Hydrolysis and Alcoholysis of Sulphonic Esters

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In a previous investigation [1] the hydrolysis and alcoholysis of sulphonic esters were studied. The experiments, however, were limited then to the esters of primary alcohols. Sulphonic esters in several respects behave like alkyl halides [Cf. 2]. It is well known [3] that the alkaline hydrolysis of methyl and ethyl halides in aqueous acetone or alcohol is predominantly bimolecular or a S_N2 reaction, while *iso*propyl and *tert.*-butyl halides undergo hydrolysis by a two-stage or S_N1 mechanism, an addition of alkali having no influence on the reaction velocity. Thus it was to be expected that the hydrolysis of the sulphonic esters of secondary and tertiary alcohols also takes place by the unimolecular mechanism, the first stage being a dissociation of the ester molecule. The main object of the investigation reported here was to elucidate this problem. In addition, the hydrolysis and alcoholysis of some other alkyl sulphonates and the solvent effect were studied.

EXPERIMENTAL

Chemicals. The esters were prepared from the respective sodium alcoholates and benzenesulphonyl chloride [Cf. 4]. To obtain products free of sulphonyl chloride, the sodium alcoholate was used in a slight excess. With *iso*propanol and *sec.*-butanol sodium reacts slowly, so that a great excess of the alcohol was needed. Finally, the mixture was heated on a water bath. On cooling the main part of these alcoholates separated as a crystal mass. The sulphonyl chloride was added to this mixture in small portions. During the process the reaction mixture was agitated and its temperature was kept between 30° and 50° C. When all sulphonyl chloride was added, the mixture was left to stay for about an hour and then heated to about 70° C. and kept at this temperature about 10 minutes. The mixture was left to stay at room temperature for an hour and then, to remove the last traces of unchanged sulphonyl chloride, vigorously shaken with a few milliliters of an approximately 10 N sodium hydroxide solution. The mixture was then poured into a large amount of cold water and the separated ester taken into a separating funnel with a small amount of ether and shaken repeatedly with pure cold water. Finally,

the ethereal solution was dried with anhydrous sodium sulphate and the ether evaporated at reduced pressure at room temperature. By this method, using benzenesulphonyl chloride and alcohols of the highest purity, esters could be obtained in a degree of purity satisfactory for this work. They were colourless and did not give any halogen reaction with silver nitrate; the total hydrolysis gave, within the experimental error, in all cases a purity of 100 per cent. Of the esters used in this work only ethyl and *n*-propyl benzenesulphonates distil at reduced pressure without decomposition. The boiling point of *n*-propyl benzenesulphonate is $153 - 154°/9$ mm.

All efforts to obtain the *tert.*-butyl ester of benzenesulphonic acid failed. The following methods were tried. (*a*) Benzenesulphonyl chloride was dissolved into a large excess of *tert.*-butanol, and an equivalent amount of pyridine was added to the solution. At room temperature a slow evolution of a gas with the smell of a hydrocarbon (i-butylene) was observed, and as on the following day when the smell of the sulphonyl chloride had disappeared, the reaction mixture was poured into cold water, only a few drops of a colourless oil were separated. These drops which had an aromatic odour disappeared rather quickly. (*b*) The method of shaking the sulphonyl chloride and *tert.*-butanol with a concentrated sodium hydroxide solution did not give any positive result. (*c*) Silver salt of benzenesulphonic acid was shaken with *tert.*-butylbromide dissolved in dry acetone (6.5 g in 50 ml of acetone) for about an hour. An evolution of heat indicated that reaction was taking place. The liquid was separated by filtration. Analysis showed that the solid phase was AgBr. From the yellow solution, acetone and unchanged butylbromide were evaporated at reduced pressure at room temperature. The residue was an oil of a reddish brown colour. In titration, 131.3 mg of the substance required 29.3 ml of 0.02 N Ba(OH)$_2$. Assuming that the oil was the *tert.*-butyl ester, the purity of the product was thus 95.5 %. The alkali was neutralized immediately, and it was impossible to decide whether the ester was completely decomposed already in the brown liquid, or whether it was instantaneously hydrolysed when it came in contact with water. A conductivity measurement showed that when a few drops of the acetone solution, directly after the filtration of the reaction mixture, were added to water, its conductivity reached ist final value in less than five seconds.

