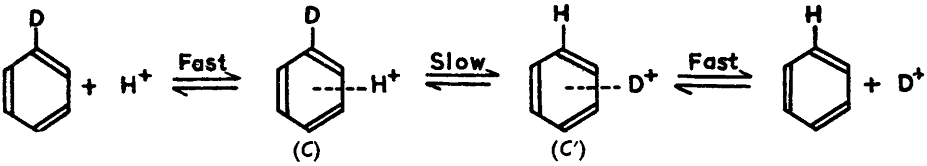
324. *The Mechanism of Aromatic Sulphonation and Desulphonation in Aqueous Sulphuric Acid.*

By V. GOLD and D. P. N. SATCHELL.

The sulphonation of benzene by aqueous sulphuric acid (77·5—87·6 wt. %) has been studied kinetically as a homogeneous reaction by application of an isotope dilution technique. These measurements and earlier data on sulphonation and desulphonation in aqueous acid are shown to be compatible with the scheme shown in (1).

WE have recently found[1] that the rate of replacement of nuclear deuterium atoms in aromatic molecules by protium derived from acidic solvents is proportional to h_0 (where $-\log h_0 = H_0$ = Hammett's acidity function[2]). The reaction is one which involves electrophilic aromatic substitution by hydrogen. We have argued that the observed kinetics are best explained on the basis of a mechanism in which the electrophilic reagent is involved in a rapid pre-equilibrium. The particular formulation which we favour is as follows:



where *C* and *C′* are non-classical structures analogous to Mulliken's "outer complexes."[3]

If such a mechanism is involved in one case of electrophilic substitution by hydrogen, then it seems likely that broadly similar mechanisms operate in other cases. This idea is supported by the example of replacement of trimethylsilyl,[4] for which the rate has, in fact, been found to be proportional to h_0, and perhaps also by those of demercuration[5] and deiodination.[6] In the last example the acidity functions of the solutions used are not known, but the rates increase with the acidity of the solvent considerably faster than does the stoicheiometric concentration of strong acid used and such a steep concentration dependence is also usually characteristic of the acidity function in mixtures of strong acids with other solvents.

These considerations are of interest in connection with the mechanism of desulphonation,

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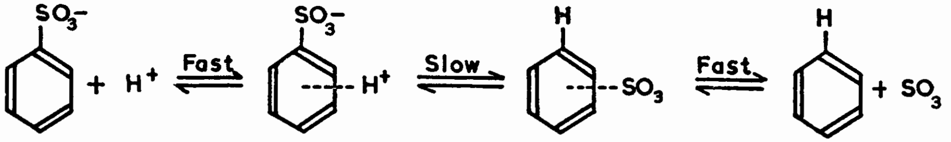
[1] (*a*) Gold and Satchell, *Nature*, 1955, **176**, 602; *J.*, 1955, 3609, (*b*) *J.*, 1955, 3619, (*c*) *J.*, 1955, 3622.
[2] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940.
[3] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.
[4] (*a*) Eaborn, *J.*, 1953, 3148; (*b*) Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353.
[5] Corwin and Naylor, *ibid.*, 1947, **69**, 1004; Kaufman and Corwin, *ibid.*, 1955, **77**, 6280.
[6] Gold and Whittaker, *J.*, 1951, 1184.

this being another reaction of the same general type. The analogy between hydrogen exchange and desulphonation is particularly close in view of the similarity of the reaction media (aqueous sulphuric and other acids) involved in the two cases. If we assume that the mechanisms are analogous, then, since the sulphonate ion is likely to be much more reactive towards electrophilic attack than the undissociated sulphonic acid, the mechanism of desulphonation can be represented as follows :



(1)

The net reaction (negligible reversal being assumed) is :

$$H^+ + Ar{\cdot}SO_3^- \longrightarrow ArH + SO_3 \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

The rate of desulphonation (v_{DS}) is then given by

$$v_{DS} = k'_-h_-[Ar{\cdot}SO_3^-] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

(square brackets implying concentration), and the first-order rate coefficient (k_{DS}) by

$$k_{DS} = v_{DS}/[Ar{\cdot}SO_3H]_{stoich.} = k'_-h_-[Ar{\cdot}SO_3^-]/[ArSO_3H]_{stoich.} \quad . \; . \quad (4)$$

