

**514.** *Acid-catalysed Ether Fission. Part II.<sup>1</sup> Diethyl Ether in Aqueous Acids.*

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The rate of fission of diethyl ether in aqueous sulphuric acid and perchloric acid increases with acid concentration even when the substrate is predominantly protonated. This holds whether the  $pK$  of diethyl ether is  $-3.59$ , as determined by solvent partition,<sup>2</sup> or  $-6.2$ , as suggested by nuclear magnetic resonance (n.m.r.);<sup>3</sup> but vapour-pressure measurements support the former value. The observed variations in rate can be explained by a change of mechanism from *A-2* in dilute acids to *A-1* in more concentrated solutions; other possibilities are also considered.

Dilution of different acids with water results in a marked levelling of their power to cleave ethers. Thus, constant-boiling hydriodic acid is not abnormally potent compared with other aqueous acids of similar acidity. Sulphuric acid and oleum are among the most effective of the anhydrous acids.

THERE is evidence that primary aliphatic ethers are hydrolysed in aqueous acids by the *A-2* mechanism.<sup>4</sup> In particular diethyl ether in perchloric acid up to 5.85M gives typical

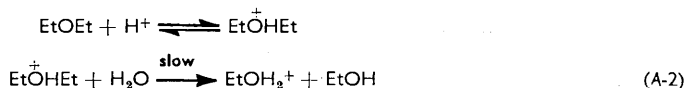
<sup>1</sup> Part I, Jaques and Leisten, *J.*, 1961, 4963.

<sup>2</sup> Atnett and Ching Yong Wu, *J. Amer. Chem. Soc.*, 1962, **84**, 1680.

<sup>3</sup> Edward, Leane, and Wang, *Canad. J. Chem.*, 1962, **40**, 1521.

<sup>4</sup> Burwell, *Chem. Rev.*, 1954, **54**, 615.

A-2 values for the parameters  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$ ,<sup>5</sup> and for Bunnett's  $w$ .<sup>6</sup> For this mechanism it is predictable that the rate should at first increase and then decrease with increasing acid concentration. The maximum should occur in the region where the acidity function of the acid is equal to the  $pK$  of the substrate, for here the acid-catalysis tails off and the change in rate should become dominated by the decreasing availability of water, which is a reactant in the slow step:



This feature is best known for amides,<sup>7</sup> but it has also been observed for esters,<sup>8</sup> and even for an ether of a rather special kind.<sup>9</sup>

The particular intention in the present work was to search for a maximum in the rate of fission of diethyl ether by relatively concentrated solutions of aqueous acids. To help interpret the kinetic results the basic behaviour of diethyl ether was studied by measurements of vapour pressure. Since this study was completed, other workers have proposed two values for the  $pK_a$  —3.59, from solvent partition measurements;<sup>2</sup> and —6.2, from n.m.r. studies.<sup>3</sup>

#### EXPERIMENTAL

*Vapour-pressure Measurements.*—The apparatus consisted essentially of a flask connected to a mercury manometer and to a vacuum line. An ether-sulphuric acid-water mixture of required composition was prepared in the flask and cooled by means of a carbon dioxide-acetone slurry. The apparatus was evacuated, sealed off from the vacuum line, transferred to a constant-temperature bath, and finally returned to the cooling mixture. The pressure was read with a cathetometer after evacuation, again when the system had reached equilibrium in the constant-temperature bath, and lastly after the final cooling (as a precaution against air leakage).

