

The Influence of the Solvent on Reaction Velocity

XII. The Solvolysis of Alkyl Benzenesulphonates in Acetone-Water and Dioxan-Water Mixtures

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Solvent effects in the uncatalysed hydrolysis of alkyl sulphonates show many similarities to those observed in the solvolysis of alkyl halides. The velocity of solvolysis of *isopropyl benzenesulphonate* is enormously increased by increasing the proportion of water in the medium, but that of ethyl, and of *n*-propyl, benzenesulphonates is affected to a much lower degree. In acetone-water and dioxan-water mixtures containing more than 50 % water, the reaction with the *iso*-propyl ester is of the sixth order but with the *n*-alkyl esters it is of the order 3.6—3.8 with respect to water. In media containing less water the order with respect to water is 2.5—1.7 with all three esters. The activation energies and frequency factors show great variations as the composition of the medium is varied. The reaction mechanism is discussed.

Parts X and XI of this series ^{1,2} dealt with the hydrolysis of alkyl halides in various acetone-water mixtures. The work described in the present paper ³ is an extension of the investigations on solvent effects in the field of nucleophilic substitution reactions. It also forms a continuation of four previous publications ⁴⁻⁷ on the hydrolysis of sulphonic esters, so that the experiments now cover the whole range of acetone-water and dioxan-water mixtures.

EXPERIMENTAL

Materials. The esters were obtained as described earlier ⁵. However, it was found that when the alcoholate was used in about 10 % excess all the sulphonyl chloride reacted within an hour and that the heating on the water bath, and shaking with sodium hydroxide solution were unnecessary. Benzenesulphonyl chloride and the alcohols used for the syntheses were of the highest purity. The esters obtained were shown to be very pure by total hydrolysis. The acetone used as solvent in the kinetic experiments was Merck "acetone pro analysi".

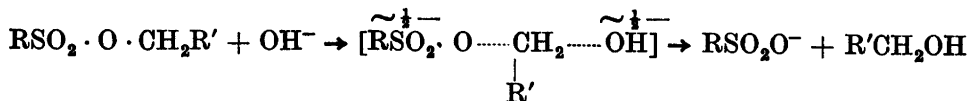
All data concerning dioxan-water mixtures are taken from the paper of Tommila and Merikallio ⁶.

Rate measurements. Two different methods were used depending on the rate of the reaction. The experiments with isopropyl benzenesulphonate in water and in mixtures containing as little as 20 % acetone utilised the conductivity method described in previous work ¹. In all other cases the rate was followed by the titration methods previously described ^{4,5}. In media of lower water content than 20 %, where reaction is slow and rather high temperatures must be used, the kinetic experiments were carried out on 10 ml samples sealed in ampoules of Pyrex glass. In all these experiments the initial concentration of the ester was 0.05 *M*. In highly aqueous media more dilute solutions were used because of the low solubility of the esters, and the reactions were carried out in glass-stoppered vessels ⁴. Since the reaction rate is somewhat dependent on the initial concentration of the sulphonic ester, all experiments in the same solvent were conducted using equal initial concentrations. In experiments of long duration at high temperatures the acetone became yellowish, but this did not seem to affect the reaction rate.

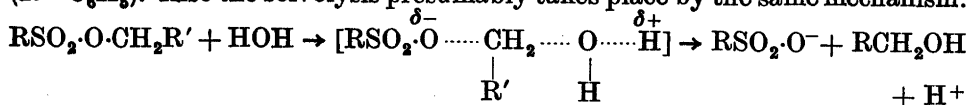
For the solvolysis, first-order kinetics were observed in all cases. From the variation of $\log k$ with $1/T$ the activation energy, *E*, and the frequency factor, *A*, were calculated by the method of least squares.

RESULTS AND DISCUSSION

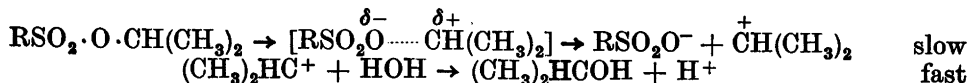
The mechanism of the reaction. In the presence of a strong base the rates of hydrolysis of *n*-alkylbenzenesulphonates in 56 wt. % aqueous acetone can be expressed by the equation $v = k_2[\text{ester}][\text{OH}^-]$. The reaction is a bimolecular one-stage reaction or, according to the terminology of Hughes and Ingold, an *S_N2* reaction:



(*R* = C₆H₅). Also the solvolysis presumably takes place by the same mechanism:



The hydrolysis of isopropyl benzenesulphonate in aqueous acetone or in aqueous dioxan is independent of the presence of hydroxyl ions: its velocity is the same in alkaline, neutral or acid solution ⁵. The rate-determining stage is the fission of the carbon-oxygen bond, the reagent intervening in a subsequent, rapid reaction ("unimolecular" or *S_N1* mechanism):



Sec.-butyl benzenesulphonate behaves similarly ⁵.

The *p*-toluenesulphonic esters are similar to the alkyl benzenesulphonates in their reactions ⁸. Thus, the unimolecular mechanism appears to be more favoured for the reactions of sulphonic esters than for the analogous reactions of alkyl halides: secondary sulphonates generally resemble tertiary halides in behaviour.

The most economical mode of the reaction



Table 1. The hydrolysis of ethyl benzenesulphonate in various acetone-water mixtures¹.