[In these expressions h_- (where $-\log h_- = H_-$) must be used [2] rather than h_0, since the base involved in the pre-equilibrium is negatively charged. However, the distinction between h_0 and h_- may in practice be relatively unimportant.[7]] The experimentally observable form of the relation between reaction velocity and acidity will depend on the extent to which the sulphonic acid is converted into the sulphonate ion in the media in question. The extent of this conversion is governed by equation (5) and therefore depends on the values

$$[Ar{\cdot}SO_3H]/[Ar{\cdot}SO_3^-] = h_-/K^a_{Ar{\cdot}SO_3H} \quad . \; . \; . \; . \; . \; . \quad (5)$$

of h_- and of the dissociation constant $K^a_{Ar{\cdot}SO_3H}$ of the sulphonic acid. According to equation (4), if $[Ar{\cdot}SO_3^-] \gg [Ar{\cdot}SO_3H]$ and therefore $[Ar{\cdot}SO_3^-] \sim [Ar{\cdot}SO_3H]_{stoich.}$, then k_{DS} should be proportional to h_-, or

$$v_{DS} = k'_-h_-[Ar{\cdot}SO_3H]_{stoich.} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

If, on the other hand, $[Ar{\cdot}SO_3H] \gg [Ar{\cdot}SO_3^-]$ and therefore $[Ar{\cdot}SO_3H] \sim [Ar{\cdot}SO_3H]_{stoich.}$ then k_{DS} should be independent of the solvent acidity, or

$$v_{DS} = k_-[Ar{\cdot}SO_3H]_{stoich.} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where $k_- = k'_- \, . \, K^a_{Ar{\cdot}SO_3H}$.

Aromatic sulphonic acids are fairly strong acids but, on the basis of structural analogies, would be expected to be appreciably weaker than sulphuric acid. The rate of desulphonation might therefore be expected to follow h_- (or h_0) in sulphuric acid solutions of low acidity, but to increase less steeply when h_0 becomes comparable in magnitude with $K^a_{Ar{\cdot}SO_3H}$. This expectation appears to be realised in practice. Crafts's work [8] on the desulphonation of *p*-xylenesulphonic acid in aqueous hydrochloric acid at 140° shows that the rate follows h_0 over a range of values [$H_0 = -0{\cdot}4$ to $-2{\cdot}4$ (at 25°)], it being assumed that h_0 at 140° is proportional to h_0 at 25° (Fig. 1). Some other data in the literature concerning desulphonation [9, 10] relate to sulphuric acid as solvent and to much higher acidities. In agreement with expectation, the increase in reaction velocity with solvent acidity is less steep in these

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[7] Brand, Horning, and Thornley, *J.*, 1952, 1374.

[8] Crafts, *Bull. Soc. chim. France*, 1907, **1**, 917.

[9] Pinnow, *Z. Electrochem.*, 1915, **21**, 380; 1917, **23**, 243.

[10] Lantz, *Bull. Soc. chim. France*, 1935, **2**, 2092.

media, and the results can be quantitatively reconciled with the proposed mechanism by assuming reasonable values ($K^{a}_{\mathrm{Ar\cdot SO_3H}} \sim 10^3$ for quinolsulphonic acid) for the dissociation constants of the sulphonic acids concerned. The experimental evidence is therefore compatible with a mechanism analogous to that which we have advanced for hydrogen exchange, involving a rapid acid–base pre-equilibrium, the actual species undergoing substitution being the sulphonate ion.

The rate of desulphonation is related to that of sulphonation through the corresponding equilibrium constant K. If the sulphonate ion is involved in the way suggested, and v_{DS} is given by equation (6) or (7) as

$$v_{\mathrm{DS}} = k_{-}[\mathrm{Ar{\cdot}SO_3H}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

then, since

$$K = \frac{k_{+}^{\circ}}{k_{-}^{\circ}} = \frac{(\mathrm{Ar{\cdot}SO_3H})}{(\mathrm{ArH})(\mathrm{SO_3})} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

(where $k_{+}^{\circ}/k_{-}^{\circ} = k_{+}f_{\mathrm{Ar\cdot SO_3H}}/k_{-}f_{\mathrm{SO_3}}\cdot f_{\mathrm{ArH}}$)

$$v_{\mathrm{S}} = k_{+}[\mathrm{ArH}][\mathrm{SO_3}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

or

$$v_{\mathrm{S}}/[\mathrm{ArH}] = k_{\mathrm{S}} = k_{+}[\mathrm{SO_3}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

(In these expressions parentheses imply activities and the f's represent activity coefficients.)

