w or by adding sodium hydrogen sulphate (concentration, c moles/l.), and is proportional to $1/w(w + c)$.

The true rate equation is therefore :

$$-\mathrm{d}[p\text{-nitrotoluene}]/\mathrm{d}t = k[p\text{-nitrotoluene}]/w(w + c) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where w includes the water produced during sulphonation.

Thus,
$$\mathrm{d}x/\mathrm{d}t = \frac{k(a - x)}{(b + x)(b + c + x)},$$

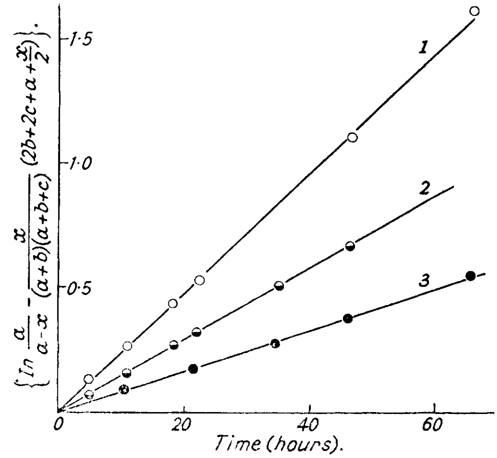
where $a = [p\text{-nitrotoluene}]$ initial, $b = [w]_{\text{initial}}$, $c = [\mathrm{HSO_4^-}]$ added, and $x = $ [sulphonic acid] at time t. This gives, on integration,

$$kt = (a + b)(a + b + c)\left[\ln\frac{a}{a - x} - \frac{x}{(a + b)(a + b + c)}(2b + 2c + a + 0{\cdot}5\,x)\right]$$

Typical experimental data are given in Table I, and test plots of t against the quantity in square brackets are shown in Fig. 1.

FIG. 1.

Sulphonation of p-*nitrotoluene in* H_2SO_4 *at* 96·5° : *lines showing course of reaction.*



	a ([p.n.t.]$_{\text{initial}}$).	b $[w]_{\text{initial}}$.	c ([$\mathrm{HSO_4}$] added).
1.	0·2	1·47	0
2.	0·2	1·47	0·906
3.	0·2	1·47	2·615

TABLE I.

Analytical data for runs at 96·5° *in sulphuric acid containing water and* $\mathrm{HSO_4^-}$.

The concentration, x, of p-nitrotoluenesulphonic acid is given as the number of c.c. of ferric alum solution equivalent to the sulphonic acid in a 10-c.c. portion of the sulphonation mixture.

Run 1. $b = 1{\cdot}47$, $c = 0$, $a = 0{\cdot}200$ mole/l. See Fig. 1.

t (hr.)	0	5·25	11·25	18·4	22·5	46·8	66·4	$k = 0{\cdot}067$
x (0·206M.)	0	8·25	16·2	23·7	27·5	41·7	48·75	

Run 2. $b = 1{\cdot}47$, $c = 0{\cdot}906$, $a = 0{\cdot}200$. See Fig. 1.

t (hr.)	0	5·1	11·1	18·35	22·35	35·1	46·7	$k = 0{\cdot}061$
x (0·206M.)	0	5·1	10·5	16·3	19·1	26·6	32·05	

Run 3. $b = 1{\cdot}47$, $c = 2{\cdot}615$, $a = 0{\cdot}200$. See Fig. 1.

t (hr.)	0	10·67	21·8	34·67	46·25	65·8	$k = 0{\cdot}059$
x (0·206M.)	0	6·6	11·5	17·0	21·7	28·0	

Run 4. $b = 3{\cdot}19$, $c = 0$, $a = 0{\cdot}200$.

t (hr.)	0	17·0	24·2	41	47·7	64·8	70·7	90·3	112·7	208·7	$k = 0{\cdot}073$
x (0·204M.)	0	7·0	8·9	14·6	17·0	22·2	23·9	27·3	31·15	45·25	

Run 5. $b = 5{\cdot}51$, $c = 0$, $a = 0{\cdot}200$.