*Kinetic Measurements.*—The reactions were followed by a non-stoichiometric analytical method, but under the conditions described the final titre is proportional to the concentration of fission products even in the presence of unchanged ether. In this respect it is an improvement on the method of Koskikallio and Whalley.<sup>5</sup>

Sulphuric acid solvent (50 ml.) and ether (1 ml.) were mixed in a vessel fitted with a pipette and a magnesium perchlorate guard-tube (to ensure that liquid removed for analysis was replaced by dry air). The solution was quickly brought to the reaction temperature and the flask then transferred to a constant-temperature bath. Samples (5 ml.) were withdrawn at intervals, and each allowed to drain on to a quantity of ice such that the final solution contained 33% by weight of sulphuric acid. This was kept at 95° under a reflux condenser for 2½ hr. to convert ethyl hydrogen sulphate to ethanol, and then made up to 250 ml. with water. (In fact this gave an equilibrium mixture containing 3% of ethyl hydrogen sulphate, which is not oxidised in the next step.) To this solution (10 ml.) was added 1% potassium dichromate (4 ml.), and 98% sulphuric acid (1 ml.) and the mixture was heated for 20 min. in a lightly-closed tube immersed in boiling water. It was then cooled under the tap, 1% potassium iodide (4 ml.) was added, and the solution was left in the dark for 5 min. The liberated iodine was titrated with 0.03N-sodium thiosulphate (titre,  $V$ ).

The final titres ( $V_\infty$ ) for the ten runs that were followed to completion were: 18.5, 18.9, 18.3, 18.5, 18.0, 18.5, 18.65, 19.2, 18.9, 18.6 ml. (The spread of these values can be accounted for by an error of  $\pm 3\%$  in transferring 1 ml. of volatile ether to the reaction flask.) In every case a good first-order plot of  $\log(V - V_\infty)$  against time was obtained. The results for 0.2M-diethyl ether in 98.4% sulphuric acid at 94.7° were as follows:

Titre (ml.)	26.50	25.67	24.47	23.36	22.61	21.22	20.09	19.10	17.99
Time (min.)	0	1.5	4	6.5	9	14	20	30	200
$10^3k$ (min. <sup>-1</sup> )	—	69.0	68.4	71.1	68.0	69.4	70.2	68.9	—

<sup>5</sup> Koskikallio and Whalley, *Canad. J. Chem.*, 1959, **37**, 788.

<sup>6</sup> Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

<sup>7</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 786.

<sup>8</sup> Jaques, Ph.D. Thesis, Sheffield University, 1959; Hall and Jaques, unpublished experiments.

<sup>9</sup> Bunnett and Burcel, *J. Amer. Chem. Soc.*, 1961, **83**, 1117.

The remaining runs were not followed to completion, and values of  $V_{\infty}$  which give the best first-order plots were assumed: these are all in the range 18.25—19.0 ml. For the reaction in 61% sulphuric acid observations made after 4 hr. depart from the first-order law in such a way as to indicate a substantial loss of ether by evaporation. Reliance is placed on the earlier points and an error of  $\pm 20\%$  is indicated in Table 2.

The sealed-tube technique was used for runs involving perchloric acid, and the hydrolysis step in the analysis was omitted.

*Materials.*—Diethyl ether was dried over sodium and fractionally distilled. The concentrations of the acids were determined by titration with anhydrous sodium carbonate. Anhydrous sulphuric acid (of maximal freezing-point) was used as an additional standard.

### RESULTS AND DISCUSSION

*Basicity of Diethyl Ether.*—The relatively low vapour pressures of the solutions at  $36.0^{\circ}$  (Table 1) suggest that in these strongly acid media the ether is largely protonated. The logarithms of these vapour pressures correlate well with the Hammett acidity function,  $H_0$ , which suggests further that the ether behaves as a Hammett base, that Henry's law is obeyed by the unprotonated ether, and that the Henry's law constant does not change greatly with acid concentration. These are necessary conditions for determining the basicity from vapour-pressure measurements.

