570. *Conductometric Investigation of Kinetics of Reactions in* 100% *Sulphuric Acid. Part I. The Decomposition of Oxalic Acid at* 25°.

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The potentialities of the conductometric method for the study of reaction rates in 100% sulphuric acid are outlined. The method has been applied to the decomposition of oxalic acid at 25°, for which kinetic data obtained by permanganate titration are available. Conductivities of solutions increase with time, because a weak base, oxalic acid, decomposes to give a strong base, water. From the initial conductances (values extrapolated to $t = 0$), the first basic ionisation constant of oxalic acid, $K_1^{25} = 1{\cdot}0 \times 10^{-3}$, has been obtained. By using this constant, the concentrations of undecomposed oxalic acid at given times were calculated from the conductivities of solutions, and it was shown that the rate of decomposition is proportional to the concentration of diprotonated oxalic acid, $(CO_2H_2)_2^{2+}$, in agreement with the conclusion reached from a plot of Lichty's rate constants against the Hammett acidity function, H_0.

Although conductometric studies of solutions of a large number of solutes in sulphuric acid have been numerous since the turn of the century, kinetic applications of conductance measurements in 100% sulphuric acid are of recent date.[1] The cryoscopic method, which has also been widely used for the study of solutions in sulphuric acid, was applied to kinetics of reactions somewhat earlier.[2] It has recently been shown [3] possible to estimate accurately, from the conductance of solutions of bases in sulphuric acid, the concentrations of the highly conducting HSO_4^- ions, and this opens wide possibilities for kinetic application of conductometric measurements to reactions in sulphuric acid in the 100% range.

For the cryoscopic method to be applicable, the change in the number of kinetically distinct particles in the course of the reaction is essential, whereas for the conductivity of a solution to change in the course of a reaction there must be a change in the concentration of the highly mobile solvent self-ions, HSO_4^- and $H_3SO_4^+$. Most reactions which result in a change of the number of particles in solution would also involve a change in the concentration of the solvent self-ions [4] and therefore could be studied by both the cryoscopic and the conductometric method. The latter would, however, be more convenient in such cases because the reaction mixture remains undisturbed at constant temperature.

Apart from these, other methods have been used to follow rates of reaction in aqueous sulphuric acid up to 100% and in oleums, *e.g.*, gas volumetric (when gases are evolved), chemical analysis or isolation of reactants or products after dilution with water, and the spectrophotometric method. The usual advantages that the conductometric method has over methods which involve sampling of the solution are even more pronounced for solutions in concentrated sulphuric acid, because secondary changes in reactants or products may take place when solutions are poured on ice before analysis. Moreover, the conductance of solutions in sulphuric acid gives information about the ionisation of reactants and products at any time in the course of the reaction, which is essential for the understanding of mechanism. The only other method which can also give such information is the spectrophotometric method, and its use for reactions in concentrated sulphuric acid and in oleum has been expanding steadily.[5]

There are several types of reactions, both organic and inorganic, that could be studied

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[1] Liler and Kosanović, *J.*, 1958, 1084.

[2] Leisten, *J.*, 1956, 1572.

[3] Liler, *J.*, 1962, 4272.

[4] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

[5] Brand, *J.*, 1950, 1004; Brand and Horning, *J.*, 1952, 3922; Vinnik, Ryabova, and Chirkov, *Zhur. fiz. Khim.*, 1959, **33**, 1992, 2677; Kilpatrick, Meyer, and Kilpatrick, *J. Phys. Chem.*, 1960, **64**, 1433; March and Henshall, *ibid.*, 1962, **66**, 840.

conductometrically. When the reactant is a weak base and the product a strong base, or when several basic species are produced from a single basic molecule, there will be an increase of conductivity with time. On the other hand, when water is abstracted from the solvent by the reactant, the highly mobile HSO_4^- ions are replaced by the much less mobile $HS_2O_7^-$ ions, and conductivity falls with time (see, *e.g.*, ref. 1). Reactions between two solutes can also be studied if they lead to a change in the concentration of solvent self-ions.