t (hr.)	0	64·5	111·75	136·5	160·5	207·5	259·5	351·5	472·5	$k = 0{\cdot}067$
x (0·204M.)	0	8·7	12·5	15·8	17·1	22·1	24·6	31·0	36·8	

The slopes of these lines (apparent rate constants) for different runs at 96·5° are plotted against $1/(a + b)(a + b + c)$ in Fig. 2; again the relation is linear. The rate constant k of equation (i) (in g.-mol.^{2}l.$^{-2}$hr.$^{-1}$) is equal to the slope of this line and is 0·066 hr.$^{-1}$ at 96·5°. Values of k from individual runs at four temperatures are shown in Table II. It will be noticed that k falls when w falls below 1·4M. ;

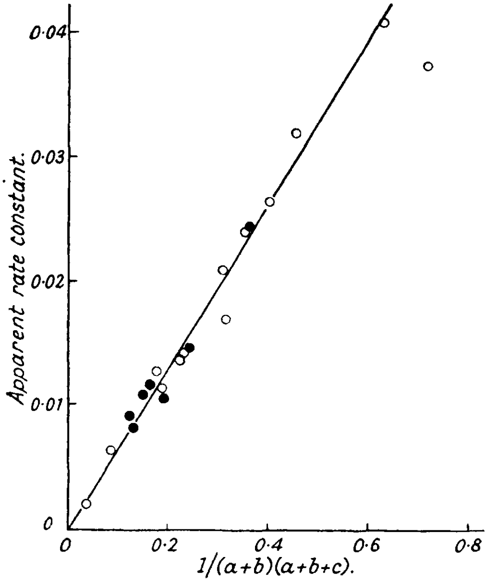
this effect is most apparent at the lower temperatures, where the higher water concentrations cannot be used, as the rate becomes too small. In obtaining mean values for k, rates at values of w less than 1·0 have been disregarded.

The mean values obey the Arrhenius law, and correspond to an activation energy of 27·4 ± 0·3 kcals. per mole.

Under the conditions of these experiments, the reverse reaction (desulphonation of nitrotoluenesulphonic acid) was shown by experiment to be negligible.

FIG. 2.

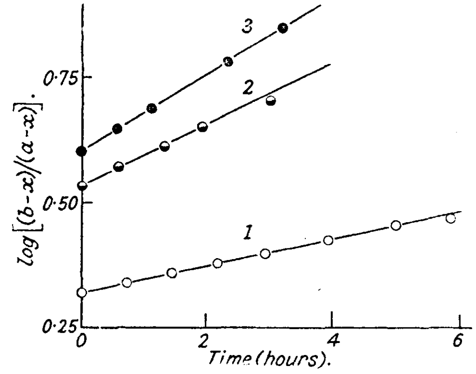
Effect of H_2O *and* HSO_4^- *on rate of* p-*nitrotoluene sulphonation at* 96·5°.



Open circles : water alone added.
Full circles : water and bisulphate added.

FIG. 3.

Sulphonation of p-*nitrotoluene by oleum at* 25° : *lines showing course of reaction.*



	$[SO_3]_{initial}$.	$[p\text{-n.t.}]_{initial}$.
1.	0·385	0·136
2.	0·685	0·199
3.	1·270	0·182

Results in Oleum.—Here the reaction is a simple bimolecular process of the first order with respect to both *p*-nitrotoluene and free sulphur trioxide (initial concentration d g.-mols.l.$^{-1}$). A few typical experimental results and second-order plots are shown in Table III and Fig. 3. The full list of rate constants k_2(g.-mol.l.$^{-1}$hr.$^{-1}$) obtained at three temperatures is given in Table IV.

TABLE II.

