The Influence of the Solvent on Reaction Velocity

XIII. Alcoholysis of Sulphonic Esters

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The velocity of the alcoholysis of *iso*propyl benzenesulphonate is greater than that of ethyl benzenesulphonate in the same solvent. This is entirely due to the greater value of the frequency factor since the activation energy is greater for the *iso*propyl ester. For ethyl benzenesulphonate the mechanism of reaction is S_N2; for *iso*propyl benzenesulphonate an intermediate mechanism between S_N2 and S_N1. In pure dry methanol the mechanism for the latter approximates to S_N1. Addition of acetone or benzene to the alcohol used as solvent causes a decrease in E and A which is especially remarkable in the case of benzene. This decrease in E and A is produced by a breaking down of the internal structure of the alcohol.

The previous paper [1] of this series dealt with the hydrolysis of alkyl benzene-sulphonates in various acetone-water and dioxan-water mixtures. For the purpose of further investigation into the solvent effect problem we have studied the solvolysis of alkyl benzenesulphonates

$$C_6H_5SO_3R + R'OH \rightarrow C_6H_5SO_3^- + ROR' + H^+$$
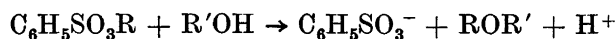
in certain binary non-aqueous mixtures. The reaction has been treated in two earlier papers [2,3] from this laboratory, but in pure alcohol only. The cases now investigated are ethyl benzenesulphonate in ethanol-acetone and ethanol-benzene mixtures and *iso*propyl benzenesulphonate in ethanol-benzene and in *iso*propanol-benzene mixtures.

EXPERIMENTAL

Chemicals. The esters were prepared as previously reported [1,3]. The alcohols used for the syntheses and as solvents in the kinetic experiments were commercial absolute ethanol and "alcool *iso*propylique pour analyse" of the firm U.C.B. Before use in the kinetic experiments they were dried: ethanol by the method of Walden [4], *iso*propanol by boiling with metallic calcium and distillation. The acetone was Merck's acetone "pro analysi"; it proved to be sufficiently dry for use as received. The benzene was a thiophene-free commercial product; before use it was dried with sodium and distilled.

Table 1. Alcoholysis of ethyl benzenesulphonate; ethanol-acetone mixtures.

EtOH ml/l	EtOH wt. %	x_{EtOH}	[EtOH] mole/l	$10^6 k$ sec.$^{-1}$				E cal.	log A	ΔS^* E.U.
				40.00°	50.00°	60.00°	75.00°			
1 000*	100	1	17.1	1.52	4.27	12.9	49.2	21 670	9.303	−18.0
900	89.9	0.918	15.4	0.980	2.99	8.02	33.5	21 800	9.217	−18.4
800	79.5	0.830	13.7	0.703	2.17	6.02	22.5	21 450	8.883	−20.1
700	69.3	0.740	12.0	0.526	1.66	4.41	17.1	21 470	8.722	−20.6
600	59.3	0.647	10.3		1.13	3.10	12.6	21 600	8.664	−20.9
500	49.5	0.552	8.6		0.733	2.12	8.07	21 400	8.344	−22.4
400	39.6	0.453	6.9		0.474	1.35	5.03	21 060	7.929	−24.3
300	29.8	0.348	5.1		0.294	0.770	2.92	21 530	7.351	−26.9
200	19.9	0.238	3.4		0.141	0.399	1.55	21 380	7.616	−25.7

* Tommila and Lindholm [3]: *E* 22 000 cal., log *A* = 9.50.

Method. The kinetic experiments were carried out in sealed tubes of Pyrex glass. Into each tube 5 ml of a 0.05 *M* solution of the ester was measured by means of a pipette, the tubes (8 − 10 in each run) were then sealed and maintained in thermostatically controlled baths the temperature of which could be held constant within about ±0.02°. Tubes were removed after various periods of time, cooled quickly by immersing in a mixture of ice and water, and analysed by titration with 0.01 *N* baryta solution, cresol red being used as indicator. The rate constants were calculated by the first order formula $k = \dfrac{1}{t}\ln\dfrac{a}{a-x}$, which in all cases gave a good constancy for *k*.