Acetone wt. %	$x_{\text{acet.}}$	$10^7 k_1 \text{ sec.}^{-1}$						E cal.	log A
		50.00°	65.00°	75.00°	80.00°	90.00°	95.00°		
0	0	1 740						22 030	11.13
3.0	0.0095	1 610						21 800	10.95
7.0	0.023	1 290						21 410	10.60
17.8	0.063	745						21 370	10.32
36.5	0.151	257						21 730	10.11
56.0	0.283	86.8		974				21 730	9.64
80.0	0.553	18.2		201				21 460	8.78
90.0	0.736	5.67	23.7		86.6			20 600	7.69
92.5	0.793	3.50	14.4		51.5			20 300	7.29
95.0	0.855	2.80		27.3		97.0		20 430	7.26
96.5	0.896	(1.04) ²	4.57		17.8	43.6 ³		21 460	7.53
98.0	0.939	(0.286) ²	1.42		6.20 ⁴		24.9	23 000	8.00

¹ The values for 0–80 % acetone are taken from the paper of Tommila and Jutila.

² By the Arrhenius equation.

³ 90.70°.

⁴ 80.80°.

is usually that in which X is forced up against the repulsion of YZ and the bond between Y and Z is simultaneously stretched until X and Z can compete for Y on equal terms⁹. Thus we can regard the activation energy as being made up of two parts: that required to overcome the repulsion of the approaching reagent, and that required to weaken the existing bond¹⁰. One or the other of these might conceivably be the determining factor. The S_N2 mechanism is clearly analogous to the case in which the repulsion energy governs the situation. If the repulsion is large, it may require less energy to extend the Y—Z bond than to force X up to Y. The extreme case is that in which the bond between Y and Z is disrupted, after which X and Y combine; the mechanism is now S_N1 . As we shall see, all three cases occur in the hydrolysis of *n*-alkyl sulphonates.

Table 2. The hydrolysis of *n*-propyl benzenesulphonate in various acetone-water mixtures.

Acetone wt. %	$x_{\text{acet.}}$	$10^7 k \text{ sec.}^{-1}$					E cal.	log A
		40.00°	50.00°	60.00°	65.00°	75.00°		
0	0	334	986	2 650			21 500	10.52
13.0	0.044	220	627	1 570			20 370	9.57
27.2	0.104	94.8	265	657			20 070	8.99
50.0	0.237	20.8	60.8	167			21 580	9.39
56.0	0.283	16.3	48.2		217		21 800	9.42
80.0	0.553		9.02	23.8		99.4	21 500	8.49
90.0	0.736		2.68	7.12		27.0	20 650	7.40

Table 3a. The hydrolysis of isopropyl benzenesulphonate in highly aqueous acetone-water mixtures. Conductometric method.

Acetone wt. %	$x_{\text{acet.}}$	$[\text{H}_2\text{O}]$ mole/l	$10^5 k_1 \text{ sec.}^{-1}$						E cal.	$\log A$
			25.00°	30.00°	35.00°	40.00°	45.00°	50.00°		
0	0	55.5		103	186	355	569	1 050	22 430	13.19
5.0	0.016	52.4			148	261	446	741	21 240	12.24
10.0	0.033	49.1		62.4	107	180		521	20 660	11.68
13.0	0.044	47.3		44.1	78.3	128	222	374	20 700	11.57
15.0	0.052	46.0	19.5	35.0	62.0	112	185	314	21 380	11.96
17.8 ¹	0.063	44.4		14.9		84.3		246	21 470	11.91
20.0	0.072	43.0	12.7	22.7	42.6	71.5		(204) ²	21 600	11.91

¹ By the titration method.² By the Arrhenius equation.

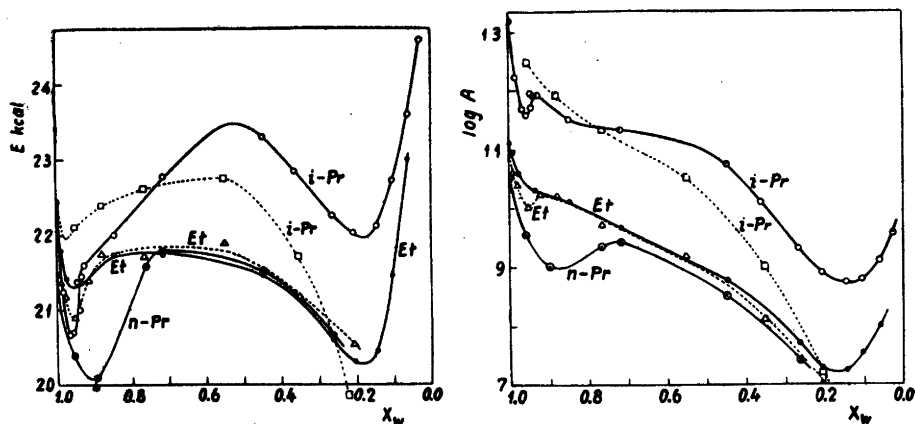
In the hydrolysis of sulphonic esters $\text{RSO}_2\text{QCHR}'\text{R}''$, the critical repulsion is that between the attacking reagent (OH^- or H_2O) and the central C atom of the alkyl group. If $\text{R}'' = \text{H}$, the repulsion is usually small and the mechanism $S_{\text{N}}2$; if R'' is an alkyl group, the repulsion is large and the reaction takes place by the $S_{\text{N}}1$ mechanism. Accordingly, $S_{\text{N}}1$ reactions should in general require higher activation energies than $S_{\text{N}}2$ reactions, for similar molecules. Also the frequency factor should be greater for an $S_{\text{N}}1$ than for an $S_{\text{N}}2$ process¹. Both of these expectations are confirmed by our experiments (Tables 1—3, Figs. 1 and 2).