Rate constants for sulphonation in < 100% *sulphuric acid.*

a, b, and c are given in mol.l.$^{-1}$

	b.	a.	c.	k.
At 96·5°.	5·51	0·2	—	0·067
	3·19	0·2	—	0·074
	2·32	0·2	—	0·073
	1·92	0·2	—	0·062
	1·59	0·2	—	0·068
	1·38	0·4	—	0·054
	1·38	0·2	—	0·066
	1·38	0·1	—	0·070
	[0·98	0·2	—	0·052]
	2·17	0·2	—	0·072
	2·17	0·2	0·195	0·072
	2·17	0·2	0·395	0·072
	2·17	0·2	0·998	0·073
	1·47	0·2	—	0·067
	1·47	0·2	0·906	0·061
	1·47	0·2	2·615	0·059
	1·061	0·2	—	0·065
	1·061	0·2	0·927	0·067
	1·061	0·2	1·998	0·060
	1·061	0·2	2·845	0·057
			Mean	0·066

	b.	a.	c.	k.
At 70·5°.	2·24	0·2	—	0·0039
	1·78	0·2	—	0·0030
	1·33	0·2	—	0·0032
	1·05	0·2	—	0·0028
	[0·78	0·2	—	0·0023]
			Mean	$0·0032_3$
At 80·5°.	2·73	0·2	—	0·0120
	2·24	0·2	—	0·0115
	1·78	0·2	—	0·0102
	1·365	0·2	—	0·0092
	1·14	0·2	—	0·0086
	[0·81	0·2	—	0·0065]
			Mean	0·0103
At 117°.	5·5	0·2	—	0·045

TABLE III.

Analytical data for sulphonation in oleum.

For value of x see Table I.

Run 6. 13·5°. $a = 0{\cdot}217$, $d = 0{\cdot}438$.

Time (hr.)	0	2·4	4·7	6·27	8·8	10·4	$k_2 = 0{\cdot}085$
x (0·200M.)	0	5·45	9·9	12·7	16·6	18·9	

Run 1. 25°. $a = 0{\cdot}182$, $d = 1{\cdot}27$ moles/l. See Fig. 3.

Time (hr.)	0	0·24	0·49	0·75	1·07	1·52	3·0	5·8	$k_2 = 0{\cdot}34$
x (0·201M.)	0	7·1	10·3	14·7	19·6	25·7	37·2	46·0	

Run 2. 25°. $a = 0{\cdot}199$, $d = 0{\cdot}685$. See Fig. 3.

Time (hr.)	0	0·56	1·27	1·89	2·96	$k_2 = 0{\cdot}30$
x (0·201M.)	0	6·9	13·3	18·5	24·4	

Run 3. 25°. $a = 0{\cdot}186$, $d = 0{\cdot}385$. See Fig. 3.

Time (hr.)	0	0·71	1·44	2·17	2·92	3·92	5·0	5·83	21·58	$k_2 = 0{\cdot}31$
x (0·201M.)	0	5·25	8·6	12·2	15·4	19·1	22·6	24·7	43·4	

Run 4. 40°. $a = 0{\cdot}212$, $d = 0{\cdot}945$.

Time (hr.)	0	0·14	0·35	0·51	0·87	$k_2 = 1{\cdot}54$
x (0·197M.)	0	10·7	25·3	32·5	43·5	

Run 5. 40°. $a = 0{\cdot}216$, $d = 0{\cdot}343$.

Time (hr.)	0	0·325	0·65	1·15	1·67	$k_2 = 1{\cdot}42$
x (0·201M.)	0	8·7	15·3	23·4	30·0	

TABLE IV.

Rate constants for sulphonation in oleum.

$a = 0{\cdot}2$ throughout.

At 40°.	d	0·34	0·53	0·81	0·95	0·95	0·98	1·16	1·51
	k_2	1·42	1·31	1·66	1·54	1·50	1·41	1·51	1·62
At 25°.	d	0·21	0·39	0·69	0·82	1·12	1·27		
	k_2	0·30	0·31	0·30	0·31	0·34	0·34		
At 13·5°.	d	0·44	0·75	0·98	1·09	1·71	2·16		
	k_2	0·085	0·094	0·080	0·110	0·120	0·143		

The activation energy derived from these values is 18·0 kcals. per mole, and the non-exponential (A) factor in the Arrhenius equation is $1{\cdot}6 \times 10^9$ g.-mol.l.$^{-1}$sec.$^{-1}$.