The reaction between the *iso*propyl ester and sodium *iso*propylate was also investigated in pure *iso*propanol. Equal quantities (5 ml) of 0.05 *M* solutions of the reagents were mixed together in the reaction vessel [3] so that the initial concentration of each was 0.025 *M*. The reaction was stopped by adding a slight excess of 0.01 *N* HCl and the acid titrated with baryta solution. The velocity constants were calculated using the equation $k = x/ta(a-x)$.

Table 2. Alcoholysis of ethyl benzenesulphonate; ethanol-benzene mixtures.

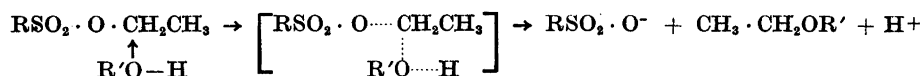| EtOH ml/l	EtOH wt. %	x_{EtOH}	[EtOH] mole/l	$10^6 k$ sec.$^{-1}$				E cal.	log A	ΔS^* E.U.
				40.00°	50.00°	60.00°	75.00°			
1 000	100	1	17.1	1.52	4.27	12.9	49.2	21 670	9.303	−18.0
900	88.8	0.944	15.4	1.12	3.29	9.47	38.0	21 870	9.314	−17.9
800	78.0	0.883	13.7	0.908	2.75	7.64	29.7	21 600	9.036	−19.2
700	67.4	0.817	12.0	0.723	2.17	6.04	23.2	21 500	8.866	−20.0
500	47.2	0.654	8.6		1.19	3.21	12.4	20 900	8.202	−23.0
300	27.6	0.449	5.1		0.536	1.40	5.01	19 960	7.228	−27.5
100	9.1	0.175	1.7			0.226	0.640*	17 150	4.590	−39.5
50	4.9	0.091	0.94			0.0667	0.177	15 100	2.728	−48.1

* 95.5°: 2.73 × 10^{-6}.

Table 3. *Alcoholysis of* isopropyl *benzenesulphonate;* isopropanol-benzene *mixtures.*

PriOH ml/l	PriOH wt. %	x_{PrOH}	[Pri OH] mole/l	$10^6 k$ sec.$^{-1}$				E cal.	log A	ΔS^* E.U.
				40.00°	50.00°	60.00°	75.00°			
1 000	100	1	13.1	1.41	4.28	11.18	46.4	21 630	9.252	−18.2
900	89.0	0.911	11.8	1.02	3.08	8.46	33.1	21 520	9.033	−19.2
700	67.1	0.726	9.2	0.616	1.71	4.67	17.8	20 900	8.370	−22.2
500	46.9	0.534	6.6	0.292	0.827	2.22	8.35	20 750	7.945	−24.2
300	27.6	0.332	3.9		0.335	0.854	3.11	19 930	7.002	−28.5

The activation energy, E, and frequency factor, A, were calculated from the variation of log k with $1/T$, the method of least squares being used in all cases. The rate constants and the parameters of the Arrhenius equation are summarised in Tables 1—4.

RESULTS AND DISCUSSION

A comparison of Tables 2 and 4 shows that for *iso*propyl benzenesulphonate the reaction is about three times as fast as for ethyl benzenesulphonate in the same solvent. For *iso*propyl benzenesulphonate, however, the activation energy is clearly higher; thus its greater reaction velocity is entirely caused by a greater frequency factor. These results resemble those observed for the un-catalysed hydrolysis of these two compounds in acetone-water, and they suggest that for the ethyl ester the reaction mechanism is S_N2,
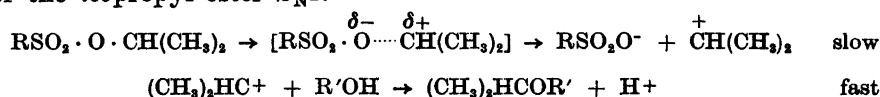
$$RSO_2 \cdot O \cdot CH_2CH_3 \rightarrow \left[RSO_2 \cdot O \cdots CH_2CH_3 \right] \rightarrow RSO_2 \cdot O^- + CH_3 \cdot CH_2OR' + H^+$$
$$\underset{R'O-H}{\uparrow} \qquad \qquad R'O \cdots H$$

and for the *iso*propyl ester S_N1:

$$RSO_2 \cdot O \cdot CH(CH_3)_2 \rightarrow [RSO_2 \cdot \overset{\delta-}{O} \cdots \overset{\delta+}{C}H(CH_3)_2] \rightarrow RSO_2O^- + \overset{+}{C}H(CH_3)_2 \quad \text{slow}$$

$$(CH_3)_2HC^+ + R'OH \rightarrow (CH_3)_2HCOR' + H^+ \qquad \text{fast}$$

Table 4. *Alcoholysis of* isopropyl *benzenesulphonate; ethanol-benzene mixtures.*