To illustrate the use of the method, the well-known decomposition of oxalic acid was studied, namely,

$$(CO_2H)_2 = CO + CO_2 + H_2O \qquad (1)$$

Lichty's careful measurements [6] of the rate of this reaction by permanganate titration could be used for comparison with conductometric results. The rates in oleum solutions were also studied by Wiig gas volumetrically.[7] The plot of the logarithm of Lichty's rate constants against H_0 led Hammett [8] to suggest that it was the diprotonated oxalic acid which was unstable. However, as Long and Paul [9] pointed out, this plot is actually curved over extended regions of H_0. In any case, the diagnostic value of the slopes of plots of log k against H_0 is now under revision.[10] It was of interest, therefore, to find what information about this reaction could be obtained from a conductometric study of its rate, which is possible because oxalic acid is only incompletely ionised in sulphuric acid [11,12] whereas water is a strong base.[13]

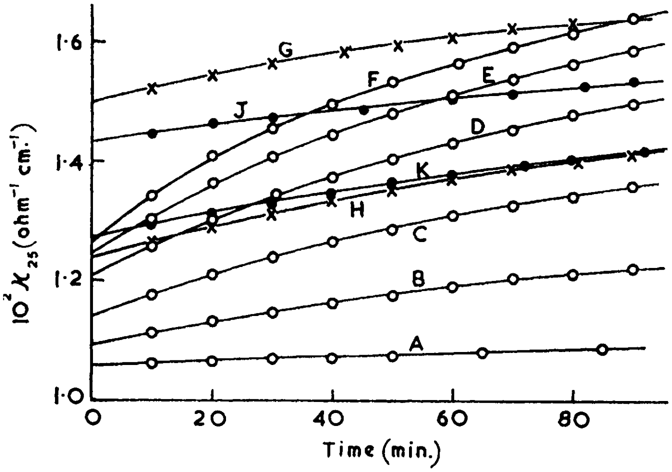

FIG. 1. Changes of conductivity with time in solutions of oxalic acid in sulphuric acid. Concentration of oxalic acid in mole $l.^{-1}$: A, 0·0265; B, 0·0717; C, 0·138; D, 0·221; E, 0·288; F, 0·338; G, 0·0669, +0·081 mole $l.^{-1}$ of $KHSO_4$; H, 0·0889, +0·034 mole $l.^{-1}$ of $KHSO_4$; J, 0·0935, +0·069 mole $l.^{-1}$ of H_2O; K, 0·1028, +0·046 mole $l.^{-1}$ of H_2O.

RESULTS

The results of conductometric measurements at 25° are given in Fig. 1, in which the conductance is plotted as a function of time for several oxalic acid solutions in pure 100% sulphuric acid, as well as in solutions containing some water or some potassium hydrogen sulphate. In

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[6] Lichty, *J. Phys. Chem.*, 1907, **11**, 225; Bredig and Lichty, *Z. Elektrochem.*, 1906, **12**, 459.

[7] Wiig, *J. Amer. Chem. Soc.*, 1930, **52**, 4737.

[8] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 284.

[9] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[10] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

[11] Oddo and Casalino, *Gazzetta*, 1917, **47**, II, 200.

[12] Wiles, *J.*, 1953, 996.

[13] Flowers, Gillespie, Robinson, and Solomons, *J.*, 1960, 4327.

calculating the concentrations of these solutions in moles l.$^{-1}$ from the weight concentrations (molons), the densities of the solutions were assumed equal to that of pure sulphuric acid.

