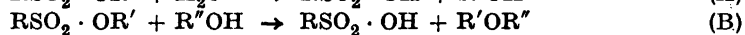
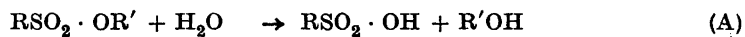


A Kinetic Study of the Reactions of Alkyl Esters of Aryl-sulphonic Acids with Water, Alcohols, Hydroxyl Ion, and Ethoxyl Ion

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Chemically, the esters of sulphonic acids differ greatly from those of carboxylic acids. The latter are stable when dissolved in the corresponding alcohol, and their hydrolysis in pure water is, in general, very slow, whereas the former react rather easily with water and also with alcohol,



These two reactions have been kinetically studied by several early workers^{1,2}, but, with one exception, at one temperature only. The present paper presents the results of a series of experiments carried out with some aromatic sulphonic esters at different temperatures.

EXPERIMENTAL

Chemicals. The esters were prepared by the method of Krafft and Roos³ from the corresponding sulphonyl chlorides and alcohols, and purified by distillation at reduced pressure in an all-glass apparatus. The physical characteristics of the esters were:

Ethyl ester of benzenesulphonic acid, b. p. 152–152.5°/12 mm,

d_{15° 1.2213, d_{20° 1.2167, d_{25° 1.2124, d_{40° 1.2083.

Methyl ester of benzenesulphonic acid, b. p. 143°/10 mm, d_{17° 1.2730.

Ethyl ester of *p*-chlorobenzenesulphonic acid, b. p. 162°/12 mm, m. p. 23.5°.

Ethyl ester of *p*-toluenesulphonic acid, b. p. 176°/16 mm, m. p. 32–33°.

These values are in good agreement with the most reliable values reported in literature. The purity of esters was also checked by complete alkaline hydrolysis.

The water used as solvent in the experiments was ordinary distilled water, freed from carbon dioxide by suction of CO₂-free air through the water for several hours. The

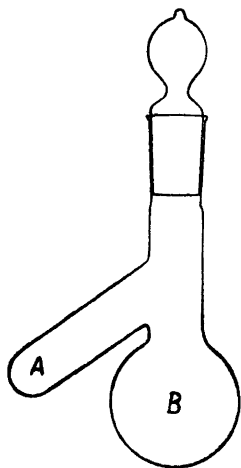


Fig. 1. Reaction vessel.

methanol, "Methanol acetonfrei", from Schering, was purified by the method of Lund and Bjerrum⁴. In the last distillation, however, instead of tribromobenzoic acid anhydrous copper sulphate was used. To get pure water-free ethanol, usual commercial 95 per cent ethanol was first dried by refluxing with calcium oxide, distilled, and treated by the method of Lund and Bjerrum. Acetone was Schering's "Aceton, reinst" which was purified by drying over potassium carbonate and subsequent slow distillation through an efficient column. It had a constant boiling point within 0.1°, and it did not give any reaction with potassium permanganate.

Benzenesulphonic acid used in some experiments was a specimen of Schering.

Method. The most kinetic experiments were carried out in glass-stoppered reaction vessels with two compartments A and B (Fig. 1). The vessel was weighed, and a few drops of ester were introduced into A; then it was weighed again. The difference between the two weighings gives the weight of the ester. A calculated amount of solvent was then

measured by means of a pipette and a micro burette into the bulb B. The vessel was closed with the stop-cock and kept in the thermostat until the reactants had acquired its temperature. Then the reaction was started by mixing the reactants by vigorous shaking, the time being recorded. After a few seconds all of the ester had always dissolved. After suitable time intervals reaction vessels were taken from the thermostat and quickly cooled by putting in a mixture of ice and water; the acid formed was titrated, cresol red being used as indicator. At temperatures in the neighbourhood of and over the boiling point of the solvent the reactions were carried out in sealed ampoules of about 12 ml capacity.

In experiments where NaOH was used as catalyst, a measured amount of the NaOH-solution was placed in B and the reaction started as given above; in this case the reaction was stopped by an excess of 0.02 N hydrochloric acid and titrated back with 0.02 N baryta solution. The reactions between ethyl benzenesulphonate and ethoxyl ion were carried out in the same reaction vessels; 5 ml of 0.1 N solution of the ester in absolute ethanol were placed in A, and in B 5 ml of 0.1 N sodium ethylate solution (prepared by dissolving sodium in absolute ethanol), thermostated, and mixed by shaking. The reaction was stopped by an excess of 0.02 N hydrochloric acid and titrated back with baryta solution, using cresol red as indicator.