It therefore follows, from the proposed mechanism for desulphonation, that the first-order rate constants for sulphonation (in excess of acid) will be proportional to the concentration of SO_3 present and, from the principle of microscopic reversibility, that SO_3 will be the only sulphonating agent operating.

The rate coefficients k_{+} and k_{-} will be subject to medium effects, which can be represented by the Brönsted–Bjerrum equation :

$$k_{-} = k_{-}^{\circ}f_{\mathrm{Ar\cdot SO_3H}}/f_{\mathrm{X}}$$

$$k_{+} = k_{+}^{\circ}f_{\mathrm{SO_3}}f_{\mathrm{ArH}}/f_{\mathrm{X}}$$

where f_{X} is the activity coefficient of the transition state of the reaction. The magnitude of these medium effects cannot be predicted from existing data, but the fact that recognisable proportionality with species concentrations has been found for the rates of reactions in aqueous sulphuric acid media of varying composition [11] encouraged us to examine the rate of aromatic sulphonation in this solvent as a function of acid concentration. It was hoped to discover in this way whether the conclusion, based on a consideration of our proposed mechanism for the desulphonation reaction, that sulphonation involves attack on the aromatic molecule by SO_3, is tenable.

Cowdrey and Davies [12] were the first to attempt a correlation between sulphonation velocity and acid concentration in terms of the concentrations of the chemical species present in sulphuric acid–water mixtures. In the absence, at that time, of information on the chemical composition of such mixtures, these authors made certain simplifying assumptions about the chemical equilibria present in these media. The most serious of these, as far as the conclusions about sulphonation in aqueous sulphuric acid are concerned, was their implicit assumption that the concentration of the species H_2SO_4 would remain constant throughout the concentration range 92—99% sulphuric acid. Although it is now clear that this particular assumption is incorrect,[13] it is not possible to allow for it entirely by reference to the recent data on the composition of aqueous sulphuric acid [14] because of the high temperature used by Cowdrey and Davies. An unambiguous analysis of their rate measurements does not seem possible at present.

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[11] *E.g.*, Lowen, Murray, and Williams, *J.*, 1950, 3318; Bonner, Bowyer, and Williams, *J.*, 1952, 3274.

[12] Cowdrey and Davies, *J.*, 1949, 1871.

[13] Young, *Record of Chem. Progress*, Spring issue, 1951, 81.

[14] Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244.

The measurements now reported relate to the rate of sulphonation of benzene in dilute homogeneous solution in aqueous sulphuric acid over the concentration range 77·5—87·6 wt. %. In addition to their interest in the present connection, the data amplify a previous statement [1b] that sulphonation did not interfere with our kinetic measurements of deuterium exchange between benzene and aqueous sulphuric acid, although in agreement with earlier work on heterogeneous hydrogen exchange between benzene and aqueous sulphuric acid, the rate of sulphonation has been found to increase more rapidly than the rate of exchange as the concentration of acid is raised.

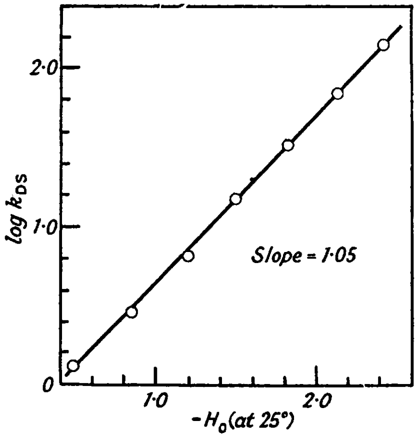

FIG. 1. *Desulphonation of* p-*xylenesulphonic acid in aqueous hydrochloric acid at* 140° (*Crafts*).

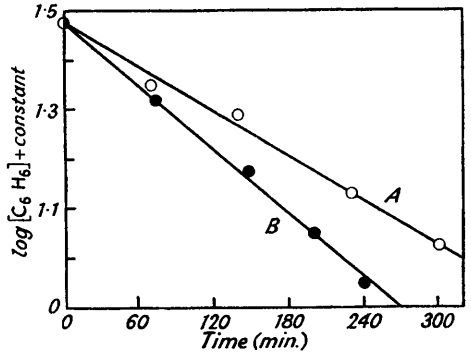

FIG. 2. *Sulphonation of benzene in excess of aqueous sulphuric acid. Specimen first-order plots.*

(*a*) 15·43M-H_2SO_4. (*b*) 15·71M-H_2SO_4.