On passing from *n*-alkyl sulphonates to isopropyl benzenesulphonate the increase in E tends to reduce the reaction velocity but its influence is more

Table 3b. The hydrolysis of isopropyl benzenesulphonate in various acetone-water mixtures¹.

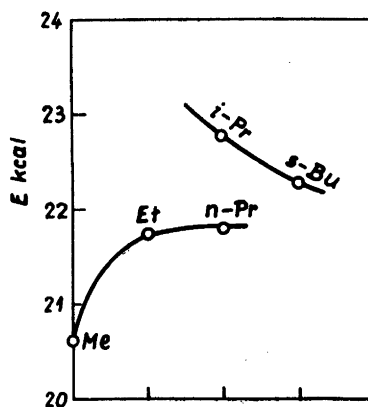
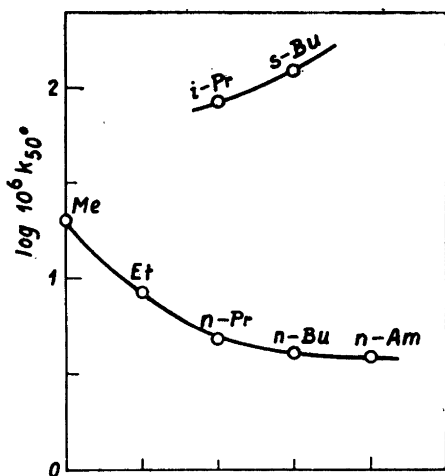
Acetone wt. %	$x_{\text{acet.}}$	$[\text{H}_2\text{O}]$ mole/l	$10^7 k_1 \text{ sec.}^{-1}$						E cal.	$\log A$
			40.00°	50.00°	65.00°	80.80°	90.00°	95.90°		
36.5	0.151	33.3	1 400	4 180					22 000	11.50
56.0	0.283	22.2	284	839					22 780	11.34
80.0	0.553	9.5	30.3	100					23 310	10.76
85.0	0.638	7.0	13.6	43.2	206				22 860	10.09
90.0	0.736	4.5	6.03	17.6	84.7				22 270	9.32
92.5	0.792	3.4		10.0	45.0	198			22 040	8.90
95.0	0.855	2.2		6.20	28.4			287 ²	22 120	8.75
96.5	0.896	1.4		2.79	12.9	60.6			22 720	8.80
98.0	0.939	0.7		1.44	7.36			80.2	23 600	9.12
99.0	0.970	0.2		(0.906) ⁴	4.93	25.9			24 600	9.60

¹ The data for 36.5—80.0 % acetone are taken from the paper of Tommila and Jutila.² 90.50°.³ 98.38°: $176 \times 10^{-7} \text{ sec.}^{-1}$.⁴ By the Arrhenius equation.



Figs. 1 and 2. Variation of E and $\log A$ with the composition of the solvent. — Acetone-water, dioxan-water.

than counterbalanced by the increase in A . The difference in mechanism manifests itself thus also in a much greater reaction velocity of the esters of the secondary alcohols. In addition, if the group $-\text{CHR}'\text{R}''$ is varied in the direction of increasing negative charge on C, the velocity of a bimolecular reaction should decrease and that of a unimolecular reaction increase. In accordance with this, in 56 wt. % acetone where, as mentioned above, the n -alkyl esters undergo hydrolysis by the bimolecular and sec -alkyl esters by the unimolecular mechanism the reaction rates follow the order $\text{Me} > \text{Et} > n\text{-Pr} > n\text{-Bu} > n\text{-Am} \ll \text{Me}_2\text{CH} < \text{EtMeCH}$ (Fig. 3). The first-order rate-con-



Figs. 3 and 4. Velocities and activation energies of the hydrolysis (solvolysis) of alkyl benzenesulphonates in 56 wt. % aqueous acetone.

stant for *n*-amyl benzenesulphonate ($k_{50} = 40.0 \times 10^{-7} \text{ sec.}^{-1}$) was determined for this particular purpose, the other data are taken from previous investigations ⁷. For *isobutyl* benzenesulphonate the reaction is very slow ($k_{50} = 4.79 \times 10^{-7} \text{ sec.}^{-1}$), partly owing to steric hindrance. The difference in mechanism is seen also from Fig. 4 which shows that the changes in the activation energy follow the course predicted by the theory.

The velocity of an S_N1 reaction should greatly increase with increasing ionising power of the solvent. In the bimolecular mechanism, too, passage from the initial state to the transition state involves development of charge and thus bimolecular reactions should also, although to a lesser degree, be favoured by increasing polarity of the solvent. These predictions have been verified in the solvolysis of alkyl halides and they are obeyed also in the solvolytic reactions of alkyl sulphonates. In pure water at 50° the velocity of the solvolysis of *isopropyl* benzenesulphonate is 4.3 times as fast as in 17.8 wt. % acetone, 1 000 times as fast as in 80 wt. % acetone, 10 000 times as fast as in 92.5 wt. % acetone, and 73 000 times as fast as in 98 wt. % acetone. The corresponding numbers for ethyl benzenesulphonate are 2.3, 96, 500, and 6 080, respectively. The ratios for *isopropyl* benzenesulphonate are considerably smaller than the corresponding values for tertiary halides, whereas for ethyl benzenesulphonate they are much greater than for ethyl bromide ¹.