The thermostat was electrically controlled and its temperature could be kept constant within 0.02°. The thermometers were checked against standard thermometers.

The formation of ether in reaction B is clearly observed by smell when a concentrated ethanol solution of ethyl benzenesulphonate is heated in an ampoule at 50° for some hours and the ampoule is broken. No decomposition was observed when a solution of ethyl benzenesulphonate in dry acetone was boiled on a water bath for several hours under a reflux condenser.

Rate calculations. The solubility of sulphonic esters in water is very poor; however, in the experiments in pure water 0.01 N solutions could be used. In the other solvents the ester was 0.05 N. As water or alcohol is in such great excess that its concentration hardly changes during the course of the reaction, for reactions (A) and (B) the rate equation

$$dx/dt = k_1 (a-x), \text{ or } k_1 = 1/t \cdot \ln [a/(a-x)],$$

where $(a-x)$ is the concentration of the ester at time t , could be used. If p is the percentage change at time t , for calculation of the first order velocity constant, the equation may be written in the very convenient form

$$k_1 = \frac{2.303}{t} \log \frac{100}{100-p}$$

This formula gave a good constancy for k_1 , as is exemplified by the following two typical runs:

Solvolysis of ethyl benzenesulphonate in pure water, $a = 0.01$ mole/liter, 60.05° .

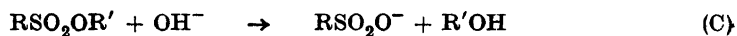
t mins.	7	12	16	20	37	40	50	60
Percentage change	17.3	27.6	35.7	42.7	65.4	68.1	76.5	80.8
$10^4 k_1$ sec. ⁻¹	4.55	4.50	4.61	4.64	4.77	4.77	4.82	4.58

Solvolysis of ethyl *p*-chlorobenzenesulphonate in abs. ethanol, $a = 0.05$ mole/liter, 75.00°

t mins.	20	36	50	72	85	95	112	122	130
Percentage change	12.1	21.0	27.8	36.8	42.7	45.6	51.2	53.9	56.4
$10^4 k_1$ sec. ⁻¹	1.07	1.10	1.09	1.06	1.10	1.07	1.07	1.06	1.07

In the other runs the constancy of k_1 was of about the same order. To save space the runs are not given in detail.

In the presence of sodium hydroxide the reaction is



but we are also concerned with the reaction (A). Thus the over-all rate of reaction is given by the expression

$$dx/dt = k_1 (a-x) + k_2 (a-x) (b-x)$$

where $(a-x)$ is the concentration of the ester, and $(b-x)$ that of hydroxyl ions at time t , k_1 the first order rate constant for (A), and k_2 the bimolecular constant for (C). However, the reaction (C) is so much faster than (A) that if a relatively great concentration of the alkali is used, the latter reaction may be neglected. To facilitate calculations,

the experiments were conducted with equimolecular concentrations of ester and hydroxyl ion, and k_2 computed from the usual expression

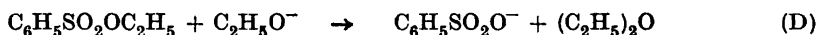
$$k_2 = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right], \text{ or } k_2 = \frac{100}{at} \left[\frac{1}{100-p} - \frac{1}{100} \right].$$

E. g. in water at 50° C, with the initial concentration $a = 0.01$ mole/liter, was obtained:

t mins.	4	7	9	11	13	16	19
Percentage change	15	23.6	27.8	32.3	35.7	42.4	45.1
$10^2 k_2$ l mole ⁻¹ sec. ⁻¹	7.29	7.39	7.15	7.24	7.16	7.69	7.21

The mean of the series is $k_2 = 0.0730$. At this temperature k_1 is only 0.000482. However, to avoid a significant decrease of the ester concentration due to reaction (A), the runs were taken only to about 50 per cent change.