The rate constant shows definite signs of increasing when the sulphur trioxide concentration is high (>1) and most markedly at the lowest temperature (13·5°); this may be due to the existence of an additional reaction of higher order in sulphur trioxide.

Discussion.

A mechanism of sulphonation is required consistent with the facts that the rate of sulphonation is proportional to $[\mathrm{RH}]/w(w + c)$ (activation energy, 27·4 kcals.) in 92—99% sulphuric acid and to $[\mathrm{SO_3}][\mathrm{RH}]$ (activation energy, 18·0 kcals.) in oleum.

The sulphonating agents which have been considered are SO_3, HSO_3^+, S_2O_6, or H_2SO_4. Possible proton-acceptors are HSO_4^-, H_2SO_4, SO_3, or $HS_2O_7^-$. The species undergoing sulphonation is almost certainly the unchanged nitro-compound; Hammett and Deyrup (*loc. cit.*) have shown that RNO_2H^+ formation is small in 100% sulphuric acid; this (and $RNO_2{\cdot}SO_3$) will sulphonate more slowly than RNO_2, and the presence of these complexes in minor proportions will be unimportant.

The concentration of the various possible reactant species can be calculated in terms of the stoicheiometric concentrations of water (w) or added HSO_4^- (c) in sulphuric acid of less than 100% strength (which, for convenience, we shall call " vitriol " in the rest of this discussion), or of sulphur trioxide (d) in oleum. Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) have shown that the equilibrium, $H_2O + H_2SO_4 \rightleftharpoons OH_3^+ + HSO_4^-$, lies almost completely to the right in concentrated sulphuric acid, *i.e.*, water is a strong base in sulphuric acid.

Hence, dissociation of sulphuric acid into sulphur trioxide or HSO_3^+ will occur according to the equations :

$$2H_2SO_4 \rightleftharpoons SO_3 + OH_3^+ + HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$3H_2SO_4 \rightleftharpoons HSO_3^+ + OH_3^+ + 2HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

(equilibrium constants, respectively, K_1 and K_2)

Since one mole of water gives rise to one mole each of OH_3^+ and HSO_4^-, and HSO_4^- dissolves unchanged, in 92—99% sulphuric acid the various concentrations are

$SO_3 = K_1/w(w + c)$
$HSO_3^+ = K_2/w(w + c)^2$
$S_2O_6 = K_1^2K_3/w^2(w + c)^2$ (K_3 being the constant for SO_3 dimerisation)
$HSO_4^- = w + c$
$HS_2O_7^- = K_2K_1/w$

In oleum, the following equilibria are important

$$SO_3 + HSO_4^- \rightleftharpoons HS_2O_7^- \quad \ldots\ldots\ldots\ldots \tag{4}$$

$$SO_3 + 2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad \ldots\ldots\ldots \tag{5}$$

$$2SO_3 + H_2SO_4 \rightleftharpoons HSO_3^+ + HS_2O_7^- \quad \ldots\ldots\ldots \tag{6}$$

(equilibrium constants, respectively, K_4, K_5, and K_6.)

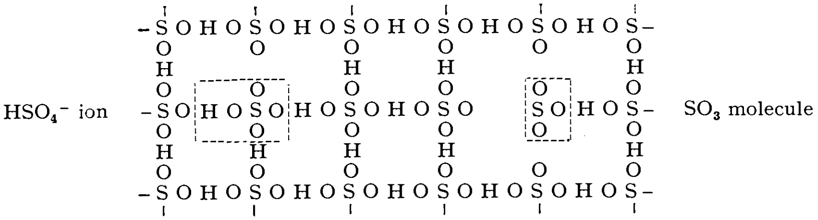
In (4), equilibrium is predominantly to the right (cf. Brand, *J.*, 1946, 880); in (5) and (6), it is predominantly to the left, since the addition of sulphur trioxide to sulphuric acid brings about only a small rise in conductivity.