For the conjugate acid ( $BH^+$ ) of a neutral molecule (B),  $pK_a$  is given by the equation

$$H_0 = pK_a + \log_{10}\{[B]/[BH^+]\} \quad (1)$$

Since in the present case B obeys Henry's law (and  $BH^+$  is obviously involatile):

$$[B]/[BH^+] = p/(p_0 - p) \quad (2)$$

where  $p$  is the observed vapour pressure of diethyl ether and  $p_0$  the vapour pressure which would be observed if all the ether were unprotonated. Combining (1) and (2):

$$H_0 = pK_a + \log_{10}\{p/(p_0 - p)\} \quad (3)$$

Values of  $p_0$  are chosen so as to give linear relations between  $H_0$  and  $\log\{p/(p_0 - p)\}$ . (The values of  $p_0$  are 800 mm. for the first set of results in Table 1, 430 mm. for the second set, and 160 mm. for the third.) The test of this procedure lies in whether the three relations give similar, and plausible, slopes and intercepts. In fact a single line can be drawn through all the points, as shown in Fig. 1, with a slope of 0.83 (the theoretical slope is

TABLE 1.

Vapour pressure of diethyl ether-sulphuric acid-water mixtures.

Temp.	Composition of mixture		Vapour pressure (mm. Hg)			
	Ether (v/v%)	H <sub>2</sub> SO <sub>4</sub> (w/w%)	Total	Water <sup>10</sup>	Ether	— $H_0$ *
36.0°	10	81.1	0.75		0.75	7.10
		77.1	2.75		2.75	6.55
		72.0	10.25	1.32	8.92	5.88
		68.4	23.05	2.64	20.41	5.43
25.6	10	77.1	1.55		1.55	6.55
		68.4	11.95	1.44	10.51	5.43
		58.3	78.0	4.56	73.4	4.29
		70.4	4.40	1.05	3.35	5.68
25.8	3.3	60.2	28.8	3.90	24.9	4.48
		51.6	80.6	7.96	72.6	3.55
		50.0	96.7	8.70	88.0	3.37
		42.7	152.3	12.65	139.7	2.62
		38.7	160.0	14.75	145.2	2.32

\* The mixtures are assumed to have the same values<sup>11</sup> of  $H_0$  as aqueous sulphuric acid containing the same weight % of sulphuric acid.

<sup>10</sup> Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1959, p. 490.

<sup>11</sup> Paul and Long, *Chem. Rev.*, 1957, **57**, 15.

unity) and an intercept of  $-3.53$ . The intercept, according to equation (3), is the  $pK_a$  of the ether oxonium ion.

The satisfactory fit of the results with equation (3) and the close agreement with the  $pK_a$  value from solvent partition measurements ( $-3.59$ ) does not support the suggestion<sup>3</sup> that the interaction between acid and ether in this region is of an indefinite kind, and that the true acid-base equilibrium is centred at  $H_0 = -6.2$ ; a further objection to this suggestion comes from the kinetic results, as will be seen later.

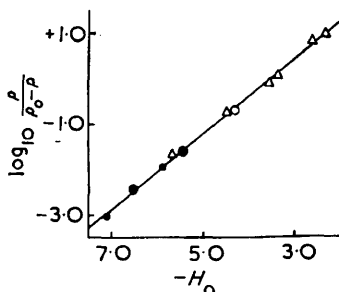


FIG. 1. Relation between the vapour pressure of ether and the Hammett acidity function.

Measurements at  $\circ$ ,  $25.6^\circ$  (Table 1);  $\Delta$ ,  $25.8^\circ$ ; and  $\bullet$ ,  $36.0^\circ$ .

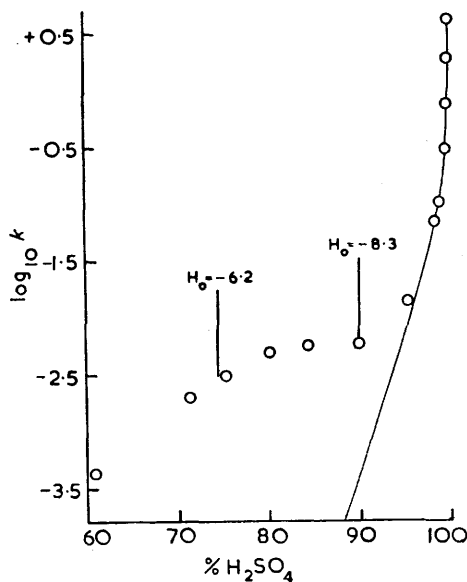


FIG. 2. Effect of acid concentration on the fission of diethyl ether in aqueous sulphuric acid. The points are experimental. The line shows rates of fission by the sulphur trioxide mechanism (see text).