DISCUSSION

Ionisation of Oxalic Acid in 100% Sulphuric Acid.—In order to interpret the changes of conductivity with time, it was first necessary to obtain information about the ionisation of oxalic acid in 100% sulphuric acid. The only experimental result so far available in that respect comes from cyroscopic investigations of Oddo and Casalino[11] and of Wiles,[12] who could find only an approximate value of the van't Hoff's factor, $i = 1{\cdot}3$, owing to decomposition. This suggests that oxalic acid ionises as a simple base to the extent of about 30%. It has also been found, by phase-diagram studies,[14] that higher dicarboxylic acids form hydrogen-bonded complexes with sulphuric acid in the molar ratio 1 : 2 (*i.e.*, one sulphuric acid molecule per carboxyl group). Hence, it is reasonable to assume that a hydrogen-bonded complex of oxalic acid with two sulphuric acid molecules represents the first stage in its protonation:

$$(CO_2H)_2 + 2H_2SO_4 \rightleftharpoons (CO_2H)_2,2H_2SO_4 \rightleftharpoons$$
$$HO_2C{\cdot}CO_2H_2^+,H_2SO_4 + HSO_4^- \rightleftharpoons (CO_2H_2)_2^{2+} + 2HSO_4^- \qquad (2)$$

The solvated monoprotonated oxalic acid and the diprotonated acid are obtained by dissociation of this complex.

The degrees of ionisation of oxalic acid in sulphuric acid can be obtained accurately from the conductivities in Fig. 1, extrapolated to zero time, by using the conductometric method for the determination of basic strength of weak bases, which was shown to give results in agreement with spectrophotometric determinations.[3] The extrapolation to zero time introduces some uncertainty, but this would not be large, especially for the more dilute solutions, where the dissolution of added oxalic acid was fast and the change of conductivity with time was slow. The results of the calculation are given in Table 1.

TABLE 1.

First basic ionisation constant of oxalic acid in 100% sulphuric acid from conductivities at zero time.

c_w (mole l.$^{-1}$)	$10^2\kappa_{25}$ (ohm^{-1} cm.$^{-1}$)	c_0 (mole l.$^{-1}$)	c_s (mole l.$^{-1}$)	α	10^3K_1
0·0717	1·094	18·43	0·024	0·33	1·13
0·1375	1·140	18·23	0·039	0·28	1·14
0·221	1·199	18·00	0·052	0·24	1·07
0·288	1·241	17·79	0·059	0·21	0·97
0·338	1·271	17·64	0·063	0·19	0·92
0·363	1·283	17·58	0·065	0·18	0·90

K_1 (mean) $= 1{\cdot}02 \times 10^{-3}$ (±12%)

This gives first the concentration of the oxalic acid solutions, c_w, their conductance at zero time, κ_{25}, the molarity of " free " sulphuric acid c_0, calculated by assuming a solvation number of 2 for oxalic acid in view of equation (2), the concentration, c_s, of the strong base $KHSO_4$ in solution in a sulphuric acid–sulphuryl chloride mixture having the same conductivity and the same molarity of " free " sulphuric acid as the oxalic acid solution the degree of ionisation $\alpha = c_s/c_w$, and finally K_1, calculated for simple basic ionisation as described before,[3] by using the definition:

$$K_1 = \frac{\alpha}{1 - \alpha} \cdot \frac{c_-}{c_{H_2SO_4}}. \qquad (3)$$

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[14] Tutundžić, Liler, and Kosanović, *Bull. Soc. chim. Beograd*, 1954, **19**, 549.

Here $c_{H_2SO_4}$ is the total molarity of sulphuric acid and c_- is the concentration of HSO_4^- ions, obtained from the equation:

$$c_- = \frac{c_s}{2} + \sqrt{\left(\frac{c_s^2}{4} + K_{ap}c_0^2\right)}, \tag{4}$$

with $K_{ap}^{25} = 2{\cdot}3 \times 10^{-6}$. It can be seen from the Table that the degrees of ionisation in the most dilute solutions are in very good agreement with the approximate cryoscopic result, and that the basic ionisation constants obtained over the whole concentration range are reasonably constant.