In the previous work ¹ it was found that for the solvolysis of alkyl halides the plot of $\log k$ against $\log [\text{H}_2\text{O}]$ is linear in the region from pure water to about 60—70 % acetone. From the slope of the graph it was deduced that for *tert.*-butyl chloride about 7 water molecules, and for *tert.*-butyl bromide about 6 water molecules, are included in the formation of the transition state whereas in the case of ethyl bromide their number is only about 2. Using the same method, *viz.* writing

$$dx/dt = k_1(a-x) = k' [\text{H}_2\text{O}]^n (a-x)$$

whence

$$\log k_1 = n \log [\text{H}_2\text{O}] + \text{const.}$$

we obtain from Figs. 5 and 6 the following values for the critical number, n , of water molecules needed for the formation of the transition state:

<i>Isopropyl</i> benzenesulphonate:	0—45 % acetone	$n = 6.0$
	45—90 % »	$n = 2.5$
	90— »	$n = 1.7$
	0—50 % dioxan	$n = 6.0$
Ethyl benzenesulphonate:	50—90 % »	$n = 2.6$
	0—50 % acetone	$n = 3.8$
	50— »	$n = 1.7$
<i>n</i> -Propyl benzenesulphonate:	0—50 % dioxan	$n = 3.6$
	50—95 % »	$n = 2.1$
	0—50 % acetone	$n = 3.8$
	50— »	$n = 1.8$

As in the case of alkyl halides the mixtures clearly fall into two distinct groups with respect to the value of n . In the region from pure water to 45 wt. % acetone or 50 wt. % dioxan $n = 6.0$ for *isopropyl* benzenesulphonate.

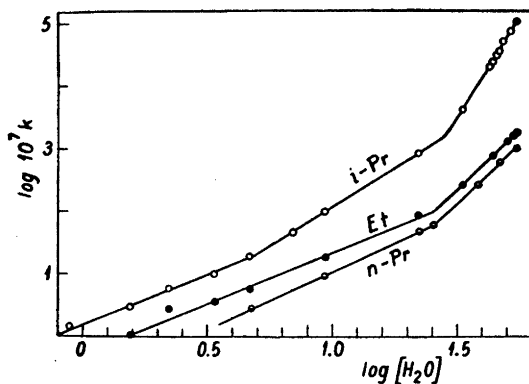


Fig. 5. Plot of $\log k$ against $\log [H_2O]$.
Acetone-water, 50° .

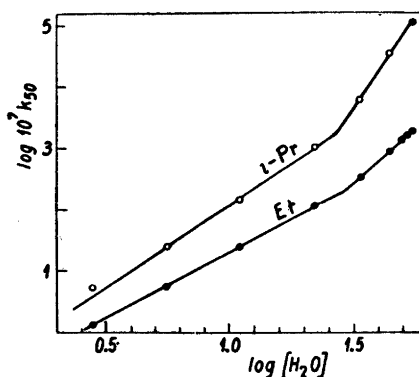
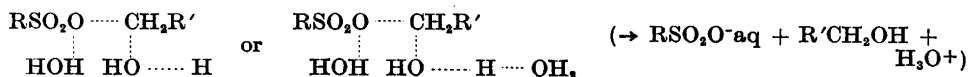


Fig. 6. Plot of $\log k$ against $\log [H_2O]$.
Dioxan-water, 50° .

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As n is about 6 for t -BuBr and about 7 for t -BuCl the values $n = 6-7$ seem to be characteristic of S_N1 reactions. The values 2.1 to 1.7 found for n -alkyl benzenesulphonates in media containing less water than 50 wt. % agree with those found for ethyl bromide in acetone-water mixtures: obviously this order of magnitude is characteristic of S_N2 reactions.

The value $n \approx 2$ indicates that in the one-stage reaction one additional water molecule, besides the attacking molecule, is involved in the formation of the transition state. In the rate-determining step one water molecule forms an incipient bond to carbon and another becomes bound by a hydrogen bond to the O atom of the group O—C. Since in some media, and especially for the solvolysis of ethyl bromide¹, n is somewhat greater than two it is reasonable to assume that a third water molecule is involved in the transition state. This third molecule would be used to accept the proton from the attacking water molecule. Thus the transition state may be represented by (cf. Ref.¹¹)



In the case of S_N1 reactions, as the value of n shows, six water molecules must contribute the solvation energy necessary for the splitting of the carbon-oxygen bond. The carbonium ion is formed within an aqueous solvation shell, and ends its life by reacting with one of these water molecules (cf. Ref.¹), a conclusion previously reached by Benfey, Hughes, and Ingold^{8,12}.

The values $n = 3.6$ to 3.8 found for the n -alkyl benzenesulphonates in the region between pure water and 50 % acetone or dioxan are distinctly greater than those deduced above for S_N2 reactions. Values of this order of magnitude do not exist in the solvolysis of ethyl bromide and they obviously suggest that in highly aqueous solvents n -alkyl benzenesulphonates have a tendency to change mechanism from an S_N2 to S_N1 reaction. Such a conclusion is supported

Table 4. The hydrolysis of ethyl benzenesulphonate in water at 40°; $\alpha = 0.01$.