EtOH ml/l	EtOH wt. %	x_{EtOH}	[EtOH] mole/l	$10^6 k$ sec.$^{-1}$			E cal.	log A	ΔS^* E.U.
				40.00°	50.00°	60.00°			
1 000	100		17.1	4.18	12.8	38.6	23 000	10.690	−11.6
900	88.8	0.944	15.4	3.42	10.8	31.0	22 800	10.470	−12.6
700	67.4	0.817	12.0	2.14	6.55	18.5	22 350	9.927	−15.1
500	47.2	0.654	8.6	1.15	3.45	9.65	22 100	9.483	−17.1

As mentioned in the experimental section, we have also studied the reaction between the *iso*propyl ester and sodium *iso*propylate

$$C_6H_5SO_2OPr^i + Pr^iONa \rightarrow C_6H_5SO_2ONa + Pr^iOPr^i$$
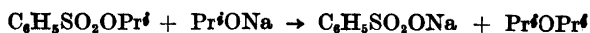
in dry *iso*propanol. For 50° the results are (p is the percentage change, $a = 0.05$ moles litre):

t min.	120	205	240	300	360	390	
p	16.8	25.6	28.8	34.0	38.4	40.0	
$10^4 k_2$ 1 mole^{-1} sec.$^{-1}$	5.61	5.60	5.62	5.72	5.77	5.70	Mean: 5.67

As may be seen the second order law is obeyed. For the whole series of experiments the values obtained are:

	40.00°	50.00°	60.00°	E_{cal}	log A
$10^4 k_2$ 1 mole^{-1} sec.$^{-1}$	2.30	5.67	13.9	18 620	8.352

For the solvolysis of the *iso*propyl ester in pure *iso*propanol the following series was obtained at 50°:

t min.	845	1 080	1 500	1 680	1 800	1 980	2 040	
p	19.4	24.4	31.6	34.8	37.2	40.0	41.2	
$10^6 k_1$ sec.$^{-1}$	4.25	4.32	4.22	4.24	4.31	4.30	4.34	Mean: 4.28

On a percentage basis the reaction with the alcoholate is about five times as fast as that with *iso*propanol suggesting an S_N2 mechanism. The concentration of *iso*propanol remains practically constant. The density of the alcohol is 0.788, and thus its concentration is 13.1 moles/litre. If the above value of k_1 is divided by the concentration we obtain for the bimolecular rate constant the value $k_2 = 3.27 \times 10^{-7}$ litres mole^{-1} sec.$^{-1}$.

In *iso*propanol and *iso*propanol-benzene mixtures the alcoholysis of *iso*propyl benzenesulphonate is slower than in ethanol and ethanol-benzene mixtures. However, the activation energy is greater in the ethanolic solutions but it is more than compensated by the frequency factor. It is probable that the lower values of E and A in the *iso*propanolic solutions are due to the greater effect of the solvation of the transition state.

If, in analogy with the treatment used in the case of the hydrolysis [1], it is assumed that the reaction rate is proportional to the nth power of the alcohol concentration,

$$\frac{dx}{dt} = k' \, [ROH]^n \, (a-x),$$

we can, since the concentration of the alcohol remains practically constant during the course of the reaction, put $k'[ROH]^n = k_1$, where k_1 is the measured first-order rate constant. Thus, $\log k_1 = n \log [ROH] + \text{const.}$, and a straight line of slope n should be obtained for the plot of $\log k_1$ against $\log [ROH]$. This is indeed the case (Fig. 1). For the *iso*propyl ester $n = 2.0$ in either series