The water used as solvent in the kinetic experiments was freshly distilled. Acetone and methanol were purified as described in the paper of Tommila and Lindholm. Dioxan was purified by the method of Hess and Frahm [5].

Method. The kinetic experiments were carried out in the same reaction vessels as were used in the work of Tommila and Lindholm, and also the method was essentially the same. At higher temperatures the reactions were conducted in sealed ampoules of Pyrex-glass. Since the velocity of the hydrolysis increases very rapidly with the water content of the solvent, the titrations in the experiments were made in the following manner. Into a 100 ml erlenmeyer flask from a burette an estimated amount of the titrating solution (0.02 N Ba(OH)$_2$ or 0.02 N HCl) was measured. The solution was cooled in a mixture of ice and water. A reaction vessel was taken from the thermostat, cooled quickly by immersing it into a mixture of ice and water, and the cold solution from the erlenmeyer flask was poured into the reaction mixture. After shaking, the solution was poured back into the erlenmeyer flask and titrated with cresol red as indicator. In this titration generally only a few tenths of a ml were required. Finally the reaction vessel was washed with the titrated solution and, if needed, titrated again to the neutral point. The whole titration took only a few seconds, during which time, at a low temperature, the progress of the reaction was negligible.

RESULTS AND DISCUSSION

The hydrolysis of isopropyl benzenesulphonate. The course of the hydrolysis of *iso*propyl benzenesulphonate in various acetone-water mixtures is expressed by the usual first order formula, as shown in Tables 1 and 2, which record the results of two typical runs. The rate constant k_1 is calculated by the formula

$$k_1 = \frac{2.303}{t} \log \frac{100}{100-p},$$ where p is the percentage change at the time t.

The amount of the ester weighed into the leg of the reaction vessel varied between 90 and 110 mg and the volume of the solvent was so calculated that, after mixing, the initial concentration of the ester was 0.05 moles/liter. In these two and in all the following tables the expressions '56 per cent acetone' *etc.* mean acetone-water mixtures containing 56 weight per cent acetone, *etc.*

Table 1. *The hydrolysis of isopropyl ben-zenesulphonate in 56 per cent acetone. Temperature 40.00° C.*

Mins.	p	$k_1 \cdot 10^4$ sec.$^{-1}$
90	14.5	0.290
120	19.2	0.296
180	25.9	0.278
240	33.5	0.282
300	39.4	0.279
420	50.2	0.276
540	60.3	0.285
720	70.8	0.285

Mean = 0.2837

Table 2. *The hydrolysis of isopropyl ben-zenesulphonate in 36.5 per cent acetone. Temperature 25.00° C.*

Mins.	p	$k_1 \cdot 10^4$ sec.$^{-1}$
120	16.1	0.243
180	22.4	0.235
300	34.5	0.235
360	39.9	0.236
480	49.0	0.234
600	57.3	0.237
620	64.4	0.239
900	72.2	0.237

Mean = 0.2370

The results of experiments carried out in the same solvents and at the same temperatures but in the presence of sodium hydroxide are given in Tables 3 and 4. A comparison of the percentage changes p shows that an addition of alkali has hardly any influence on the rate of the hydrolysis. The reaction is of the first order even in the presence of alkali. The small differences in the values of p and k, between Tables 1 and 3, and 2 and 4, are fully accounted for by experimental errors in the kinetic measurements and by eventual variations of the composition of the solvent. As will be seen later on, the rate of the reaction is extremely sensitive to the water content of the medium. The independence of the rate of the hydrolysis on the alkali was further confirmed

by the experiments made with different initial concentrations c of the ester and alkali (Table 5).

Table 3. *The hydrolysis of isopropyl benzenesulphonate in 56 per cent acetone in the presence of alkali. Ester: $c = 0.05$; NaOH: $c = 0.05$. Temperature 40.00° C.*

Mins.	p	$k_1 \cdot 10^4$ sec.$^{-1}$
90	15.0	0.302
120	19.1	0.294
180	27.5	0.298
240	33.9	0.287
270	38.3	0.298
420	53.2	0.301
540	62.4	0.302
720	73.5	0.307

Mean 0.2986

Table 4. *The hydrolysis of isopropyl benzenesulphonate in 36.5 per cent acetone in the presence of alkali. Ester: $c = 0.05$; NaOH: $c = 0.05$. Temperature 25.00° C.*