In similar manner, for evaluation of the velocity constant of the reaction between ethyl benzenesulphonate and sodium alcoholate in absolute ethanol:



the reaction (B) can be omitted and the simple bimolecular formula used, as show the following values obtained at 40° C with equal initial concentrations of both reactants:

t mins.	30	45	60	75	90	110	120	170
Percentage change	15.2	21.2	27.0	31.4	35.2	39.2	41.2	50.4
$10^3 k_2$ l mole ⁻¹ sec. ⁻¹	1.99	2.00	2.05	2.04	2.01	1.94	1.94	2.00

The mean is $k_2 = 2.00 \cdot 10^{-3}$. For the reaction (B) is at this temperature $k_1 = 1.40 \cdot 10^{-6}$. Morgan and Cretcher⁵, in their investigation on the reaction, also used this simplified method for the evaluation of k_2 .

The rate constants were determined at four or five temperatures and are means of 6 to 10 determinations representing 10 to 60 percentage change. From the k -values, corresponding different temperatures, the parameters A and E of the Arrhenius equation

$$k = Ae^{-E/RT}$$

were calculated using the method of the least squares. The Arrhenius equation was always obeyed within the experimental error. The results are summarized in Tables 1—3.

Table I. Solvolysis of sulphonic esters.

Ester	Solvent	Temp. °C $10^5 k_1 \text{ sec}^{-1}$.		<i>E</i> cal	$\log_{10} A$
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	Pure water	25.0	1.03	22 030	11.13
		30.0	1.60		
		40.0	5.77		
		50.0	17.4		
		60.0	47.3		
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	Abs. methanol	40.0	0.263	22 090	9.84
		50.0	0.800		
		60.0	2.29		
		74.9	9.62		
		80.0	14.2		
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	Abs. ethanol	40.0	0.139	22 000	9.50
		50.2	0.421		
		60.0	1.22		
		74.9	4.82		
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	0.01 <i>N</i> $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$ in water	40.0	6.41	22 080	11.22
		50.0	18.6		
		60.0	52.9		
		75.0	226		
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	0.05 <i>N</i> KCl	40.0	6.13	22 130	11.24
		50.0	19.3		
		60.0	52.9		
		64.8	83.4		
$\text{C}_6\text{H}_5\text{SO}_2\text{OEt}$	Acetone-water con- taining 56 weight per cent acetone	40.0	0.291	21 730	9.64
		50.0	0.868		
		60.0	2.42		
		75.0	9.74		
$\text{C}_6\text{H}_5\text{SO}_2\text{OMe}$	Pure water	25.0	1.15	21 030	10.48
		40.0	6.45		
		50.1	18.5		
		60.0	48.4		
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OEt}$	Abs. ethanol	40.0	0.0875	22 320	9.52
		50.0	0.265		
		64.8	1.25		
		75.0	3.17		
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OEt}$	56 per cent acetone	40.0	0.177	21 860	9.58
		50.0	0.530		
		64.8	2.39		
		75.0	6.11		

Table 1 continued.

<i>p</i> -Cl.C ₆ H ₄ SO ₂ OEt	Abs. ethanol	40.0	0.300	} 22 670	10.31
		50.0	0.919		
		60.0	2.83		
		75.0	11.5		
<i>p</i> -Cl.C ₆ H ₄ SO ₂ OEt	56 per cent acetone	40.0	0.749	} 21 250	9.71
		50.0	2.16		
		60.0	6.05		
		75.0	23.0		

Table 2. The reaction $C_6H_5SO_2OEt + NaOH \rightarrow C_6H_5SO_2ONa + EtOH$ in water.

Temp. °C	$10^3 k_2$ l mole ⁻¹ sec. ⁻¹	<i>E</i> cal	log ₁₀ <i>A</i>
40.0	9.20	} 21 120	12.70
50.2	25.2		
60.0	74.1		
75.0	273.0		

Table 3. The reaction $C_6H_5SO_2OEt + EtONa \rightarrow C_6H_5SO_2ONa + EtOEt$ in absolute ethanol

Temp. °C	$10^3 k_2$ l mole ⁻¹ sec. ⁻¹	<i>E</i> cal	log ₁₀ <i>A</i>
25.0	0.372	} 20 880	11.87
40.0	2.04		
49.9	5.78		
60.1	15.2		