EXPERIMENTAL

General Procedure.—Benzene was dissolved in various sulphuric acid–water mixtures. After various periods of time the unchanged hydrocarbon was equilibrated with a definite amount of a suitable C_6H_5D–C_6H_6 mixture. The composition of the resulting mixture was determined by infrared analysis [1b] from which the amount of C_6H_6 remaining in the acid was calculated. We found it impossible with our equipment to analyse C_6H_5D–C_6H_6 mixtures accurately by using a band characteristic of the species C_6H_6, as there is none sufficiently free from overlap with bands found in C_6H_5D. Further, benzene is sparingly soluble in aqueous sulphuric acid, and it is also necessary to add a sufficient amount of the C_6H_5D–C_6H_6 mixture to permit phase separation. For these reasons the accuracy of the analytical method is not high. The quoted rate constants have limits of error of the order of ±20%. From the point of view of the general dependence of sulphonation rate on acid composition, the large range of velocities measured makes this error in the absolute values of the individual rate constants of minor importance.

Detailed Procedure.—Measured samples (~0·30 ml.) of " AnalaR " benzene were dissolved in samples (400 ml.) of a given sulphuric acid–water mixture contained in flasks fitted with ground-glass stoppers and having an additional sealing of Apiezon " Q compound." Four or five samples were used for each acid–water mixture, and altogether eight different acid–water mixtures were studied covering the range 77·5—87·6 wt. % (13·43—16·09M).

After an appropriate period in a thermostat at 25°, a flask was opened, the acid mixture diluted with water, and a measured amount (~1·0 ml.) of a C_6H_5D–C_6H_6 mixture of known composition added to its contents, which, after re-sealing of the flask, were agitated for 15 min. The benzene and acid phases were now separated, and the benzene stored over a little calcium chloride and barium carbonate in a sealed flask (5 ml.) and then subjected to isotopic analysis.[1b]

Appreciable desulphonation was shown to be absent in the following manner : (i) the addition of samples of calcium benzenesulphonate to similar acid–water mixtures showed no benzene to be formed even after long periods of time; (ii) the kinetics of sulphonation showed no evidence of the presence of residual benzene remaining in equilibrium when the reaction was followed over many half-lives.

Specimen first-order plots are shown in Fig. 2. The rate constants are collected below.

Stoich. concn. of H_2SO_4 (M) ...	13·43	13·87	14·61	14·68	15·10	15·43	15·71	16·09
$10^5 k_S$ (sec.$^{-1}$)	0·026	0·075	0·65	1·13	2·5	5·7	8·3	32

The monodeuterobenzene was prepared as previously described.[15] The strengths of the acid–water mixtures were determined by titration.

DISCUSSION

In order to test the rate equation (11) for sulphonation in aqueous sulphuric acid, it is necessary to express the unknown concentration of SO_3 in terms of known concentrations of other species. By considering the equilibrium

$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

(with an equilibrium constant K_H) we obtain

$$[SO_3] = [H_2SO_4]f_{H_2SO_4}/K_H(H_2O)f_{SO_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and hence, from (11),

$$k_S = k_+[H_2SO_4]f_{H_2SO_4}/K_H(H_2O)f_{SO_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Values for the activity of water in aqueous sulphuric acid can be derived from data in the literature, as previously reviewed.[14, 16] In the evaluation of $[H_2SO_4]$, two approaches seem possible. In the first place, we may refer to the concentrations of various chemical species in the acids as derived from direct measurements of Raman spectra.[13] Unfortunately, the existing measurements are comparatively inaccurate for $[H_2SO_4]$ in the region of interest in the present study. We have, therefore, used instead the indirectly obtained mass-law equation :

$$[H_3O^+][HSO_4^-]/[H_2O][H_2SO_4] = 50 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which appears to lead to a consistent picture of the composition of sulphuric acid above 75% by weight.[14] If equation (14) represents the rate of sulphonation of benzene, the rate constant k_S should be proportional to $[H_2SO_4]/[(H_2O)$, provided that the ratio $f_{H_2SO_4}/f_{SO_3}$ stays reasonably constant. Because of the large range of rates covered, the concentration dependence of the velocity of sulphonation is more clearly tested by logarithmic graphs. Curve I (Fig. 3) is a graph of $\{\log [H_2SO_4]/(H_2O) + \text{Constant}\}$ against the weight percentage of sulphuric acid in the solvent, and the circles represent the experimental points of ($\log k_S$ + Constant), the additive constants in these two quantities being adjusted so as to make the functions meet at the lowest point. The discrepancy between the experimental points and curve I is clearly appreciable and, if the proposed mechanism and manner of calculation of $[H_2SO_4]/(H_2O)$ are correct, it implies that the term $\log (f_{H_2SO_4}/f_{SO_3})$ increases by $\sim$0·7 unit on going from 77·5 to 87·6% acid.

