977. *Acid-catalysed Ether Fission. Part I. A New Mechanism, in Sulphuric Acid.*

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The rates of fission in 99·6% sulphuric acid of 13 alkyl ethers and 4 alkyl aryl ethers have been measured, enabling structural effects on both sides of the breaking bond to be assessed. The variation in rate with the concentration of water and potassium hydrogen sulphate has been studied for two alkyl ethers and one alkyl aryl ether in sulphuric acid containing total solute concentrations of up to 0·3 mole/kg.

The results suggest that alkyl ethers are solvolysed in concentrated sulphuric acid by a previously unsuspected mechanism: the conjugate acid of the ether reacts with sulphur trioxide in a mobile equilibrium to form a complex which, in the rate-determining stage, breaks up into a carbonium ion and an alkyl hydrogen sulphate molecule. The fission of alkyl aryl ethers, however, appears to be a simple *A*-1 reaction. This difference in mechanism is discussed.

MOST ethers are rather resistant to hydrolysis by aqueous acids; and the reaction is not a very easy one to follow by chemical analysis. Consequently there have been few kinetic studies, and there is a dearth of information on which ideas concerning mechanism can be formed.[1] In contrast, much light has been thrown on the hydrolysis of esters and amides by determining, for example, the variation in rate with acid concentration, the effect of substituents in different parts of the molecule, and the dependence of these substituent effects upon the reaction medium.[2] It is hoped in this series to provide some similar information for the hydrolysis (or, more generally, the solvolysis) of ethers, in a wide range of protonic media. The present Part is concerned with the reaction in concentrated sulphuric acid. No kinetic studies have previously been reported.[3]

RESULTS AND DISCUSSION

Cryoscopic Results for Aliphatic Ethers in 99·6% *Sulphuric Acid.*—van't Hoff *i*-factors of 2·0 to 1·4 (Table 1, col. 4) show that aliphatic ethers ionise as strong or moderately strong bases in 99·6% sulphuric acid: the lower values are reasonably associated with incomplete ionisation according to equation (1), since they are found for the more negatively substituted ethers:

$$\mathrm{RR'O + H_2SO_4 \rightleftharpoons RR'OH^+ + HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Solvolysis should lead to approximately four-fold freezing-point depressions, because in this solvent alcohols are converted into alkyl hydrogen sulphates, which behave as non-electrolytes, and water is a strong base:

$$\mathrm{RR'O + 3H_2SO_4 \longrightarrow RHSO_4 + R'HSO_4 + H_3O^+ + HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Table 1 summarises the results obtained by following changes in freezing point with time, at temperatures sufficient to cause fission. First-order rate constants (k_1) were calculated by assuming infinity values (i_∞) of the van't Hoff *i*-factor. The difference between these and the experimentally determined final *i*-factors (in col. 5) are measures of the reliability of the rate constants. The experimental value is generally a little greater than i_∞ because the products of solvolysis are not completely stable: the products from the butyl ethers are so unstable that the rate constants had to be calculated from initial slopes.

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[1] Burwell, *Chem. Rev.*, 1954, **54**, 615.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 751.

[3] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 51.

Constitutional Effects on the Solvolysis of Aliphatic Ethers.—The relative order of rates shown by results 1—10 in Table 1 can be understood on the basis of three ideas. (i) The rate-determining step is a unimolecular fission of the conjugate acid [equation (3)] or of some other complex formed from the solvent and the ether:

$$R\text{—}OH^{+}\text{–}R' \longrightarrow R^{+} + R'OH \qquad (3)$$

(ii) Fission occurs so as to produce the more stable carbonium ion; and this decides which of the two carbon–oxygen bonds will break. (iii) Constitutional effects are greater in the potential carbonium ion than in the remote branch of the ether, but positive or negative inductive effects in the remote branch respectively retard or accelerate the heterolysis.