The constant K_1 was defined and calculated as the first basic ionisation constant of oxalic acid, rather than as the overall basic ionisation constant. This can be justified by the large difference in the basicities of the oxalic acid molecule and the monoprotonated oxalic acid ion. In the light of recent work on the position of protonation of the carboxyl group,[15] the diprotonated oxalic acid ion, $(CO_2H_2)_2^{2+}$, is probably symmetrical, one proton being attached to each of the four oxygen atoms, rather than asymmetrical as assumed by Hammett.[8] The average distance between the charges in this ion must be of the same order as the distance between the charges in the oxalate ion. The symmetry numbers are the same in the two acid dissociations in aqueous solution as in the two basic ionisations in sulphuric acid. Since, moreover, both water and sulphuric acid are solvents of high dielectric constant, it would follow from the Kirkwood–Westheimer theory[16] that the ratio of the first and the second basic ionisation constant of oxalic acid in sulphuric acid should be of the same order as the ratio of the first and the second acid dissociation conconstant of oxalic acid in aqueous solution, which is approximately 10^3. The second basic ionisation constant of oxalic acid in sulphuric acid would thus be of the order of 10^{-6}, which means that in 100% sulphuric acid the concentration of the diprotonated oxalic acid is very small and the contribution to conductance from the second basic ionisation negligible.

If we use the same method of estimating HSO_4^- concentrations and assume that oxalic acid undergoes complex ionisation:

$$(CO_2H)_2 + 2H_2SO_4 \rightleftharpoons HO_2C{\cdot}CO^+ + H_3O^+ + 2HSO_4^- \tag{5}$$

the calculated equilibrium constant varies by a factor of 5 over the same concentration range. Therefore, complex ionisation is ruled out as the pre-equilibrium in the decomposition of oxalic acid. The pre-equilibrium is simple basic ionisation.

Calculation of Concentrations of Oxalic Acid from Conductance.—Calculation of the rate of the reaction from the conductivity of sulphuric acid solutions is based on the statement that solutions of bases in sulphuric acid, having equal conductivity and equal molarity of " free " sulphuric acid, have also equal concentrations of HSO_4^- and $H_3SO_4^+$ ions. Its correctness is demonstrated by the success of the conductometric determination of basic ionisation constants of weak bases.[3] In the solution of a strong base, we have

$$c_- = c_+ + c_s, \tag{6}$$

where c_- and c_+ are the molarities of the solvent self-ions, HSO_4^- and $H_3SO_4^+$, respectively, and c_s is the molarity of the strong base. In the decomposition of oxalic acid, equation (1), each mole of oxalic acid, a weak base, produces one mole of water, a strong base. Therefore, in the course of the reaction we have:

$$c_- = c_+ + c_{H_2O} + \alpha c_t, \tag{7}$$

where c_{H_2O} is the molarity of water formed (water taken to be a strong base[13]), c_t is the molarity of oxalic acid at time t, and α is its degree of ionisation, which can be obtained from eqn. (3). In order to estimate the molarity of " free " sulphuric acid in solutions

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[15] Ross, Stewart, and Yates, *J. Amer. Chem. Soc.*, 1960, **82**, 4059.

[16] Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, **6**, 506.

in which the reaction proceeds, a solvation number of 2 was taken for water, because of the reaction:

$$H_2O + 2H_2SO_4 = H_3O^+,H_2SO_4 + HSO_4^- \qquad (8)$$

there being good evidence for the solvation of the hydroxonium ion.[17] Since a solvation number of 2 was also assumed for oxalic acid because of reaction (2), the molarity of " free " sulphuric acid was constant in the course of this reaction (possible small changes of density of the solutions were neglected). When the conductivity of an oxalic acid solution, in which the reaction takes place, is equal to that of the solution of a strong base in a solvent mixture of equal molarity of " free " sulphuric acid (conductivities of $KHSO_4$ in sulphuric acid–sulphuryl chloride mixtures [3] were also used here), then the concentrations of solvent self-ions are equal in both solutions, and one obtains from eqns. (6) and (7):