Time, min.	[NaOH] = 0		[NaOH] = 0.01			[NaOH] = 0.02		
	Change %	$10^5 k_1$	Change %	$10^5 k_2$	$10^5 k_1$	Change %	$10^5 k_2$	$10^5 k_1$
60	18.0	5.50	20.0	6.95	6.18	20	6.54	6.20
90	25.0	5.33	28.5	7.35	6.20			
120	33.0	5.56	36.8	8.32	6.36			
180	44.5	5.45	48.5	8.70	6.14	52.0	8.02	6.79
210	49.5	5.42	53.5	9.12	6.08	57.0	8.06	6.73
240	55.0	5.55	59.0	10.0	6.19	62.0	8.28	6.71
270	60.0	5.66	62.5	10.2	6.06	66.5	8.52	6.73

Table 5. The hydrolysis of ethyl benzenesulphonate in 7.0 wt. % acetone. Temperature 40.00°; $\alpha = 0.01$, [NaOH] = 0.01.

Time, min.	70	100	120	150	180	210	240	360
Change %	18.5	25.0	28.9	34.7	37.3	42.6	47.2	61.1
$10^5 k_2$	5.40	5.52	5.62	5.88	5.52	5.87	6.20	7.27
$10^5 k_1$	4.87	4.79	4.73	4.73	4.32	4.40	4.44	4.37

(In absence of alkali $k_1 = 4.65 \times 10^{-5}$ sec.⁻¹)Table 6. The hydrolysis of ethyl benzenesulphonate in 17.8 wt. % acetone. Temperature 25.00°; $\alpha = 0.02$, [NaOH] = 0.02.

Time, hours	3	8	19 $\frac{1}{2}$	24	27	33	43	50
Change %	5.5	13.7	30.5	36.2	40.0	46.5	54.5	59.4
$10^5 k_2$	2.70	2.76	3.16	3.27	3.43	3.66	3.88	4.07
$10^5 k_1$	5.22	5.12	5.23	5.20	5.25	5.26	5.09	5.00

(In absence of alkali $k_1 = 4.58 \times 10^{-6}$ sec.⁻¹).Table 7. The hydrolysis of ethyl benzenesulphonate in 30 % acetone. Temperature 25.00°; $\alpha = 0.02$, [NaOH] = 0.02.

Time, hours	21	24	32 $\frac{1}{4}$	43	48	70
Change %	22.0	24.8	31.7	40.0	43.4	55.0
$10^5 k_2$	1.85	1.91	1.98	2.15	2.21	2.42
$10^5 k_1$	3.29	3.30	3.28	3.30	3.29	3.17

Table 8. The hydrolysis of ethyl benzenesulphonate in 36.5 wt. % acetone. Temperature 25.00°; $\alpha = 0.05$, [NaOH] = 0.05.

Time, hours	21	24	43	50	69	96
Change %	15.5	17.5	28.8	32.0	41.2	51.0
$10^5 k_2$	1.20	1.22	1.31	1.31	1.40	1.50
$10^5 k_1$	2.23	2.23	2.70	2.14	2.14	2.07

(In absence of alkali $k_1 = 1.51 \times 10^{-6}$ sec.⁻¹)

by the fact that in highly aqueous solvents first order kinetics were followed even in the presence of alkali (Tables 4—8). Reasons for the small increase of reaction velocity in the presence of alkali will be mentioned later. On the other hand, one is not justified in assuming that the mechanism is S_N1 since in that case n should be about six and the reaction velocity of the n -propyl ester should be greater than that of the ethyl ester. This is not the case. Thus we must conclude that the solvolysis of n -alkyl esters in highly aqueous solvents takes place in the following way. The introduction of a methyl group into ethyl benzenesulphonate increases the repulsion on the hydroxyl group in the approaching water molecule and causes the sulphonyl group to be held less tightly. The fact that the activation energy is lowered (Fig. 1) shows that the change in the bond energy governs the trend of the activation energy. In the transition state we have thus a relatively great bond stretching, the entropy of activation being less negative (A greater) for ethyl benzenesulphonate than for n -propyl benzenesulphonate. The fact that the reaction is of the order 3.6—3.8 with respect to water indicates that four water molecules are intimately included in the formation of the transition state. The solvation of the alkyl benzenesulphonate molecule with these water molecules contributes the energy necessary for the stretching of the bond O—C between the sulphonyl and alkyl groups and after a sufficient extension of the bond one of the water molecules of the solvation layer can compete on equal terms with the sulphonyl group for the alkyl group. Thus the transition state is formed within an aqueous solvation shell of four water molecules and an exterior layer of less oriented water molecules. The observation that in highly aqueous solvents the hydrolysis of ethyl benzenesulphonate is almost unaffected by alkali, shows that the hydroxyl ion in general cannot penetrate through the solvation layer. Benfey, Hughes, and Ingold¹² reached the same conclusion when examining unimolecular substitution reactions, and they assume that the hydroxyl ion will take a proton from the outside of the solvation shell. The slight increase of the reaction velocity in our case is probably caused by a leakage of hydroxyl ions through the solvation layer or by normal salt effects, *cf.* Ref.⁸

In mixtures containing water less than 50 % by weight the hydrolysis of the two esters is powerfully accelerated by alkali and, as mentioned above, in 56 wt. % aqueous acetone the reaction is a second-order process⁷. For ethyl benzenesulphonate and n -propyl benzenesulphonate the activation energy is reduced in the presence of alkali and in alkaline and neutral solutions $E_{n-Pr} > E_{Et}$ (in the alkaline solution the values are 20 950 and 20 800 cal, respectively). Thus the reaction proceeds by a normal S_N2 mechanism. The change in the behaviour of the esters in these predominantly organic solvents is not solely due to the weaker solvation of the transition state by water ($n \approx 2$), but also to the decrease of the dielectric constant of the medium.