Thus,

$[SO_3] = d$
$[HSO_3^+] = K_6/\sqrt{(K_6d^2 + K_5d)}$
$[HS_2O_7^-] = \sqrt{(K_6d^2 + K_5d)}$
$[HSO_4^-] = \sqrt{K_6d^2 + K_5d}/K_4d = \sim 0$, as K_6 and K_5 are small and K_4 is large.

It is assumed that an acceptable mechanism is one in which the product of the concentrations of sulphonating agent and proton-acceptor depends on the same functions of medium concentration as does the rate of reaction. This condition is only fulfilled by the combinations, SO_3/H_2SO_4 and HSO_3^+/HSO_4^-.

Although these represent formally different mechanisms, it is doubtful whether there is any physical distinction between them, for the following reason. Sulphuric acid, like water (Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515), almost certainly has a hydrogen-bonded structure in the liquid state; it has a high dielectric constant and, as in water, the hydrogen ions are exceptionally mobile (Hammett and Lowenheim, *J. Amer. Chem. Soc.*, 1934, **56**, 2620). Sulphur trioxide and HSO_4^- will not exist as independent entities, but will be incorporated in the lattice and there constitute a kind of lattice defect. A typical micro-crystalline region containing these defects might schematically be represented as follows:



In the critical act of sulphonation, the two species responsible for substitution and proton removal are likely to be hydrogen-bonded together, either directly or through a solvent molecule. The difference, therefore, between mechanisms involving (*a*) SO_3 and H_2SO_4 or (*b*) HSO_3^+ and HSO_4^- depends upon the assignment of a proton involved in an O—H—O bond to one or other of the bound oxygen atoms, and such a distinction may lack physical justification. In the rest of this discussion the SO_3/H_2SO_4 formulation is used; the arguments apply with equal force to the HSO_3^+/HSO_4^- mechanism.

There remains for consideration the connection between the rate constants in vitriol and in oleum. If the true rate constant k_1 for the SO_3/RH reaction were the same in both cases, then, since the apparent rate constant in concentrated sulphuric acid is k_1K_1 and that in oleum is k_1, the quotient at a given temperature should be equal to the equilibrium constant K_1, and the difference in apparent activation energies to the heat, ΔH_1, of the reaction

$$2H_2SO_4 \rightleftharpoons SO_3 + OH_3^+ + HSO_4^-.$$

Although K_1 is not known and no method for its determination is readily available, ΔH_1 (which is simply the heat of reaction of one mole of water with one mole of sulphur trioxide, both dissolved in an infinite amount of sulphuric acid) has been found to be 20·0 kcals. per mole (Miles, Niblock, and Smith, *Trans. Faraday Soc.*, 1944, **40**, 281). Since the observed difference in activation energy is only 9·4 kcals. per mole, it follows that the true rate constants in vitriol and oleum are different, and that the true activation energy in the former case (7·4 kcals. per mole) is 10·6 kcals. less than in the latter (18·0 kcals. per mole). Further, there is only one combination of sulphonating agent and proton-acceptor in accord with the kinetics, so that this activation energy difference must be ascribed (*a*) to a change in the species being sulphonated or (*b*) to a change in the physical characteristics of the medium, on passing from 98% sulphuric acid to 1% oleum.

Hypothesis (*a*) demands that RNO_2 be almost quantitatively converted into RNO_2H^+ or $RNO_2{\cdot}SO_3$ in oleum, but not in vitriol. Although $^-NO_2{\cdot}SO_3$ and $^-NO_2H^+$ will be more strongly electron-attracting than $^-NO_2$, it is difficult to believe that the consequent increase in activation energy could be as great as 10·6 kcals. Further, as well as affecting the properties of RNO_2, such complex formation would seriously change the concentration of the sulphonating agent, sulphur trioxide; such changes are not consistent with the observed second-order kinetics.