$$c_s = c_{H_2O} + \alpha c_t. \qquad (9)$$

From the equation of the reaction (1) it follows that

$$c_{H_2O} = c_{\text{initial}} - c_t, \qquad (10)$$

where c_{initial} is the initial molarity of oxalic acid in solution. From eqns. (9) and (10) we obtain

$$c_t = (c_{\text{initial}} - c_s)/(1 - \alpha), \qquad (11)$$

where α is calculated from K_1, the first basic ionisation constant of oxalic acid from Table 1. The concentration of undecomposed oxalic acid at various times was calculated in this way for all experiments from Fig. 1, and an example of the calculation for solution D is given in Table 2. In the calculation of the rate in the presence of a strong base (experiments G, H, J, and K in Fig. 1) the concentration of the strong base, c_b, must be added to the right-hand side of equation (9):

TABLE 2.

Calculation of the rate of decomposition of oxalic acid in pure sulphuric acid from conductivities at 25°.

(Data for solution D from Fig. 1.)

Time	$10^2\kappa_{25}$	c_s	c_-		c_t	$-10^4 dc_t/dt$
(min.)	(ohm^{-1} cm.$^{-1}$)	(mole l.$^{-1}$)		α	mole l.$^{-1}$	mole l.$^{-1}$ min.$^{-1}$
0	1·199	0·052	0·064	0·23	0·220	
10	1·256	0·060	0·071	0·21	0·204	13·0
20	1·302	0·066	0·076	0·20	0·193	9·7
31	1·345	0·072	0·081	0·19	0·183	7·5
45	1·389	0·077	0·086	0·18	0·175	5·5
60	1·429	0·082	0·090	0·17	0·168	4·5
90	1·496	0·091	0·098	0·16	0·155	3·4

$$c_s = c_{H_2O} + c_b + \alpha c_t. \qquad (12)$$

The rest of the calculation is the same as for solutions in pure sulphuric acid.

Comparison with Lichty's Results.—This is possible only for the most dilute solution A, whose concentration, 0·0265 mole l.$^{-1}$, is very close to the concentration of Lichty's solutions, 0·025M. It is difficult, however, to assess the zero time of Lichty's experiments. He assumed that the reaction was of first order with respect to oxalic acid, which is nearly true for solutions in sulphuric acid–water mixtures, with more than 0·5% of water, where the amount of water produced in the reaction does not alter the acidity of the solution. In the 100% sulphuric acid range, however, this certainly is not true and his first-order " constants " are far from being constant. On the assumption that the reaction is of the first order, the zero time of the reaction is of no importance and therefore all Lichty's

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[17] Young and Walrafen, *Trans. Faraday Soc.*, 1961, **57**, 34.

solutions were kept at 10° for some unspecified time before being heated to the reaction temperature. After 15 min. at that temperature the first sample was taken for analysis. Lichty's results, together with the results obtained in this work for the solution A, are plotted in Fig. 2. The times for Lichty's experiment are measured from the time when the solution was brought to the reaction temperature. It can be seen that a shift along the time axis of about 10 minutes brings his curve into close agreement with the curve for solution A. This means that the time that Lichty's solution had spent at 10° plus the time taken in the heating are equivalent from the point of view of the progress of the reaction to about 10 minutes at 25°. When the difference in zero time is taken into account, the agreement between the two sets of results, obtained by different methods, is very good.

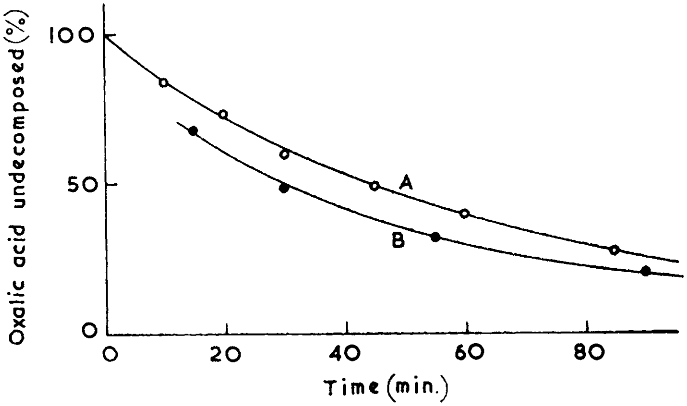

FIG. 2. Comparison with Lichty's results (25°).[6]
A, Solution A, 0·0265 mole l.$^{-1}$.
B, Lichty's solution, 0·0250 mole l.$^{-1}$.