*Rates of Fission in Aqueous Acids of Intermediate Concentration.*—Table 2 shows first-order rate constants for the fission of diethyl ether in sulphuric acid-water mixtures. The four results with 98.4% acid and the five with 80.2% acid give good Arrhenius plots: at 98.4%,  $\log_{10} A$  is  $14.1 \text{ min.}^{-1}$  and  $E$  is  $25.6 \text{ kcal./mole}$ ; at 80.2%,  $\log_{10} A$  is  $14.3 \text{ min.}^{-1}$  and  $E$  is  $27.9 \text{ kcal./mole}$ . The first of these activation energies is used in Fig. 2, which shows the variation in the rate of fission from 61 to 100% sulphuric acid at  $94.7^\circ$ .

The sharp rise in the rate of fission in concentrated sulphuric acid was ascribed in Part I

TABLE 2.

First-order rate constants for the fission of diethyl ether in aqueous sulphuric acid solutions. Ether concentration 0.2M.

Solvent (% $\text{H}_2\text{SO}_4$ )	Temp.	$10^3k$ ( $\text{min.}^{-1}$ )	Solvent (% $\text{H}_2\text{SO}_4$ )	Temp.	$10^3k$ ( $\text{min.}^{-1}$ )	Solvent (% $\text{H}_2\text{SO}_4$ )	Temp.	$10^3k$ ( $\text{min.}^{-1}$ )
100.00	$54.8^\circ$	57.8	98.4	$84.8^\circ$	28.4	80.2	$80.3^\circ$	0.90
99.90	54.8	26.3	98.4	94.7	68.6	80.2	84.9	1.61
99.74	54.8	10.4	95.3	94.7	13.1 †	80.2	89.8	2.63
99.55	54.8	4.20	95.3	94.7	13.7 †	80.2	99.85	7.56
98.91	54.8	1.42	90.0	94.7	5.71	75.4	94.7	3.06
98.4	54.8	1.01	84.4	94.7	5.53	71.4	94.7	1.97
98.4 *	54.8	1.07	80.2	94.7	4.84	61.0	94.7	$0.43 \pm 0.08$
98.4	74.8	9.30						

\* Ether concentration 0.1M. † Duplicate measurements.

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to a mechanism involving sulphur trioxide, because ether fission in this region has close parallels with aromatic sulphonation. For the present purpose it is necessary to determine the contribution made by this mechanism to the rate constants in less concentrated acids. The Arrhenius parameters at 98.4 and 80.2% are too alike to be useful in detecting a point of mechanistic change: kinetic studies have shown, however, that over a wide range of sulphuric acid and water mixtures the rate of aromatic sulphonation varies in a similar way for different substrates,<sup>12</sup> and, assuming that the parallel between sulphonation and ether fission by the sulphur trioxide mechanism persists in more aqueous acid, these results enable us to predict the rate of ether fission by this mechanism from the region (around 100% sulphuric acid) where it has been shown to dominate,<sup>1</sup> to the region of intermediate concentration, as far as 72% sulphuric acid. The predicted rates, shown by the line in Fig. 2, indicate a sharp change of mechanism. In 95.3% sulphuric acid fission occurs mainly by the sulphur trioxide mechanism; yet if the contribution of this mechanism is subtracted from the results in more aqueous acids, the rate constant at 90.0% is reduced by 8% (which lowers the corresponding circle in Fig. 2 by one third of its diameter) and the rate constants measured in more aqueous acids are unaffected. This shows in particular that the shoulder in Fig. 2, extending from 61 to 90% sulphuric acid, is not caused by the superposition of a falling rate due to the *A-2* mechanism and a rising rate due to the sulphur trioxide mechanism.

TABLE 3.