Mins.	p	$k_1 \cdot 10^4$ sec.$^{-1}$
120	15.7	0.236
180	21.9	0.229
300	35.7	0.245
480	51.2	0.249
720	65.1	0.244
900	71.5	0.232

Mean 0.2391

Table 5. *The hydrolysis of isopropyl benzenesulphonate in 56 per cent acetone at 50.00° C.*

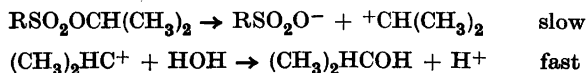| c_{Ester}	0.0712	0.0712	0.0674	0.0673	0.0648	0.0633	0.0607
c_{NaOH}	0.100	0.070	0.050	0.030	0.020	0.010	0.000
Mins.	90	90	90	90	90	90	90
p	39.0	37.9	37.7	37.2	36.4	37.6	36.6
$k_1 \cdot 10^4$sec.$^{-1}$	0.916	0.885	0.878	0.861	0.841	0.874	0.845

For a unimolecular reaction the time of half-completion must be independent of the initial concentration, according to the formula $t_{1/2} = (\ln 2)/k_1$. That this condition is fulfilled is seen from Table 6. The time of half-completion

Table 6. *The hydrolysis of isopropyl benzenesulphonate. Time of half-completion at 25° and 50° C. Solvent 56 per cent acetone.*

c_{Ester}	c_{NaOH}	25.00°		50.00°	
		Mins.	p	Mins.	p
0.100	0.100	2 220	47.9	130	50.2
0.050	0.050	2 220	49.0	130	51.3
0.025	0.025	2 220	49.7	130	50.0
0.010	0.010	2 220	50.0	130	49.8

is quite independent of the initial concentration of the ester, and the presence of alkali has no effect.

All these results show that the hydrolysis of the *iso*propyl ester of benzene-sulphonic acid is a two-stage reaction with the S_N1 mechanism, the rate-determining stage being ionization of the ester molecule:

$$RSO_2OCH(CH_3)_2 \rightarrow RSO_2O^- + {}^+CH(CH_3)_2 \qquad slow$$
$$(CH_3)_2HC^+ + HOH \rightarrow (CH_3)_2HCOH + H^+ \qquad fast$$

The hydrolysis of *n*-propyl ester of benzenesulphonic acid is much slower than that of the *iso*propyl ester. *E.g.* in 56 per cent acetone at 40° C, for the latter $k_1 = 0.284 \cdot 10^{-4}$ sec.$^{-1}$, for the former only $0.0163 \cdot 10^{-4}$ sec.$^{-1}$ (Table 7). Besides, the former reaction is powerfully catalysed by alkali *, the latter not at all. These facts, too, indicate that the mechanisms cannot be the same in the two cases. The *n*-propyl ester like the other *n*-alkyl esters undergoes hydrolysis by the one-stage or S_N2 reaction.

The hydrolysis of *sec.*-butyl ester of benzenesulphonic acid occurs faster than that of *sec.*-propylester. In 56 per cent acetone at 40° C the value of the rate constant is $k_1 = 0.390 \cdot 10^{-4}$ sec.$^{-1}$ (Table 7). An addition of sodium hydroxide had no influence on the speed of the reaction. Obviously all the sulphonates of secondary alcohols undergo hydrolysis by a two-stage mechanism.

The Arrhenius equation. — The mean values of k for various temperatures are given in Table 7. Activation energies and frequency factors were obtained from the variation of log k with $1/T$, the simple Arrhenius equation $k = Ae^{-E/RT}$ being obeyed within the limits of the experimental error in all cases. In the calculation the method of the least squares was used. Table 7 contains also the values of E and log A. Because of the poor solubility of *iso*propyl benzene-sulphonate in water and the great rapidity of the reaction in this solvent, a direct measuring of the rate of its hydrolysis in water was not possible. The values of k_1 for pure water given in the Table are obtained by extrapolating to the acetone content zero on the ground of Fig. 1 which shows that log k_1 is practically a linear function of the acetone percentage of the solvent. From these extrapolated values, which give a good Arrhenius plot, E and log A were calculated.