The Rate of Reaction.—The rates of decomposition, $-dc_t/dt$, were obtained from plots of the concentration of undecomposed oxalic acid, c_t, against time. The results obtained for solution D are given in Table 2. To find out whether the monoprotonated or the diprotonated species decomposes, the rates were plotted first against αc_t, the concentration of the monoprotonated species, and the correlation was found not to be linear. The concentration of the diprotonated species cannot be calculated without the knowledge of the second basic ionisation constant, but it is possible to find a quantity proportional to it if the degree of second ionisation is small. For the second ionisation of the base B (here oxalic acid at time t) we have:

$$\underset{\alpha c_t(1-\beta)}{BH^+} + H_2SO_4 \rightleftharpoons \underset{\beta\alpha c_t}{BH_2^{++}} + HSO_4^-, \qquad (13)$$

where β is the degree of second ionisation. The second ionisation constant is given by:

$$K_2 = \frac{\beta\alpha c_t \,.\, c_-}{\alpha c_t(1-\beta)\,.\, c_{H_2SO_4}}. \qquad (14)$$

Since K_2 is of the order of 10^{-6}, β must be very small. For $\beta \ll 1$, we obtain

$$c_{BH_2^{2+}} = \beta\alpha c_t = K_2 \cdot \frac{c_{H_2SO_4}}{c_-} \cdot \alpha c_t. \qquad (15)$$

In a given solution K_2 and $c_{H_2SO_4}$ (total molarity of sulphuric acid) are constant, and the concentration of the diprotonated oxalic acid is proportional to $\alpha c_t/c_-$. This quantity can readily be calculated from the values used in the calculation of c_t (see Table 2). The rates of the reaction were plotted against $\alpha c_t/c_-$ for all solutions in Fig. 3. It can be seen that the points for all the solutions define a single straight line passing through the origin, as should be the case if the diprotonated oxalic acid is the unstable species:

$$-\frac{dc_t}{dt} = k\,.\,c_{BH_2^{2+}} = kK_2\,.\,c_{H_2SO_4}\,\alpha c_t/c_-. \qquad (16)$$

This result is consistent with Hammett's conclusion,[8] reached by the concept of the acidity function. The product of the three constants on the right-hand side of equation (16) is the slope of the line in Fig. 3, and the value obtained is $1{\cdot}9 \times 10^{-3}$ mole l.$^{-1}$ min.$^{-1}$. The rate constant, k, is obtained by dividing this value by $K_2c_{H_2SO_4}$, which is of the order of 18×10^{-6} mole l.$^{-1}$. The rate constant is hence of the order of 100 min.$^{-1}$, and the half-life of the unstable diprotonated species about 0·4 sec. Diprotonated oxalic acid is therefore a highly unstable species, which decomposes probably to the even more unstable carbonium ion $^+H_2O_2C{\cdot}CO^+$. It has recently been shown [18] by isotope techniques that the slow stage in the decompositions of formic, benzyoylformic, and triphenylacetic acid is also probably the carbonium-ion formation, whereas pre-equilibria involve only simple mono- and di-protonated species. Isotopic studies of the decomposition of oxalic acid itself [19] have shown that the breaking of the C–C bond is not rate-determining.