To apply these principles it is first necessary to decide for each ether which branch can form the more stable carbonium ion. We have taken the order to be: Pr^i > Bu^n > Et > 2-chloroethyl > 2-sulphatoethyl > Me. The first part of the series is straightforward; 2-chloroethyl follows ethyl because the inductive effect of the chlorine atom opposes the dispersal of positive charge; and 2-sulphatoethyl comes later still because the sulphato-group is more strongly electron-attracting than chlorine. On the basis of inductive effects methyl should lie between ethyl and 2-chloroethyl, but for the rather similar heterolysis of acetals and ketals Kreevoy and Taft[4] have shown the importance of hyperconjugation by β-hydrogen atoms: since 2-chloroethyl and 2-sulphatoethyl each have two β-hydrogen atoms to stabilise the carbonium ion and methyl has none it is at least defensible to place methyl last in the series. In Table 1 the groups which should separate as carbonium ions on the basis of this series are designated R, and in order to provide comparable figures (k') for the rate of fission at one carbon–oxygen bond the rate constants for symmetrical ethers have been halved. Ethers 1—5 have the same group R′, and the importance of constitutional effects in R is shown by the large differences required to bring about reaction at a convenient rate (from 25° for methyl n-butyl ether to 90° for methyl ether): the order of rates follows the stability series.

TABLE 1.

Cryoscopic results for aliphatic ethers (RR′O) in 99·6% sulphuric acid.

No.	R	R′	Initial i-factor	Final i-factor	i_∞	Reaction temp.	10^3k_1 (min.$^{-1}$)	k'
1 *	Me	Me	1·80	4·38	4·05	90·0°	3·41	1·70
2 †	$CH_2{\cdot}CH_2{\cdot}SO_4H$	Me	1·4	3·7	4·0	65·0	1·69	1·69
3	$CH_2{\cdot}CH_2Cl$	Me	1·79	4·28	4·15	65·0	3·4 ‡	3·4
4 *	Et	Me	1·90	—	4·11	55·0	13·8	13·8
5	Bu^n	Me	1·93	—	—	25·0	16	16
6	Et	Et	2·00	4·42	4·25	55·0	6·93	3·46
7	Et	$CH_2{\cdot}CH_2Cl$	1·95	—	4·10	55·0	18·8	18·8
8 †	Et	$CH_2{\cdot}CH_2{\cdot}SO_4H$	1·6	—	4·0	55·0	24·2	24·2
9	Bu^n	Bu^n	2·04	—	—	25·0	6	3
10	Pr^i	Pr^i	2·24	4·38	4·25	25·0	40	20
11	$CH_2{\cdot}CH_2Cl$	$CH_2{\cdot}CH_2Cl$	1·56	4·54	4·45	65·0	4·96	2·49
12	$CH_2{\cdot}CH_2Br$	Me	1·82	3·66	3·65	25·8	27·2	27·2
13	$CH_2{\cdot}CH_2Br$	Et	2·02	—	4·00	25·8	4·90	4·90

* For these volatile ethers the i-factors in cols. 4, 5, and 6 are in the correct ratios, but the absolute magnitudes are uncertain.

† The sulphato-ethers were prepared *in situ* from corresponding hydroxy-ethers, a process which produces water. The i-factor for water (1·9) has been subtracted from the observed values.

‡ Derived from a measurement at 70·0° (k = 5·8 × 10^{-3}) by assuming an activation energy of 25 kcal./mole. (This value was found for 2-chloroethyl ethyl ether from measurements in 99·6% H_2SO_4 at four temperatures.)

The effect of substituents in the remote branch, R′, should be purely inductive, and for ethers with the same group R the rate should decrease in the following order of groups R′, without ambiguity: 2-sulphatoethyl > 2-chloroethyl > Me > Et. Ethers 6, 4, 7, and 8

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[4] Kreevoy and Taft, *J. Amer. Chem. Soc.*, 1955, **77**, 5590.

constitute such a series (R = ethyl). The order of rates is that predicted, and the effects are sufficiently small that the whole series can be studied at the same temperature.

Of the remaining ethers di-n-butyl ether reacts more slowly than n-butyl methyl ether as expected, and di-isopropyl ether reacts the fastest of the whole series. Comparison of the results for di-(2-chloroethyl) ether and 2-chloroethyl methyl ether reveals a small anomaly which might be ascribed to a second-order effect, such as the difference in basicity (see Table 1, col. 4). The bromo-ethers on the other hand depart seriously from their predicted behaviour. The Taft σ^* values for chloromethyl and bromomethyl (+1·050 and +1·030) are such that no detectable difference in rate would be forecast for corresponding chloro- and bromo-ethers. In fact, however, the bromo-ethers are much more reactive, and in contrast to the corresponding chloro-ethers 2-bromoethyl methyl ether is cleaved more easily than 2-bromoethyl ethyl ether. Ethyl 2-iodoethyl ether was found to liberate iodine immediately on dissolution. This raises the interesting possibility for the bromo-ethers that some interaction with solvent occurs which greatly modifies the polar character of the bromine atom without actually causing it to separate. These observations clearly require a special explanation: the results in general support our assumption of a rate-determining unimolecular dissociation, and we next consider the nature of the dissociating species.