Hypothesis (*b*) is more attractive; the transfer of a proton to the solvent may well be more difficult in oleum than in less than 98·5% sulphuric acid, where there is at least one HSO_4^- " lattice defect " for every fifteen sulphuric acid molecules. These " defects," as well as being points at which protons can very readily be accepted, will be extremely mobile; their movement involves only proton transference. It can therefore be postulated that during sulphonation in vitriol there is always a HSO_4^- " defect " near enough to any SO_3/RH collision for the proton to be transferred to the $^-O^-$ group if the collision is activated. Although HSO_4^- would be involved in the critical step, its concentration would not enter into the kinetics. On the other hand, there will be very few HSO_4^- groups in 100% sulphuric acid or oleum. Here, the proton must be transferred to a neutral oxygen atom, possibly with local disruption of the lattice, and this would involve an addition to the energy of activation.

There are signs of a drop in rate constant as the water concentration falls below 1%; this may be due to the increasing scarcity of HSO_4^-, whose concentration may increasingly affect the rate as the water concentration approaches zero.

The value of $1{\cdot}6 \times 10^9$ for the non-exponential A factor in the Arrhenius equation, derived from the measurements in oleum solution, is of the correct order of magnitude for a process involving uncharged reactants such as sulphur trioxide and RH (cf. Bell, *J.*, 1943, 629). It is also relevant that it is in this type of reaction that salt effects are least important; the variations in ionic strength in the vitriol experiments are therefore unlikely to be of major importance.

The increase in apparent order of reaction when the sulphur trioxide concentration is high ($>$M.) may be due to thermodynamic complexities because of the large concentrations, or simply to the appearance of $HS_2O_7^-$ (a possible proton-acceptor). This would introduce an additional reaction whose rate was $k_3[RH][SO_3]\sqrt{(K_6[SO_3]^2 + K_3[SO_3])}$, the relative importance of which would be greatest (*a*) at high sulphur trioxide concentration and (*b*) at low temperature (since the activation energy would probably be less than that of the main reaction).

Interpretation of Previous Work on Sulphonation and Desulphonation.

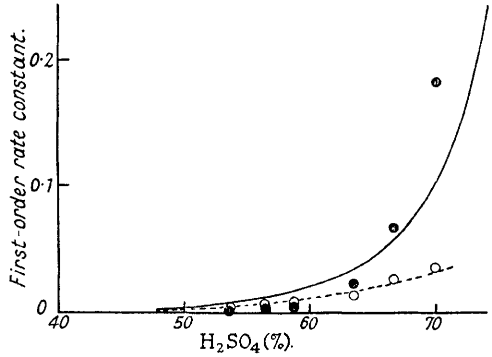
The results of Pinnow (*loc. cit.*) show that the rate of sulphonation of quinol becomes perceptible only when the sulphuric acid concentration exceeds 55%; above this concentration, the rate increases very sharply (see Fig. 4). The rate of hydrolysis of quinolsulphonic acid becomes perceptible at about the same sulphuric acid concentration, but increases with the acid concentration less sharply than the forward reaction (Fig. 4). Lantz (*Bull. Soc. chim.*, 1935, **2**, 2092) found that the rate of hydrolysis of naphthalene-α-sulphonic acid varied similarly with sulphuric acid concentration (Fig. 5). Crafts (*Ber.*, 1901, **34**, 1350; *Bull. Soc. chim.*, 1907, **1**, 917) found that the rate of hydrolysis of xylenesulphonic acids in hydrochloric acid was insignificant at low acid concentrations, but that it subsequently rose sharply (see Fig. 6).

These facts are inconsistent with the older view that the sulphonation–desulphonation equilibrium can be written as $H_2SO_4 + RH \rightleftharpoons RSO_3^- + OH_3^+$, for in this case the hydrolysis rate should be directly proportional to the acid concentration from the lowest values upward. Lantz (*Bull. Soc. chim.*, 1945, **12**, 1004) has advanced the very reasonable idea that desulphonation, which involves substitution by a proton, should be brought about best by the strongest acid in the system (sulphuric acid) and that other undissociated strong acids such as hydrochloric acid should also be effective. Such a postulate is in fact the logical counterpart of the mechanism established in this paper for sulphonation in vitriol, the complete equilibrium being $SO_3 + RH + HSO_4^- \rightleftharpoons RSO_3^- + H_2SO_4$.