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* In the presence of alkali the hydrolysis of the *n*-propyl ester is a reaction of second order; in 56 per cent acetone $k_2 = 0.000125$ 1 mol^{-1}sec.$^{-1}$ at 40.00 °C.
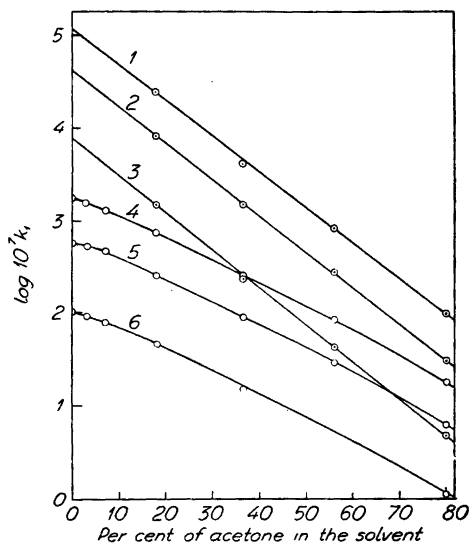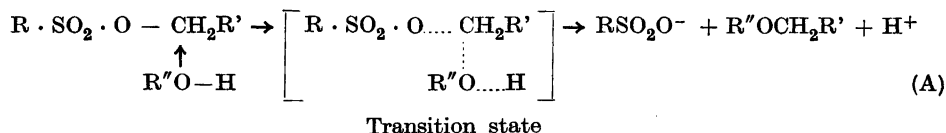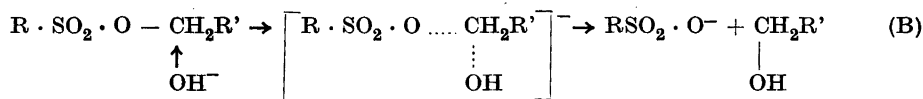
Fig. 1. Influence of solvent. 1, 2 and 3 the hydrolysis of isopropyl benzenesulphonate, 4, 5 and 6 the hydrolysis of ethyl benzene-sulphonate at 50°, 40°, and 25° C.

The data of Table 7 give further justification for the following mechanism of the solvolysis of sulphonates of primary alcohols proposed in the paper of Tommila and Lindholm:

$$R \cdot SO_2 \cdot O - CH_2R' \rightarrow \begin{bmatrix} R \cdot SO_2 \cdot O ..... CH_2R' \\ \\ R''O....H \end{bmatrix} \rightarrow RSO_2O^- + R''OCH_2R' + H^+$$

$$\uparrow$$
$$R''O-H$$

Transition state

(A)

(R″ = H or an alkyl radical), or in the presence of alkali:

$$R \cdot SO_2 \cdot O - CH_2R' \rightarrow \begin{bmatrix} R \cdot SO_2 \cdot O ..... CH_2R' \\ \\ OH \end{bmatrix}^- \rightarrow RSO_2 \cdot O^- + CH_2R'$$

$$\uparrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$OH^- \qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

(B)

In the same solvent, e.g. in 56 per cent aqueous acetone, the specific reaction rate follows the order

$$CH_3 > C_2H_5 > n-C_3H_7$$

i.e. the order of increasing electron-repulsive character of the alkyl group in the alcohol side. We have also seen, above, that the sec.-butylester is hydro-lysed more rapidly than the sec.-propylester. This is in harmony with the predictions of the theory. Groups which facilitate the electron release from the C atom of the -O-C-group facilitate the ionization and have an accelerating effect on the S_N1 mechanism. In the one-stage bimolecular mechanism, such a group, on the one hand, weakens the bond which must be broken, on the

Table 7. The values of k, E and A.

Ester and solvent	$10^7 \cdot k_1$ sec.$^{-1}$					E cal.	log A
	25.00°	40.00°	50.00°	60.00°	75.00°		
$C_6H_5SO_2OMe$: 56.0 % acetone		71.0	201	529		20 600	9.25
$C_6H_5SO_2OEt$: Pure water	103	577	1 740			22 030	11.13
3.0 % acetone	93.0	530	1 610			21 800	10.95
7.0 » »	79.3	465	1 290			21 410	10.60
17.8 » »	45.8	259	745			21 370	10.32
36.5 » »	15.1	90.4	257			21 730	10.11
56.0 » »		29.1	86.8		974	21 730	9.64
80.0 » »	1.10	6.40	18.2		201	21 460	8.78
$C_6H_5SO_2OPr(n)$: 56.0 % acetone		16.3	48.2	21.7 (65.0°)		21 800	9.42
$C_6H_5SO_2OPr(iso)$: Pure water	7 750	42 200	120 000			21 000	12.27
17.8 % acetone	1 490	8 430	24 600			21 470	11.91
36.5 » »	237	1 400	4 180			22 000	11.50
56.0 » »	43.1	284	839			22 780	11.34
80.0 » »	4.75	30.3	100			23 310	10.76
65.9 » dioxan			646				
$C_6H_5SO_2OBu(sec.)$ 56.0 % acetone	66.7	390	1 230			22 280	11.15