TABLE 2.

Rates of solvolysis of aliphatic ethers in sulphuric acid containing hydroxonium, potassium, or ammonium hydrogen sulphate.

Diethyl ether at 45·0°.

Molality				10^3k_1
Water	$KHSO_4$	Ether	HSO_4^- *	(min.$^{-1}$)
0·214		0·033	0·247	2·17
0·153		0·033	0·186	3·50
0·074		0·049	0·124	8·13
0·072		0·044	0·117	8·29
0·072		0·029	0·103	10·4
0·074		0·025	0·101	11·1
0·036		0·022	0·062	25·6
0·000		0·063	0·067	27·4
0·000	0·186	0·044	0·230	14·5

Di-2-chloroethyl ethyl ether at 39·0°.

Molality				10^3k_1
Water	$KHSO_4$	Ether	HSO_4^- *	(min.$^{-1}$)
0·230		0·052	0·282	2·64
0·190		0·052	0·242	4·12
0·130		0·052	0·182	6·67
0·064		0·052	0·117	16·0
0·051		0·057	0·109	22·5
0·037		0·054	0·093	31·9
0·000		0·053	0·057	59·8
0·000		0·071	0·074	41·0
0·000	0·145	0·053	0·198	26·1
0·000	0·193	0·052	0·245	23·7
0·000	0·241	0·054	0·295	20·1
0·000	0·086 †	0·056	0·142	35·4

* The sum of the molalities of water, potassium hydrogen sulphate, and ether, with a small correction (maximum 0·004) for the self-dissociation of the solvent (Bass, Gillespie, and Robinson, *J.*, 1960, 821).

† Ammonium hydrogen sulphate.

Variation of Rate with Acid Composition for Aliphatic Ethers.—Rate constants for the solvolysis of ethyl ether and 2-chloroethyl ethyl ether in solutions containing different amounts of water (hydroxonium hydrogen sulphate) and of potassium and ammonium hydrogen sulphate are given in Table 2; and the important features are displayed in Fig. 1. It is clear that in concentrated sulphuric acid the rate of fission of alkyl ethers is very sensitive to hydrogen sulphate concentration, but that it is much more sensitive to hydroxonium hydrogen sulphate (line A) than other hydrogen sulphates (line B). (These solutions contain a significant amount of hydrogen sulphate ion derived from the basic ionisation of the ethers, and the points which define line A actually show the combined effects of large variations in water concentration and small variations in the concentration of hydrogen sulphate ion from the ether. The present results, however, are insufficiently precise to enable us to separate the small effect of the ether from the large effect of water, and for this reason and to simplify discussion we shall refer to these results as though they show the effect of water alone on the rate of fission.)

Since aliphatic ethers exist predominantly as conjugate acid in these solutions the relative concentration of conjugate acid can vary little from one solution to another, and if this were the species undergoing fission the points in Fig. 1 would lie on a horizontal straight line. Suppose next that the doubly protonated ether were the reactive intermediate: by equation (4) the rate would be inversely proportional to the hydrogen sulphate concentration, and Fig. 1 would show a single straight line of unit negative slope.

$$RR'OH^+ + H_2SO_4 \rightleftharpoons RR'OH_2^{++} + HSO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

In seeking other explanations for the observed pattern we noticed a similarity between our results and those obtained by Cowdrey and Davies for aromatic sulphonation in 92—99% sulphuric acid.[5] We therefore carried out experiments in sulphonation in similar solutions to those used in the ether solvolyses and using the same cryoscopic technique. The results (Fig. 2) show definite similarity to those for ether fission, the solutions containing water being associated with sharper rate-dependence than the potassium hydrogen sulphate solutions. Results of this type [5] can be understood if the sulphonating agent is sulphur trioxide (or one of its solvates [6]) for the rate should then be proportional to the concentration of sulphur trioxide formed by dissociation of the solvent, and this dissociation is suppressed more sharply by hydroxonium sulphate than by other hydrogen sulphates:

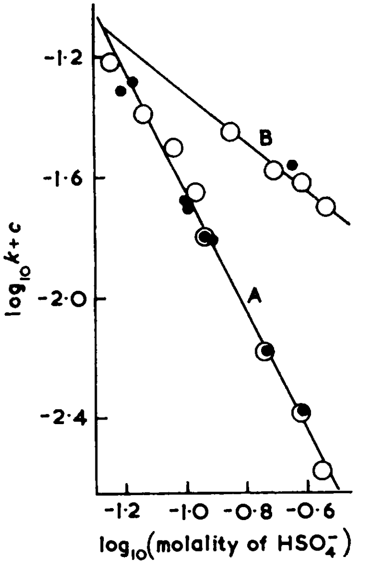

FIG. 1. Effect of hydrogen sulphate concentration on the solvolysis of aliphatic ethers in sulphuric acid.

○ Di-2-chloroethyl ether at 39·0° (c = 0·00).
● Diethyl ether at 45·0° (c = 0·32).
A, hydroxonium hydrogen sulphate.
B, potassium or ammonium hydrogen sulphate.

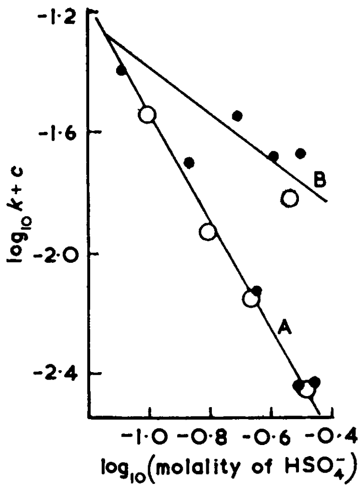

FIG. 2. Effect of hydrogen sulphate concentration on the rate of sulphonation in sulphuric acid.

○ p-Nitrotoluene at 96·5° (c = 0·05).
● Benzylideneacetone at 54·8° (c = 0·00).
A, hydroxonium hydrogen sulphate.
B, potassium hydrogen sulphate.

$$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The same assumption, that the rate is proportional to the concentration of sulphur trioxide, is equally successful in explaining our results on ether fission. If the variations

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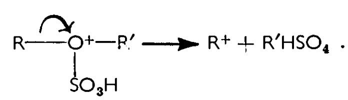
[5] Cowdrey and Davies, *J.*, 1949, 1871.
[6] Ref. 2, p. 300.

in rate are controlled by dissociation (5) the lines in Figs. 1 and 2 for aqueous solutions should have slopes of -2, and the other lines slopes of -1: the observed slopes for sulphonation are $-1{\cdot}80$ and $-0{\cdot}77$ ($\pm 0{\cdot}4$), and for ether fission $-2{\cdot}02$ and $-0{\cdot}81$. The results for sulphonation show greater experimental scatter than those for solvolysis, and they have a limitation similar to that described for the ether results in that the aromatic substrate and the solvent produce a significant concentration of hydrogen sulphate ions. The similar sensitivity of these two reactions to the composition of the solvent is nevertheless apparent, and it is difficult to ascribe it to any factor other than the concentration of sulphur trioxide.

The Mechanism of Solvolysis for Aliphatic Ethers.—In concentrated sulphuric acid ether fission appears to be a unimolecular process, but the overall rate is proportional to the concentration of sulphur trioxide. To reconcile these conclusions we propose a two-step mechanism: a pre-equilibrium (6) which accounts for the solvent effects, and a heterolysis (7) on which the observed constitutional effects depend:

$$RR'OH^+ + SO_3 \rightleftharpoons RR'SO_4H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$



$$R{-}\underset{SO_3H}{\overset{\curvearrowright}{O^+}}{-}R' \longrightarrow R^+ + R'HSO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The carbonium ion formed by the heterolysis unites rapidly with a hydrogen sulphate ion.

The pre-equilibrium is so sensitive to solvent composition that one may reasonably consider solvent effects on the heterolysis to be negligible by comparison: on the other hand, constitutional effects on the pre-equilibrium are probably small (since it is difficult even to predict their direction) and so the observed effects of substituents are virtually those exerted on the heterolysis.