In the acid concentrations under consideration (40—70%), water and not sulphuric acid is the medium, so it is likely here that the rate of the forward reaction will depend on the HSO_4^- concentration.

FIG. 4.

Pinnow's results for sulphonation of quinol and reverse reaction in moderately concentrated H_2SO_4.



Full circles : sulphonation of quinol
Open circles : hydrolysis of quinolsulphonic acid } 100°.

Full line : theoretical line for sulphonation $\left[\frac{0{\cdot}015s^3}{(w - s)^2}\right]$.

Broken line : theoretical lines for hydrolysis $\left[\frac{s^2}{30(w - s)}\right]$.

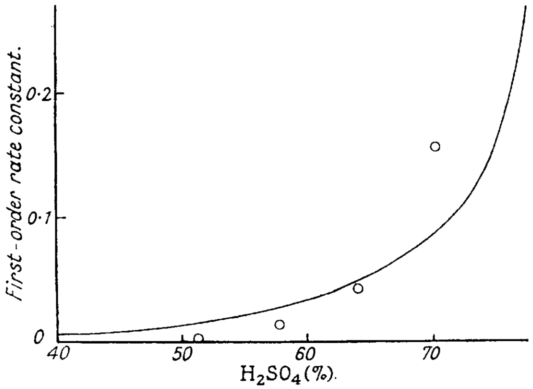
By simple and perhaps somewhat naïve mass-action considerations a solution with analytical contents w and s ($w > s$) of water and sulphuric acid respectively should contain various species in the following concentrations :

$H_2O = w - s$
$OH_3^+ = HSO_4^- = s$
$H_2SO_4 = s^2/K_7(w - s)$, K_7 being the first dissociation constant of sulphuric acid.
$SO_3 = K_1s^2/K_7^2(w - s)^2$

The rates of sulphonation and hydrolysis on this view should depend respectively on $s^3/(w - s)^2$ and $s^2/(w - s)$. Lines showing these two functions are plotted in Figs. 4 and 5, and, although agreement is not accurate (the experimental rates rise more sharply than predicted), the main features (rate negligible at low acid concentration, subsequently rising sharply) are represented. The deviations may be due to ionic interaction (the electrolyte concentrations are

FIG. 5.

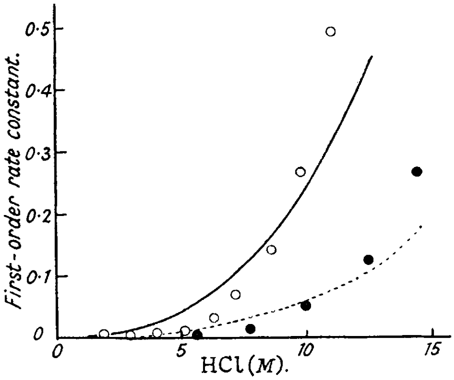
Hydrolysis of naphthalene-α-sulphonic acid (Lantz).



Line represents $s^2/10(w - s)$.

FIG. 6.

Hydrolysis of sulphonic acids in HCl (*Crafts*).



Full circles : m-*xylenesulphonic acid.*
Open circles : p-*xylenesulphonic acid.*
Broken line : $\frac{0{\cdot}02s^2}{w - s}$. *Full line :* $\frac{0{\cdot}08s^2}{w - s}$.

between 5 and 15M.); at high acid concentrations the discrepancy may be due to the conversion of RSO_3^- into RSO_3H (which will hydrolyse at a different, unpredictable rate).

Hydrolysis rates in hydrochloric acid should, on similar grounds, depend on $s^2/(w - s)$ (s being the analytical hydrochloric acid content). Again, the main features of the reactions are shown (see Fig. 6) although there are quantitative discrepancies which could be due to the breakdown of ordinary equilibrium laws.

It can thus be claimed that a reasonable extension of the mechanism of sulphonation in 92% H_2SO_4—6% oleum provides a satisfactory and coherent working hypothesis for interpreting sulphonation and desulphonation rates in moderately concentrated acids.

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