Fig. 1. Plot of log k *against log* [H_2O]. *Temperature 50°.*

1. *Ethyl ester, ethanol-acetone*
2.　*»　　　»　　ethanol-benzene*
3. Iso*propyl ester, isopropanol-benzene*
4.　*»　　　»　　ethanol-benzene*
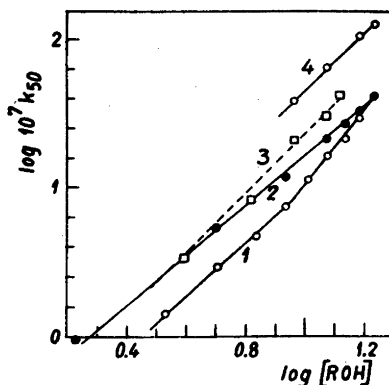
of solvents. For the ethyl ester $n = 1.7$ in ethanol-benzene mixtures but in ethanol-acetone mixtures the graph has two linear parts with $n = 1.7$ and $n = 2.5$. In the solvolysis of alkyl benzene sulphonates in acetone-water or in dioxan-water, and in the solvolysis of alkyl halides in acetone-water, two or probably three water molecules are included in the formation of the transition state if the mechanism is S_N2, but if the mechanism is S_N1 their number is six or seven. However, in the alcoholysis of 1-halogenoethers where the reaction takes place by an S_N1 mechanism plotting of log k against log [ROH] has given straight lines with slopes from 3.2 to 5.2 in alcohol-dioxan mixtures, and from 1.5 to 2.0 in alcohol-benzene and alcohol-carbon tetrachloride mixtures [6].

It is obvious that for the alcoholysis of ethyl benzenesulphonate the mechanism is S_N2. For *iso*propyl benzenesulphonate the mechanism cannot be S_N2 since its alcoholysis is more rapid than that of ethyl benzenesulphonate in the same solvent. However, the following facts are not consistent with an S_N1 mechanism: (a) the reaction is accelerated by presence of alkali (see also Ref.[3]); (b) the increase of the reaction velocity with increasing proportion of ethanol in the solvent is about the same with the isopropyl ester as with the ethyl ester, whereas in acetone-water S_N1 reactions are much more influenced by changes in the composition of the solvent than are S_N2 reactions [1,5]; (c) the value of n is only about 2; (d) although the values of A are greater for *iso*propyl benzenesulphonate than for ethyl benzenesulphonate, they are still distinctly lower than those found for S_N1 reactions in acetone-water and in dioxan-water [1,5]. It is unlikely that the two mechanisms occur simultaneously. The kinetic relationships would then be complex. If the ester disappears in two simultaneous reactions, each with its individual energy of activation, the rate constants for various temperatures would hardly be expected to conform to a simple Arrhenius equation in all solvents.

As in the case of the water solvolysis of sulphonic esters a coherent interpretation of the experimental results can be given if, as suggested by Hinshelwood, Laidler, and Timm [7], we regard the activation energy as being made up of two parts: that required to overcome the repulsion of the approaching reagent (ROH) and that required to weaken the existing bond (O—CHR'R"), *i. e.*, to stretch it from its normal length to the length in the transition state.

In ethyl benzenesulphonate the carbon atom which is the reaction centre is only weakly negative; thus the repulsion is small and the mechanism is S_N2. In *iso*propyl benzenesulphonate the introduced methyl group enhances the repulsion of the hydroxyl group in the approaching alcohol while causing the sulphonyl group to be held less tightly. The fact that the activation energy is increased in ethanolic solutions shows that the change in repulsion is the most important. This view is supported also by the fact that in pure absolute methanol, the activation energy of the alcoholysis is greater for the *iso*propyl ester than for the ethyl ester, *viz.* 23 000 and 22 100 cal., respectively [2],[3]. The most economical mode of reaction will then be that in which the alcohol molecule is forced up against the repulsion and the bond O—C in the ester is stretched at the same time until the alcohol molecule and the RSO_2O-group can compete on equal terms for the —$CHMe_2$ group. As the calculations of Eyring and Polanyi [8] show, such cases are very common. Thus the structure of the transition state will be less rigid, *i. e.* the entropy of activation less negative and the frequency factor greater than in the case of ethyl acetate in the same solvent. This is in accordance with the experimental results.