Nothing is known at present about the activity coefficients of H_2SO_4 and SO_3 in aqueous sulphuric acid. However, we may perhaps take the ratio of the activity coefficients of another pair of solutes whose molecular formulæ differ only by the elements of water, as a rough guide to the direction in which $f_{H_2SO_4}/f_{SO_3}$ may be expected to vary. As one of us has shown,[17] the difference between the acidity function J_0 and certain approximations to J_0 may be used to evaluate certain combinations of activity coefficients in aqueous sulphuric acid. In particular, the result [17] that :

$$J_0 - J_0' = \log (f_B f_{R^+}/f_{BH^+} f_{ROH}) \approx -\log (f_{ROH_2^+}/f_{R^+}) \quad . \quad . \quad . \quad (16)$$

where J_0' is a certain approximation to J_0, is of interest in the present connection, since R^+ and ROH_2^+ are two solutes related to each other in the required manner. [For the

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[15] Bryce-Smith, Gold, and Satchell, *J.*, 1954, 2743.
[16] Gold and Hawes, *J.*, 1951, 2102.
[17] Gold, *J.*, 1955, 1263.

acidity range considered R = $(NO_2{\cdot}C_6H_4)_3C$.] Two independent sets of experimental data [18, 19] are available which give the values of J_o and, according to both, $f_{ROH_2^+}/f_{R^+}$ increases as the proportion of sulphuric acid in the solvent rises. The discrepancy between the experimental points and curve I could thus appear to be in the right direction. Unfortunately, the two sets of data show a marked and puzzling quantitative disagreement over the particular range of interest. According to the data of Williams *et al.*,[11] $\log f_{ROH_2^+}/f_{R^+}$ increases by about 0·7 unit between 77·5 and 81·6% H_2SO_4, but according to those of Deno *et al.*[19] the increase amounts to only 0·1 unit. It is tempting to choose the set of data which gives the difference of 0·7 unit, since this is precisely the change we wish to ascribe to $f_{H_2SO_4}/f_{SO_3}$, but at the moment there does not appear to be any other reason for preferring this set, and in any case an exact parallelism between $f_{H_2SO_4}/f_{SO_3}$ and $f_{ROH_2^+}/f_{R^+}$ is hardly to be expected. Curve II (Fig. 3), which is seen to pass through the experimental points, is, however, a plot, based on Williams's data,[18] of $\{\log [H_2SO_4]/(SO_3) + J_o' - J_o +$ Constant$\}$, and, although we do not wish to over-stress the significance of this close fit, it seems to us that the experimental data are compatible with the mechanism outlined.

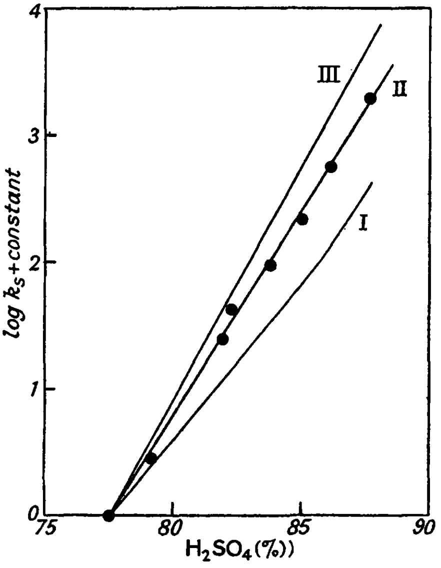

FIG. 3. *Dependence of sulphonation velocity for benzene on acid composition.*

I, $Y = \log \{[H_2SO_4]/(H_2O)\}$ + Constant.
II, $Y = \log \{[H_2SO_4]/(H_2O)\} + J_o' - J_o$ + Constant.
III, $Y = \log \{h_o[H_2SO_4]/(H_2O)\}$ + Constant.
●, Experimental points ($\log k_S$ + Constant).

We shall now examine whether the data are sufficiently diagnostic to rule out other mechanisms for sulphonation.