other hand it augments the repulsion between the attacking reagent and the said C atom. The latter effect is more powerful and the net result is opposite to that in S_N1. Steric effects also may hinder S_N2 reaction.

When the repulsion between the attacking reagent and the seat of reaction is relatively small, the energy of activation is determined by this repulsion energy. Such is the case in the hydrolysis of the sulphonates of primary alcohols. If the group $-CH_2R'$ be sufficiently varied in the direction of increasing negative charge on C, the energy of activation will no longer be determined primarily by the repulsion between this C atom and attacking reagent, for it may now require less energy to extend the bond O—C than force a hydroxyl ion or the negative portion of a water dipole right up to C. This means a change of mechanism ($S_N2 \rightarrow S_N1$). The data of Table 7 actually show that in the

same solvent, e.g. in 56 per cent acetone, the energy of activation for the hydrolysis of esters of primary alcohols follows the order

$$CH_3 < C_2H_5 < C_3H_7$$
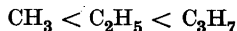
i.e. the order of increasing negative charge on the C atom, but is considerably lower than E for the hydrolysis of *iso*propyl ester. On the other hand, the energy of activation is, as required by the theory, less for the hydrolysis of *sec.*-butylester than for *sec.*-propylester.

The influence of the solvent. Table 7 shows that in acetone-water mixtures the specific reaction rate k_1 of the water hydrolysis decreases enormously with decreasing water content of the solvent. From Fig. 1 we see that in the range between 0 and 80 per cent acetone log k_1 for the *iso*propyl ester is practically a linear function of the acetone percentage. The effect of the solvent is appreciably greater in the hydrolysis of *iso*propyl benzenesulphonate than in that of ethyl benzenesulphonate. Although for both reactions the curves in Fig. 1 are greatly similar, the parameters of the Arrhenius equation behave differently in the two series. For the hydrolysis of *iso*propyl benzenesulphonate E increases continuously with the percentage of the acetone in the solvent, whereas for the hydrolysis of ethyl benzenesulphonate E in low acetone contents has a trough and in high acetone contents falls again. In the latter case A changes in the same direction as E, whereas in the hydrolysis of the *iso*propyl ester the changes of A and E take place in opposite directions. This entirely different behaviour of E and A is clearly an indication of different reaction mechanisms in the two cases. The trough in E is also found for the alkaline hydrolysis of carboxylic esters, which, too, is a bimolecular reaction.

The influence of the solvent may be assessed by considering the total solvation of the transition state in relation to those of the reactants, which solvation depends on the magnitude and distribution of the charges in the two states. If the transition state is solvated to a greater extent than the reactants, the activation energy is lowered. There is no doubt that solvation plays a part in the bond fission of the mechanism S_N1, and that the ionizing effect of the water-acetone mixtures increases with the water content. Thus the reaction is the faster the greater the water content of the solvent. In the case of the bimolecular (S_N2) mechanism the observed changes of E and A have an opposite effect on the reaction velocity, and thus the solvent effects are more complicated.

The inhibiting effect of dioxan is somewhat greater than that of acetone. Table 7 shows the value of k at 50° C in a 65.9 per cent dioxan-water, in which mixture the mole fraction of water is the same ($x_{water} = 0.717$) as in 56 per

cent aqueous acetone. This different effect is probably, partly at least, due to the formation of hydrogen bonds between water and the organic solvent component from which it comes, so that only a part of the water molecules are quite free to participate in the reaction or in the solvation phenomena. This part becomes smaller with the decrease of the water content of the solvent, and is, at the same water content, smaller in dioxan-water than in acetone-water, since a dioxan molecule with its two oxygen atoms can join two water molecules with hydrogen bonds, while an acetone molecule can join only one.