First-order rate constants for the cleavage of diethyl ether in acid solutions.

Solvent: HClO <sub>4</sub> -H <sub>2</sub> O		Solvent: SO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub>		
% HClO <sub>4</sub> .....	60.6      72.2	% SO <sub>3</sub> .....	0.00      0.53      1.24	
Temp. ....	94.7°    94.8°	Temp. ....	25.6°    25.4°    25.4°	
10 <sup>3</sup> k (min. <sup>-1</sup> ) .....	3.11      5.03	10 <sup>3</sup> k (min. <sup>-1</sup> ) .....	0.92      68      250	

*The Mechanism of Fission in Aqueous Acids of Intermediate Concentration.*—Surprisingly, the kinetic results lack concordance with the *A-2* mechanism, which would require a continuous fall in rate from 61 to 90% sulphuric acid if the  $pK_a$  of the oxonium ion were -3.5, or a sharp maximum in the region of 75% sulphuric acid if the  $pK_a$  were -6.2. We have considered three explanations. First, that as the activity of water falls and the activity of hydrogen sulphate ion rises, hydrogen sulphate steadily replaces water as the effective nucleophile. This is an attractive theory because in more dilute solutions the *A-2* mechanism is well supported, and the amount of ethyl hydrogen sulphate produced increases with the acid concentration.<sup>13</sup> However, the superiority of perchloric acid to sulphuric acid observed in more aqueous solutions<sup>5</sup> should then be reversed at higher concentrations, since the perchlorate ion is a particularly weak nucleophile, but the results in Table 3 show that this is not the case. If the comparison is made at equal values of  $H_0$ , the ratio of the rate in perchloric acid to that in sulphuric acid actually increases in more concentrated solutions:

% HClO <sub>4</sub>	% H <sub>2</sub> SO <sub>4</sub>	- $H_0$	Rate ratio
28.4	26.0	1.44	1.61
60.6	67.2	5.30	2.63

(A comparison cannot be made for 72.2% perchloric acid, since the corresponding sulphuric acid is in the region where fission occurs by the sulphur trioxide mechanism.)

A second possibility is suggested by the fact that the rates of *A-1* reactions increase with acid concentration more rapidly than those of *A-2* reactions. Fission by the *A-2* mechanism in dilute solutions could therefore give way to the *A-1* mechanism in more

<sup>12</sup> Cowdrey and Davies, *J.*, 1949, 1871; Gold and Satchell, *J.*, 1956, 1635; Eaborn and Pande, *J.*, 1960, 1480; Kilpatrick, Meyer, and Kilpatrick, *J. Phys. Chem.*, 1960, **64**, 1433; 1961, **65**, 1189; Kilpatrick and Meyer, *J. Phys. Chem.*, 1961, **65**, 530.

<sup>13</sup> Williams and Clark, *J.*, 1956, 1304.

concentrated acids. This occurs for amides<sup>14</sup> and esters,<sup>8</sup> but the rate then passes through a maximum, and the *A-1* mechanism is observed only when the *A-2* reaction rate has fallen considerably. In the present case the *A-2* reaction would be overtaken, as it were, while still increasing with acid concentration, between the ranges of acids studied here and by Koskikallio and Whalley. If the  $pK_a$  is taken to be  $-3.59$ , the Bunnett  $w$  plot<sup>6</sup> from 61 to 90% sulphuric acid is a smooth curve: but the slopes at the extremities (0.0 and  $-1.4$ ) are both within the range expected for an *A-1* reaction. This interpretation cannot therefore be discounted. (The Bunnett  $w$  plot with a  $pK_a$  of  $-6.2$  might be considered as evidence against this value for the basicity of ether. It consists of two horizontal lines with a steep step between them.)

There is a third, and more general, interpretation of these results. When different measurements indicate interactions of a substrate with the solvent in different regions of acidity, as with diethyl ether and acetone,<sup>15</sup> there may be correspondingly complex relations between acid concentration and chemical reactivity. To attribute the acid-catalysis of ether fission to a single acid-base equilibrium centred at an  $H_0$  value of either  $-3.59$  or  $-6.2$ , and to ignore the interaction at the other value, may be too crude a procedure. If this is true, a greater knowledge of the structure of these solutions will be needed to interpret the results.