In methanol, where the kinetics in presence of alkali are between the orders one and two [3], the reaction very likely proceeds by a mechanism which approaches S_N1. This is obviously due to the fact that methanol is a more ionising solvent than are ethanol and *iso*propanol. Furthermore in methanol the ratio k_{Pr}/k_{Et} is greater than in ethanol, *e. g.* at 50° the values are 9.9 and 3.0, respectively.

A comparison of the parameters of the Arrhenius equation for the solvolysis in various pure solvents is given in Table 5. In each solvent E and A are higher for the *iso*propyl ester than for the ethyl ester, the difference increasing with the decrease of the ionizing power of the solvent and ΔE is 400, 900, and 1 330 calories in H_2O, MeOH, and EtOH, respectively. In water, where the solvolysis of the *iso*propyl ester proceeds by an S_N1 mechanism, its frequency factor is conspicuously high but high values of A are found also for the solvolysis of ethyl benzenesulphonate in water and for the alcoholysis of *iso*propyl benzene-sulphonate in methanol, *i. e.* for cases where the mechanism is not "pure" S_N2.

With an increasing proportion of acetone or benzene in the solvent the activation energy and frequency factor decrease. This phenomenon is most

Table 5. The reaction $C_6H_5SO_2OR + R'OH \rightarrow C_6H_5SO_2O^- + H^+ + ROR'$ in various pure solvents.

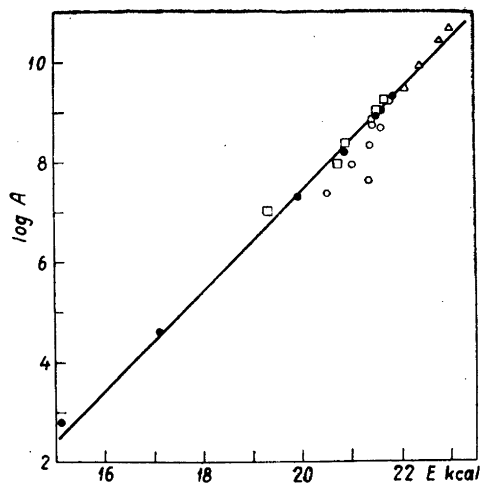| R	Et		i-Pr	
Solvent	E cal.	log A	E cal.	log A
H_2O	22 030	11.3	22 430	13.19
MeOH	22 100	9.84	23 000	11.13
EtOH	21 670	9.30	23 000	10.69
i-PrOH			21 630	9.25

Fig. 2. Plot of log A against E. O Ethyl ester, ethanol-acetone. ● Ethyl ester, ethanol-benzene. △ Isopropyl ester, ethanol-benzene. ☐ Isopropyl ester, isopropanol-benzene.

simply explained by the change in the internal structure of the solvent. On addition of acetone or benzene to the alcohol the internal structure of the alcohol will be gradually broken down, the chains formed by the alcohol molecules being split to shorter chains and finally to single molecules distributed among the molecules of the added component. The alcoholysis of alkyl benzene-sulphonates is a reaction of the type where the transition state is more polar and, consequently, more solvated than the initial state. Before the solvent can solvate the transition state the molecular bonds between the solvent molecules must presumably be broken and the heat of solvation is reduced by the amount of energy required to break these bonds. The decrease of E by solvation is therefore reduced but the further the splitting of the alcohol chains proceeds the greater will be the decrease. In ethanol-acetone mixtures there exist between the ethanol and acetone molecules weak hydrogen bonds which must in general be broken before the solvent can solvate the transition state; indeed, there is only a slight lowering of the activation energy with an increasing proportion of acetone. The formation of the mixture is endothermic in all three cases [9] but is much more so for the alcohol-benzene than for the alcohol-acetone mixtures. The variation of the activation energy is in good agreement with this state of affairs, which may explain much of the decrease of E with a decreasing proportion of alcohol in the solvent.

The more the internal structure of the pure alcohol is broken down the greater is the disorder of the molecules in the mixture and the greater will be the entropy decrease which the molecules of the solvent suffer in 'freezing' around the transition state; hence the decrease of A with the decrease of the proportion of the alcohol in the solvent. As in many other cases, there exists a linear relationship between log A and E (Fig. 2).

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