Since the rate of the reaction for the *isopropyl* ester, at least in solutions containing up to 56 wt. % acetone is not affected by the presence of alkali⁵ the mechanism must be S_N1 . The great reduction in n in passing to solvents containing less water than 50 % by weight suggests that in these solvents the S_N1 reaction is less favoured. A similar change at much lower water percentages can be observed in the solvolysis of *tert.*-butyl chloride and bromide¹. It is unfortunate that because of the insolubility of sodium hydroxide in mixtures

containing more than 60 % acetone or dioxan the reaction in the presence of strong alkali cannot be investigated in this region.

That the unimolecular mechanism is less favoured as the proportion of water in the solvent is decreased is also seen from the fact that the ratios k_{i-Pr}/k_{Et} and k_{i-Pr}/k_{n-Pr} decrease rapidly with decreasing water content, whereas the ratio k_{Et}/k_{n-Pr} remains nearly constant or increases slightly (Table 9). This is true also in the solvolysis of alkyl halides (Table 10), but in this case the absolute values of the ratios and their decrease are much greater. However, also at low water concentrations the reaction velocities of the isopropyl ester

Table 9. The ratios of the rate constants, 50° C.

Acetone, wt. %	0	13.0	17.8	36.5	56.0	80.0	90.0	95.0
k_{i-Pr}/k_{Et}	60		33	16	9.7	5.5	3.1	2.2
k_{i-Pr}/k_{n-Pr}	106	61			17	11	6.6	
k_{Et}/k_{n-Pr}	1.76				1.80	2.02	2.12	

Table 10. The solvolysis of alkyl halides, 40° C.

Acetone, wt. %	0	17.8	27.2	36.5	56	76.7	85
k_{t-BuCl}/k_{EtBr}	88 500	18 100	8 500	4 600	870	190	
k_{t-BuBr}/k_{EtBr}					34 600	8 000	6 000

and of the tertiary halides are considerably greater than those of the *n*-alkyl compounds, whereas they should be smaller if the mechanism were S_N2 .

Reaction velocity and the dielectric constant of the medium. The plots of $\log k$ against $(D-1)/(2D+1)$ (Fig. 7) or against D (Fig. 8) are of about the same form as those for the hydrolysis of alkyl halides. It is remarkable that in acetone-water the plot of $\log k$ against D is linear in the region from pure water to about 80 wt. % acetone. The slopes of the graphs for isopropyl benzenesulphonate are clearly greater than those for the *n*-alkyl esters. Similarly, in the solvolysis of alkyl halides the slopes of the curves for *tert.*-butyl bromide and

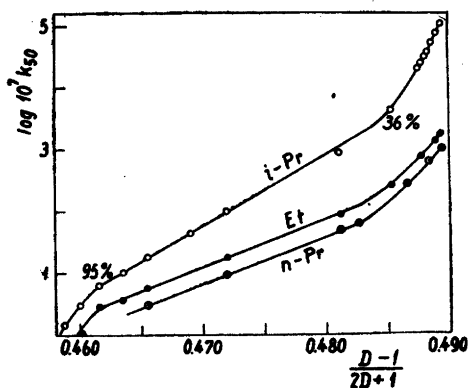


Fig. 7. Plot of $\log k$ against $(D-1)/(2D+1)$. Acetone-water, 50°.

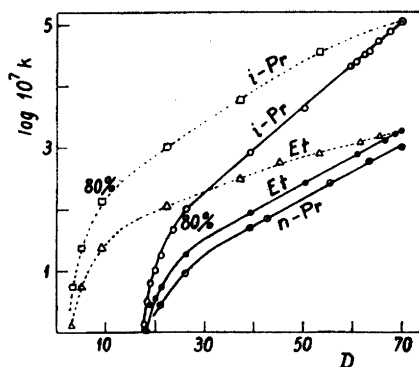


Fig. 8. Plot of $\log k$ against D , 50°. — Acetone-water, dioxan-water.

chloride are greater than that for ethyl bromide. In solvents containing only a few per cent of water the slopes of the curves approach each other.

Parameters of the Arrhenius equation. The plots of E and $\log A$ against the composition of the solvent (Figs. 1 and 2) have about the same general shape as in the case of alkyl halides¹. For all three esters, the second minimum appears for the same composition of acetone-water mixtures, $x_w \approx 0.18$, whereas for alkyl halides great variations occur in its position. Greater differences between the curves in acetone-water and dioxan-water appear for the solvolysis of *isopropyl benzenesulphonate*, whereas for ethyl benzenesulphonate the curves lie close together. The great difference in E and A between *isopropyl benzenesulphonate* and *n-propyl benzenesulphonate* throughout the whole set of acetone-water mixtures, and between ethyl benzenesulphonate and *n-propyl benzenesulphonate* in highly aqueous solvents, is especially noticeable.