*The Relative Efficiency of Acid Catalysts in Ether Fission.*—The characteristics of different acids have been summarised by Burwell,<sup>4</sup> but some explanations have necessarily been tentative and further understanding is now possible. One result to be explained is that while hydrogen iodide cleaves ethers much more rapidly than does hydrogen bromide in anhydrous or nearly anhydrous solutions, the aqueous constant-boiling acids are almost equally effective. (The constant-boiling acids under reflux provide the highest reaction temperatures possible without the use of sealed tubes.) With the anhydrous acids equimolar amounts of alcohol and alkyl halide are formed, and it is reasonable to suppose that the relative efficiency of the hydrogen halides depends upon the nucleophilic power of the halide ion,  $X^-$ :



If the same initial products are formed in the constant-boiling acids, as Burwell assumes, the similar efficiency of hydriodic and hydrobromic acid is unexpected. If, on the other hand, the halide ions are not directly involved in the actual fission, the relative reactivity of the aqueous acids can be correctly predicted from the data in Table 4, reaction temperature and acidity being assumed to be the important factors. The hydriodic and hydrobromic azeotropes have similar boiling points and similar values of  $H_0$ : constant-boiling

TABLE 4.

Some data on the hydrogen halide-water azeotropes.

Acid	Molality	B. p.	$-H_0$
Hydrochloric .....	6.94	110°	2.2
Hydrobromic .....	11.30	126	3.7
Hydriodic .....	10.36	127	3.6 ± 0.2 *

\* Estimated from the molality,<sup>16</sup> HI being assumed to be stronger than HBr.<sup>17</sup>

hydrochloric acid, with the lowest boiling-point and acidity, is in fact the least effective for ether fission.

This explanation is consistent with our finding that the hydrogen sulphate ion, even in

<sup>14</sup> Duffy and Leisten, *J.*, 1960, 853.<sup>15</sup> Nagakura, Minegishi, and Stanfield, *J. Amer. Chem. Soc.*, 1957, **79**, 1033; Campbell and Edward, *Canad. J. Chem.*, 1960, **38**, 2109.<sup>16</sup> Bell, "The Proton in Chemistry," Methuen & Co., Ltd., London, 1959, p. 81.<sup>17</sup> Schwarzenbach and Stensby, *Helv. Chim. Acta*, 1959, **42**, 2342.

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quite concentrated solutions of sulphuric acid, plays no direct part in cleaving diethyl ether; and it requires that all acids of similar acidity should cleave aliphatic ethers effectively at 127°. This appears to be true, for a moderate extrapolation of Koskikallio and Whalley's results shows that the fission of diethyl ether in aqueous perchloric acid of  $H_0 = -3.6$  at 127° would be 90% complete in 1.5 hr., and we have already seen that sulphuric acid has a comparable effect to perchloric. A typical procedure for cleaving aliphatic ethers with hydriodic acid recommends boiling for 2 to 3 hr.<sup>18</sup>

The foregoing discussion will suggest modifications to the statement<sup>19</sup> that "...sulphuric acid is not of much use in the cleavage of ethers, probably because of the relatively slight nucleophilic displacing tendency of the bisulfate ion." A better reason why sulphuric acid is not used may be that alcohols and alkyl hydrogen sulphates are harder to isolate than alkyl halides, for aqueous sulphuric acid is effective, and anhydrous sulphuric acid and oleums are extremely effective, for cleaving ethers. The half-life of diethyl ether in 100.3% sulphuric acid (1.24% oleum) is less than 3 minutes at room temperature (see Table 3).

The experiment with 72.2% perchloric acid was carried out by Dr. D. N. Kershaw.

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<sup>18</sup> Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 314.

<sup>19</sup> Ref. 4, p. 632.

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