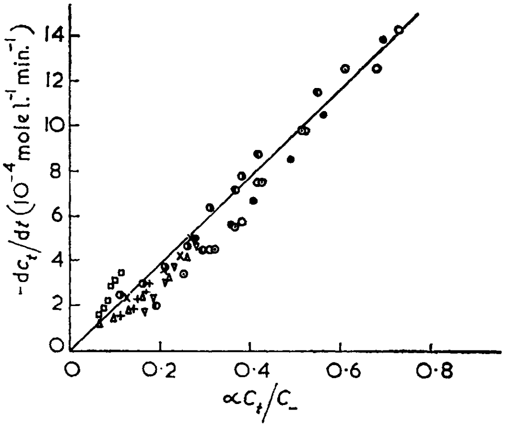

FIG. 3. Rate of decomposition plotted against $\alpha c_t/c_-$, which is proportional to the concentration of diprotonated oxalic acid. Results refer to solutions from Fig. 1: A (△), B (◑), C (◐), D (⊙), E (●), F (○), G (□), H (×), J (+), and K (▽).

In view of the negligibly small concentrations of the diprotonated species in 100% sulphuric acid, which follow from conductometric results, it seems very improbable that a limiting rate of decomposition, reported by Wiig,[7] would be reached in oleum, at an acidity which, according to Brand,[20] is only about one H_0 unit higher than that of pure sulphuric acid. It is more likely that Wiig's results are due to the inadequacy of his gas-volumetric method for fast reactions.

EXPERIMENTAL

Sulphuric acid was prepared as previously described [3] and had a conductivity of $\kappa_{25} = 1{\cdot}044 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$.

Oxalic acid dihydrate (B.D.H. laboratory reagent) was dried at ~80° to reduce sublimation, and was repeatedly ground in order to obtain small crystals which would dissolve rapidly. The anhydrous acid was stored above phosphorus pentoxide.

The solutions were prepared by adding anhydrous oxalic acid, weighed in tightly stoppered, small test-tubes, to weighed amounts of sulphuric acid (30—40 g.) in stoppered conical flasks, kept in a thermostat-bath at 25° ± 0·05°. Dissolution was complete within 1 min. for dilute, and within 2—3 min. for more concentrated solutions. After the addition of oxalic acid, the

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[18] Ropp, *J. Amer. Chem. Soc.*, 1960, **82**, 842.
[19] Fry and Calvin, *J. Phys. Chem.*, 1952, **56**, 897.
[20] Brand, *J.*, 1950, 999.

conical flask was stoppered with a calcium chloride tube, to allow the gases to escape. Since the reaction begins as soon as some oxalic acid is dissolved, and since in any case the major part of the solid dissolved within a minute, the zero time for the reaction was taken to be the time of addition of oxalic acid to the solvent. As soon as dissolution was complete, the solutions were transferred very quickly into an empty conductance cell, also kept in the thermostat-bath, and this was then stoppered with a calcium chloride tube. The first measurement of resistance was made after 10 min. and subsequent measurements at 10-or-more minutes' intervals. Owing to the tendency of sulphuric acid to form supersaturated solutions of carbon monoxide and dioxide, the cell was shaken 1—2 min. before the measurements, to allow all gas bubbles to leave the solution and to achieve a bubble-free narrow part of the conductance cell at the time of the resistance measurement. The narrow part of the cell was always kept at an angle to the horizontal for the same reason. The Jones and Bollinger type of cell was used, but with the two side-tubes joined at the upper end,[21] so that the solution, which only reaches half-way up these tubes, has a considerable mobility within the cell. This is important when the cell is shaken to liberate the gases. The cell constant was 20·24 cm.$^{-1}$, and the electrodes were not platinised. Preliminary tests had shown that carbon dioxide and monoxide, in so far as they dissolve in sulphuric acid, do not affect its conductivity, and that platinum electrodes do not catalyse the reaction, although their surface provides better nucleation centres for bubble formation than do the glass walls of the cell. However, good reproducibility of the results and small scatter of points (see Fig. 1) show that this did not have an adverse effect on the accuracy of measurements, which in any case was no better than 0·1%. The conductance bridge used was described previously.[3]

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[21] Tutundžić and Liler, *Bull. Soc. chim. Beograd*, 1953, **18**, 521.