The alcoholysis. In pure absolute methanol the alcoholysis of *iso*propyl benzenesulphonate

$$C_6H_5SO_2OPr(i) + MeOH \rightarrow C_6H_5SO_2OH + MeOPr(i)$$
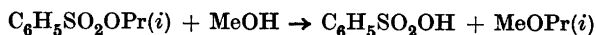
is a first order reaction (Table 8). The most probable values obtained are:

	25.00°	40.00°	50.00°	E cal	log A
$10^6 k_1$ sec.$^{-1}$	1.95	12.5	39.2	22 980	11.13

This reaction is also much (at 50° about five times) faster than the corresponding reaction of ethyl benzenesulphonate. As in hydrolysis, the activation energy and the frequency factor are higher than for the reaction of ethyl benzenesulphonate, for which alcoholysis in methanol[1] $k_{50°} = 8.00 \cdot 10^{-6}$, $E = 22\,090$ cal, log $A = 9.84$. Alkali affects alcoholysis, as will be seen from Tables 8 and 9, but in the presence of an equivalet concentration of sodium hydroxide the second order formula gives for k values which continuously increase *,

Table 8. *The alcoholysis of isopropyl benzenesulphonate in abs. methanol at 50.00° C.*

t mins.	90	120	180	240	360	420	480
p	19.2	24.5	34.6	43.2	57.0	62.7	67.1
$10^5 k_1$ sec.$^{-1}$	3.97	3.91	3.94	3.93	3.91	3.92	3.86

Table 9. *The alcoholysis of isopropyl benzenesulphonate in abs. methanol in presence of alkali at 50.00°. $c_{Ester} = c_{NaOH} = 0.05$ moles/liter.*

t mins.	45	60	90	120	150	180	210	300	360
p	15.3	20.5	26.9	34.2	41.1	46.3	49.7	61.9	66.4
$10^5 k_1$ sec.$^{-1}$	6.14	6.39	5.81	5.82	5.88	5.76	5.45	5.36	5.05
$10^5 k_2$ l mol^{-1} sec.$^{-1}$	133	134	137	145	155	160	157	181	183

* Owing to the equilibrium $CH_3OH + NaOH \rightleftharpoons CH_3ONa + H_2O$ the alkaline solution contains a little of water. However, experiments in absence of alkali, in methanol containing 60 mg of water in 50 ml, showed that in this solution the reaction velocity is approximately the same as in water free methanol. Thus the small water content of the solution cannot cause the shift in k

the first order formula values which continuously decrease. This indicates that in the presence of alkali, alcoholysis takes place partly by $S_N 1$, partly by $S_N 2$ mechanism. A transesterification, catalyzed by the alkali, may in a measure occur, but it cannot seriously disturb the picture. In the absence of alkali, the alcoholysis of *iso*propyl benzenesulphonate is very likely to occur predominantly by $S_N 1$ mechanism, inasmuch as it is so much faster than the corresponding reaction of the ethyl ester.

In *iso*propyl alcohol the velocity of the alcoholysis of *iso*propylbenzene sulphonate is only about one tenth of that in methanol (observed: $k_1 = 0.388$ 10^{-5} sec.$^{-1}$ at 50°). The acceleration by alkali is greater (at 50° from the first order formula $k_1 < 20 . 10^{-5}$, from the second order formula $k_2 \approx 45 \cdot 10^{-5}$, the latter early constant) than in methanol, in accordance with the fact that *iso*propanol is a less ionizing solvent than methanol.

With sodium *iso*propylate in isopropanol *iso*propyl benzenesulphonate reacts with about the same velocity as with sodium hydroxide and the reaction is mainly bimolecular (at 50° $k_2 = 46 \cdot 10^{-5}$ l mol^{-1} sec.$^{-1}$).

SUMMARY

The hydrolysis of *iso*propyl benzenesulphonate and *sec.*-butyl benzenesulphonate in aqueous acetone is a two-stage reaction. The alcoholysis of these esters takes place partly by a unimolecular, partly by a bimolecular mechanism. The solvolyses of *n*-alkyl sulphonates are presumably one-stage reactions. The solvent effects in the hydrolytic reactions of sulphonic esters were studied.

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