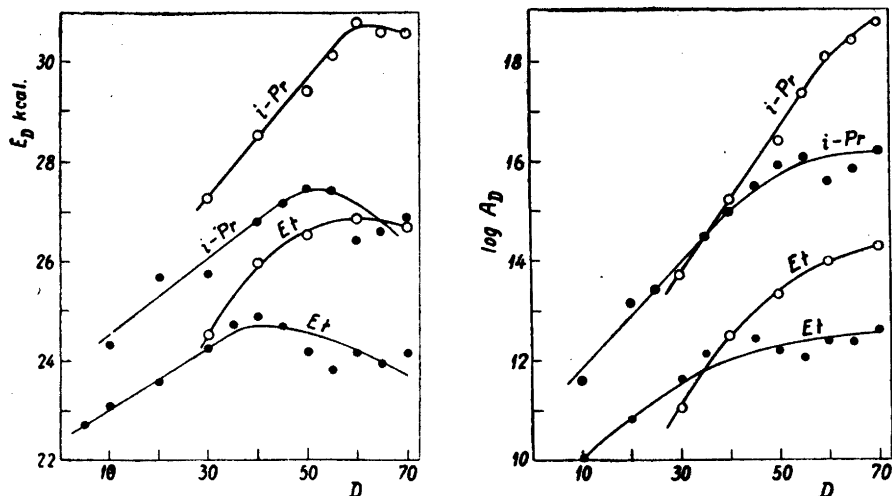
The dependence of E and A on the composition of the mixture used as solvent can be discussed in terms of the solvation of the initial state and of the transition state and of changes in the internal structure of the solvent. This has been described in a previous paper¹. Especially noteworthy is the deep minimum in highly aqueous solvents, which indicates that the transition state is highly solvated and much more polar than the initial state.

Isodielectric solutions. The rate constants for isodielectric solutions, k_D , were obtained from the k 's of Tables 1—3 and those given in Ref.⁶ by graphical interpolation¹. Plots of $\log k_D$ against $1/T$ are linear within the experimental error. The isodielectric activation energies, E_D , and frequency factors, A_D , are given in Table 11.

The dependence of E_D and A_D on D is illustrated in Figs. 9 and 10. For comparison it may be mentioned that the plots of $\log A_D$ vs. D are linear for the

Table 11. Isodielectric activation energies and frequency factors.

D	Acetone-water				Dioxan-water			
	Ethyl benzene-sulphonate		<i>Isopropyl</i> benzene-sulphonate		Ethyl benzene-sulphonate		<i>Isopropyl</i> benzene-sulphonate	
	E , cal.	$\log A$	E , cal.	$\log A$	E , cal.	$\log A$	E , cal.	$\log A$
70	26 660	14.28	30 560	18.71	24 150	12.60	26 900	16.23
65			30 600	18.40	23 940	12.35	26 600	15.87
60	26 820	13.98	30 680	18.09	24 150	12.39	26 440	15.61
55			30 150	17.36	23 800	12.03	27 420	16.11
50	26 500	13.33	29 240	16.38	24 180	12.19	27 480	15.95
45					24 690	12.42	27 180	15.52
40	25 940	12.50	28 520	15.22	24 870	12.41	26 790	15.00
35					24 701	12.14	26 420	14.51
30	24 500	11.02	27 270	13.69	24 200	11.63	25 720	13.78
20					23 530	10.80	25 700	13.22
10					23 100	10.04	24 340	11.63



Figs. 9 and 10. Variations of E_D and $\log A_D$ with D . \circ Acetone-water, \bullet dioxan-water.

alkyl halides, the positive slope being very small for EtBr. The plots of E_D° vs. D are also linear, with a positive slope for *t*-BuCl and *t*-BuBr, but with a small negative slope for EtBr.

For *isopropyl benzenesulphonate* as well as for *ethyl benzenesulphonate* the isodielectric activation energies and frequency factors are much higher than the corresponding values for the solvents of constant composition. For *t*-BuCl and *t*-BuBr E_D and A_D are always much higher than are E and A for the constant composition. However, for EtBr the isodielectric activation energy is a little smaller in highly aqueous solvents, but slightly greater in other solvents than that for constant composition. For EtBr A_D is only somewhat greater than A .

The relationship between $\log A_D$ and E_D is linear (Fig. 11) for $D < 60$. The ratio $\Delta \log A_D / \Delta E_D$ is equal, *viz.* 1.30, for both esters and both sets of mixtures. A linear relationship between $\log A_D$ and E_D was found also for alkyl halides in acetone-water mixtures¹, the values of $\Delta \log A_D / \Delta E_D$ being: *t*-BuCl 2.4, *t*-BuBr 1.9, EtBr ≈ -1 .

For ethyl bromide and the tertiary halides the difference in mechanism thus manifests itself very clearly in the isodielectric activation energies and activation entropies, whereas there are no so great differences in the behaviour of the isodielectric quantities between ethyl benzenesulphonate and *isopropyl benzenesulphonate*. The behaviour of E_D and A_D for the latter resembles closely that for the tertiary halides, and the behaviour of E_D and A_D for ethyl benzenesulphonate is little different.