If the pre-equilibrium lay to the right-hand side, the ethers would produce a four-fold depression of the freezing point:

$$RR'O + 3H_2SO_4 \longrightarrow RR'HSO_4^+ + H_3O^+ + 2HSO_4^-$$

It is clear from the cryoscopic results that the sulphur trioxide complexes can only be formed in fractional amounts, and it is interesting to consider why fission occurs through these intermediates rather than the conjugate acids which are the predominant species. The fission of a sulphur trioxide complex produces a carbonium ion and an alkyl hydrogen sulphate which is stable, whereas the conjugate acid would yield the same carbonium ion and an alcohol which is rapidly converted into, and is therefore less stable than, the alkyl hydrogen sulphate. It follows that for the heterolysis of the sulphur trioxide complex the free-energy change must be less, and the free energy of activation will probably be less, than that for the conjugate acid. This consideration does not allow us to predict the dominance of mechanism (6)—(7) since we do not know the relative concentration of sulphur trioxide complex and conjugate acid; but it does give the mechanism a rational basis.

Aromatic Ethers.—Preliminary experiments in which solutions of alkyl aryl ethers in sulphuric acid were heated and then poured on ice showed that *m*-nitroanisole, *p*-nitroanisole, and *p*-nitrophenetole form water-soluble sulphonic acids, but that 2,4-dinitroanisole, 3,5-dinitroanisole, 2,4-dinitrophenetole, and 2-methyl-5-nitrophenetole undergo fission. Cryoscopic results (Table 3) show that whereas 2,4-dinitroanisole splits at measurable speed at 85°, 2,4-dinitrophenetole reacts readily at only 25°. This large difference in ease of fission suggests that the alkyl–oxygen bond is broken in each case, for if the methyl and ethyl groups were not directly involved in heterolysis the ethers would differ little in reactivity. Results for the other two ethers lead to the same conclusion.

The order of rates in this series suggests the same mechanism as for alkyl ethers, but there are significant differences between the two series, for initial *i*-factors (Table 3, col. 3) show that the alkyl aryl ethers are weak bases in sulphuric acid, and the *i*-values show a tendency for the aryl group to remain in solution as a phenol rather than as the phenyl hydrogen sulphate. If the phenol produced in the fission of an alkyl aryl ether behaves as a non-electrolyte the final *i*-factor should be approximately 2:

TABLE 3.

Cryoscopic results for alkyl aryl ethers in 99·6% sulphuric acid.

R	R′	Initial *i*-factor	Final *i*-factor	i_∞	Reaction temp.	10^3k_1
Me	$2,4\text{-}(NO_2)_2C_6H_3$	1·23	3·24	3·0	85·0°	32·1
Me	$3,5\text{-}(NO_2)_2C_6H_3$	1·14	3·34	3·0	85·0	9·16
Et	$2,4\text{-}(NO_2)_2C_6H_3$	1·29	2·45	2·4	25·6	38·7
Et	$2\text{-Me-}5\text{-}NO_2{\cdot}C_6H_3$	1·36	—	4·0	25·6	12·1

$$RR'O + H_2SO_4 \rightleftharpoons RHSO_4 + R'OH \qquad (8)$$

In fact 2,4-dinitrophenol is about one-third ionised as a base in 100% sulphuric acid,[8] and so the final *i*-value in the fission of alkyl 2,4-dinitrophenyl ethers should be about 2·3, in good agreement with the observed results for 2,4-dinitrophenetole. The high value of i_∞ (3·0) for both 2,4- and 3,5-dinitroanisole suggests side reactions, which are not unexpected in this solvent at 85°, but the still higher value (of 4·0) for the solvolysis of 2-methyl-5-nitrophenetole at 25° shows that the phenol forms a hydrogen sulphate, a conclusion which might be predicted from the similar behaviour of *m*-nitrophenol.[8]