If the attacking entity were SO_3H^+, the rate constant of sulphonation would be given by:

$$v_S/[ArH] = k_S = k_+'[SO_3H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which is analogous to (11). If we assume that the concentrations of SO_3 and SO_3H^+ are related to each other through Hammett's acidity function, the equation (17) becomes

$$k_S = k_+'[SO_3]h_o/K^a_{SO_3H^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where $K^a_{SO_3H^+}$ is the acidity constant of SO_3H^+. Substituting for $[SO_3]$ from (13), we find

$$k_S = \frac{k'_+}{K^a_{SO_3H^+}K_H} \cdot h_o \cdot \frac{[H_2SO_4]}{(H_2O)} \cdot \frac{f_{H_2SO_4}}{f_{SO_3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

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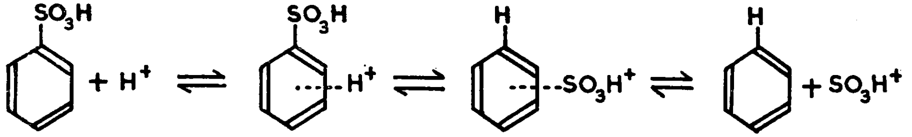
[18] Murray and Williams, *J.*, 1950, 3322; Williams and Bevan, *Chem. and Ind.*, 1955, 171.

[19] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044; cf. *idem*, *J. Org. Chem.*, 1954, **19**, 155.

The function $h_0[H_2SO_4]/(H_2O)$ can now be calculated as before. Its logarithm (+ Constant) is plotted in curve III (Fig. 3), and is seen to increase more steeply with acid concentration than the experimental points. However, the divergence of these points from curve III is no more marked than their divergence from curve I; but, as we have seen, it seems likely that $f_{H_2SO_4}/f_{SO_3}$ increases with sulphuric acid concentration and this will accentuate the disagreement for curve III, whereas it reduces it for curve I. For this reason equation (14) appears preferable to equation (19). The mechanism on which equation (19) is based (involving attack by SO_3H^+) could be written, together with its



(20)

reversal, as in (20). This mechanism requires the velocity of desulphonation in 77·5—87·6% sulphuric acid to be proportional to h_0, since in this region one expects $[Ar{\cdot}SO_3H]$ to be $\gg$ $[Ar{\cdot}SO_3^-]$. The experimental data do not entirely rule this out. A further requirement of the mechanism is that the rate of electrophilic attack on the sulphonic acid is more important than the attack on the sulphonate ion which is present in much lower concentration. This again is conceivable but seems unlikely, on intuitive grounds, over the particular range of acidities. In solutions of higher acidity (such as oleum) it may be expected that the mechanism (20) would assume greater importance since, with increasing acidity, the concentration of sulphonate ions will progressively fall and that of SO_3H^+ ions will rise. Accordingly, we do not regard our conclusions as incompatible with those of Brand and Horning,[20] according to whom SO_3H^+ is the active sulphonating species in oleum.

A number of other mechanisms for sulphonation have recently been considered. According to these, the sulphonation reaction and its reversal are to be written

$$H_3SO_4^+ + ArH \rightleftharpoons Ar{\cdot}SO_3H + H_3O^+ \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$S_2O_6 + ArH \rightleftharpoons Ar{\cdot}SO_3H + SO_3 \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$H_2S_2O_7 + ArH \rightleftharpoons Ar{\cdot}SO_3H + H_2SO_4 \quad . \quad . \quad . \quad . \quad (23)$$

$$HS_2O_7^- + ArH \rightleftharpoons Ar{\cdot}SO_3^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad (24)$$

Schemes (21) and (22) seem to be incompatible with experimental results on desulphonation in requiring the rate to be proportional to the concentration of either H_3O^+ or SO_3. Schemes (23) and (24) predict a concentration-dependence for sulphonation which, over the range studied by us, is almost indistinguishable from schemes (1) and (20) respectively, and we have no direct experimental grounds for rejecting them. Our reason for not putting them forward as probable alternative mechanisms is entirely based on the postulated analogy between desulphonation and dedeuteration, discussed on p. 1936, and would be void if this analogy should later be found to be incorrect. For the same reason we have not explicitly considered the termolecular mechanisms discussed by Cowdrey and Davies.[12]

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[20] Brand, *J.*, 1950, 997; Brand and Horning, *J.*, 1952, 3922