Conclusions concerning the reaction mechanism. Summing up, it can be said that judging from solvent effects the mechanism of the hydrolysis of alkyl halides and sulphonic esters can be interpreted in terms of the general theory put forward by Hinshelwood, Laidler and Timm¹⁰. According to this theory

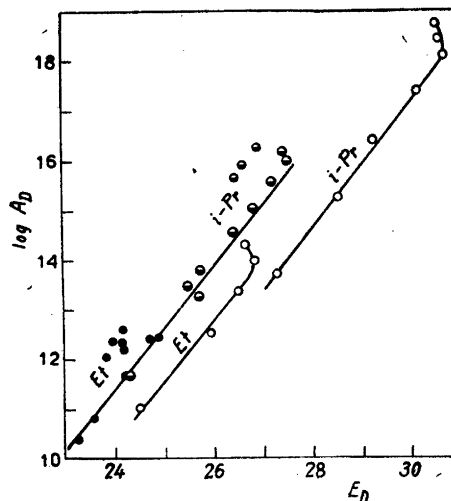


Fig. 11. Plot of $\log A_D$ against E_D . \circ Acetone-water, \bullet , \bullet dioxan-water.

there is a graded series of mechanisms, with S_N1 and S_N2 as the extremes. All observations substantiate the view that a borderline reaction need not take place by two distinct (S_N1 and S_N2) and concurrent mechanisms, but only by one mechanism of intermediate type.

In all aqueous solvents ethyl bromide is hydrolysed by an S_N2 mechanism. The tertiary halides undergo hydrolysis by an S_N1 mechanism, but in media where the proportion of water is very small the conditions for the unimolecular mechanism are less favourable than in more aqueous solvents. Ethyl benzenesulphonate and *n*-propyl benzenesulphonate react in highly aqueous solvents by an intermediate mechanism; in solvents where the proportion of water is less than about 50% by the bimolecular mechanism S_N2 . Isopropyl benzenesulphonate undergoes hydrolysis by the unimolecular mechanism, but in solvents where the proportion of water is small this mechanism is greatly impeded.

These conclusions are essentially in agreement with the suggestions of Swain *et al.*^{11,13}, Winstein, Grunwald and Jones¹⁴, von Doering and Streitwieser¹⁵, and Hudson *et al.*¹⁶, who have put forward arguments that there is a gradual transition from S_N2 to S_N1 . This was also mentioned as a possibility by Hughes, Ingold *et al.*¹⁷, but was not pursued. On their formulation, intermediate cases are interpreted as due to occurrence of simultaneous reactions involving the two mechanisms. Robertson in a recent investigation¹⁸ has concluded that in the reaction $XC_6H_5SO_3R + Y \rightarrow XC_6H_5SO_3^- + RY$ (where *Y* is nucleophilic agent and *X* a *para* substituent) there are changes from S_N2 to S_N1 , or *vice versa*, as the nucleophilic nature of *Y*, the character of *R* and the ionizing power of the solvent are changed.

REFERENCES

1. Tommila, E., Tiilikainen, M. and Voipio, A. *Ann. Acad. Sci. Fennicae AII* (1955) No. 65.
2. Tommila, E. and Antikainen, P. J. *Acta Chem. Scand.* **9** (1955) 825.
3. Preliminary report: Tommila, E. *XIIIth International Congress of Pure and Applied Chemistry, Stockholm 1953, Abstract of Papers*, p. 141.
4. Tommila, E. and Lindholm, M. *Acta Chem. Scand.* **5** (1951) 647.
5. Tommila, E. and Jutila, J. *Acta Chem. Scand.* **6** (1952) 844.
6. Tommila, E. and Merikallio, E. *Suomen Kemistilehti B* **26** (1953) 79.
7. Tommila, E. and Heinonen, O. *Suomen Kemistilehti B* **27** (1954) 27.
8. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, G. Bell and Sons Ltd. London 1953, p. 341, 362, 367.
9. Eyring, H. and Polanyi, M. *Z. physik. Chem. B.* **12** (1931) 279.
10. Hinshelwood, C. N., Laidler, K. J. and Timm, E. W. *J. Chem. Soc.* **1938** 848.
11. Swain, C. G. *J. Am. Chem. Soc.* **70** (1948) 1119.
12. Benfey, O. T., Hughes, E. D. and Ingold, C. K. *J. Chem. Soc.* **1952** 2494.
13. Swain, C. G. and Langsdorf, W. P. *J. Am. Chem. Soc.* **73** (1951) 2813.
14. Winstein, S., Grunwald, E. and Jones, H. W. *J. Am. Chem. Soc.* **73** (1951) 2700.
15. v. Doering, W. and Streitweiser, A. *Abstr. 119th Meeting Am. Chem. Soc. 1951*, 45M; *Ann. Repts on Progr. Chem. (Chem. Soc. London)* **1951** 122.
16. Brown, D. A. and Hudson, R. F. *J. Chem. Soc.* **1953** 883, 3352; Archer, B. L., Hudson, R. F. and Wardill, J. E. *Ibid.* **1953** 888.
17. Gleave, J. L., Hughes, E. D. and Ingold, C. K. *J. Chem. Soc.* **1935** 236; Hughes, E. D. and Ingold, C. K. *Trans. Faraday Soc.* **37** (1941) 657.
18. Robertson, R. E. *Can. J. Chem.* **31** (1953) 589.

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