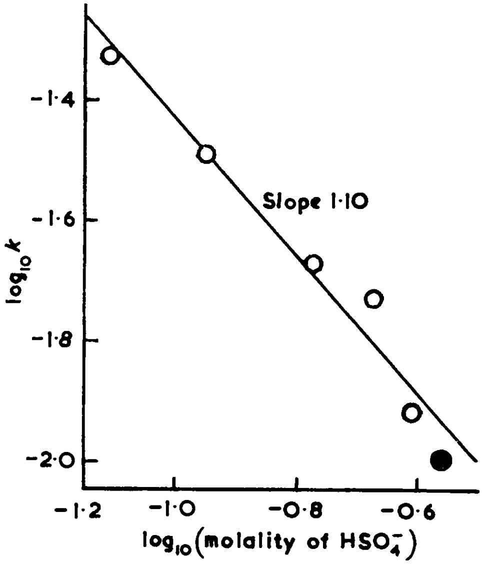


FIG. 3. Effect of hydrogen sulphate concentration on the solvolysis of 2-methyl-5-nitrophenetole in sulphuric acid.

○ Aqueous sulphuric acid.
● Sulphuric acid containing $KHSO_4$.

The rationale for the sulphur trioxide mechanism depends on a much greater stability in sulphuric acid of an alkyl hydrogen sulphate than the corresponding alcohol. Facts presented above suggest that the difference in stability between phenols and their hydrogen sulphates is small, since a relatively small change in the substituents can swing the equilibrium (8) from one side to the other. We should therefore be prepared for alkyl

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[7] Bass, Gillespie, and Robinson, *J.*, 1960, 821.
[8] Gillespie and Oubridge, *J.*, 1959, 2804.

aryl ethers to be solvolysed by a different mechanism, and results for 2,4-dinitrophenetole in Table 4 show that this is certainly the case. Suppose that the conjugate acid were the species which undergoes heterolysis: its concentration should vary inversely with the hydrogen sulphate ion concentration according to equation (9) regardless of whether the hydrogen sulphate ion is derived from water or potassium hydrogen sulphate. The single line of nearly unit negative slope in Fig. 3 is consistent with this mechanism for 2-methyl-5-nitrophenetole, and the apparent insensitivity to hydroxonium ion of the rate of fission of 2,4-dinitrophenetole (Table 4) suggests the same conclusion for this ether. The prevalence of a different mechanism for these ethers provides interesting support for our interpretation of the solvolysis of alkyl ethers in the same solvent.

$$RR'O + H_2SO_4 \rightleftharpoons RR'OH^+ + HSO_4^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

TABLE 4.

Rates of solvolysis of alkyl aryl ethers in sulphuric acid containing hydroxonium and potassium hydrogen sulphates.

2-Methyl-5-nitrophenetole at 25·6°.

Molality				10^3k_1
Water	$KHSO_4$	Ether	HSO_4^- *	(min.$^{-1}$)
0·220		0·053	0·246	12·1
0·186		0·052	0·212	18·5
0·142		0·053	0·168	21·2
0·084		0·052	0·111	32·1
0·049		0·052	0·077	47·0
0·058	0·204	0·031	0·277	9·90

2,4-Dinitrophenetole at 25·6°.

Molality				10^3k_1
Water	$KHSO_4$	Ether	HSO_4^- *	(min.$^{-1}$)
0·220		0·052	0·246	38·7
0·058	0·159	0·052	0·243	40·9

* The sum of the molalities of water and potassium hydrogen sulphate, plus half the molality of the ether.

EXPERIMENTAL

Cryoscopic Measurements.—The measurements of *i*-factors and of rate constants were carried out as in previous work.[9] The concentration of water in the solvent was determined by reference to the freezing point. Potassium and ammonium hydrogen sulphate were added as the normal sulphates.

Product Analysis.—Proof of the solvolysis of ethyl ether was obtained by hydrolysing the ethyl hydrogen sulphate and then estimating the ethyl alcohol by volumetric oxidation. The procedure has been used for determining the rate of fission in other media and will be described fully in a later Part. Solutions in which bromo- and chloro-ethers had been solvolysed all gave negative tests for halide ions. Proof of fission was obtained for alkyl aryl ethers by diluting the reaction mixtures so as to precipitate phenols which were then purified and identified.

Materials.—A number of the ethers were obtained commercially, and the preparations of all the remainder have been previously described. Reasonable care was taken in purifying and testing for purity: *e.g.*, all liquids were dried and fractionated. Satisfactory analyses were obtained for the bromo-ether.

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