DISCUSSION

General. From Table 1 we see that the specific rate of the solvolytic reaction of ethyl benzenesulphonate with water is about 20 times as great as that of the reaction with methanol and about 40 times as great as that of the reaction with ethanol. The solvolysis of methyl ester is a little faster than that of ethyl ester. Chlorine as substituent in the aromatic nucleus has an accelerating influence, while methyl group reduces the reaction velocity, as already demonstrated in Demeny's study of the effect of a substituent upon the rate at which an alkyl sulphonate hydrolyzes^{1a}. The independence of k_1 on the acid formed in the reaction and the experiments carried out in the presence of added benzenesulphonic acid show that the hydrolysis is not catalyzed by acids. This is consistent with previous observations^{1e,g,6}. However, in the

presence of added sulphonic acid k_1 is a little greater than in pure water. This result and the observation of McCleary and Hammett⁶ that in 60 per cent dioxane-water k_1 slightly increases during the reaction is easily explained by the dependence of activity coefficients on the concentration.

One conspicuous point is that the activation energies of the solvolytic reactions of ethyl benzenesulphonate with water, methanol, and ethanol are practically equal, about 22 000 cal, and that the differences in the k -values are solely due to differences in the parameter A of the Arrhenius equation. For the (bimolecular) reactions between ethyl benzenesulphonate and hydroxyl ion (in water) or ethoxyl ion (in absolute ethanol) the activation energy is only about 1 000 calories lower (Tables 2 and 3). For the latter reaction Morgan and Cretcher⁵ found that $E = 21\,750$ cal and $\log A = 12.56$, which values are somewhat greater than those of the Table 3. Morgan and Cretcher estimated k_2 at two temperatures only.

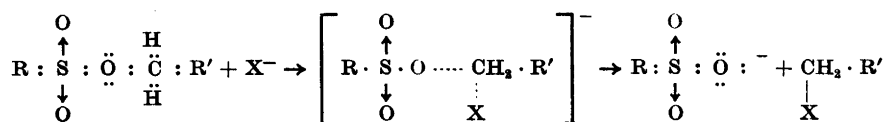
Concerning the parameters of the Arrhenius equation, the alkaline hydrolysis of ethyl benzenesulphonate differs greatly from that of ethyl benzoate. As is generally the case for the alkaline hydrolysis of carboxylic esters, the activation energy and frequency factor have markedly low values for the latter reaction; in water $E = 12\,700$ cal and $\log A = 7.76$ (unpublished results). For the alkaline hydrolysis of ethyl benzenesulphonate in water $E = 21\,100$ cal and $\log A = 12.70$ or $A = 5 \times 10^{12}$. This value of A is somewhat greater than the theoretical collision frequency $Z \approx 3 \times 10^{11}$, so that in the expression $A = PZ$ the probability factor P is about 17. For the reaction between ethoxyl ion and ethyl benzenesulphonate $E = 20\,880$ cal and $\log PZ = 11.87$ or $P \approx 2$. For the alkaline hydrolysis of ethyl benzoate in water we obtain from $\log PZ = 7.76$ the value $P \approx 2 \cdot 10^{-4}$.

Acetone in the solvent reduces the reaction velocity very much. This effect is entirely due to a decrease of the frequency factor, the activation energy remaining practically constant or rather decreasing somewhat.

The mechanism of the reaction. The values of E and A indicate that the mechanism of the hydrolysis of sulphonic esters differs greatly from that of carboxylic esters. The hydrolysis carried out in water enriched in ^{18}O has shown that in the latter case the cleavage is in the C—OR link⁷. Sulphonic esters, again, hydrolyse, as suggested even as early as 1912 by Ferns and Lapworth⁸, and as the experiments⁹ with ^{18}O show, with O—C and not S—O bond-fission. Hinshelwood, Laidler, and Timm¹⁰ have shown, in a theoretical treatment, that one 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 bond, *i. e.*, to stretch it from its normal length to the length in the transition state. In alkaline hydrolysis

of carboxylic esters the repulsion is least at the carbonyl carbon, and therefore the hydroxyl ion attacks this atom; the over-all reaction is of the type where the repulsion energy governs the situation¹⁰. Since the repulsion is weak, the activation energy is small.

In the sulphonic acids two oxygen atoms are bound to sulphur with semi-polar links, the two lone electron pairs of the sulphur atom being shared with oxygen. Thus the sulphur atom carries a positive charge. However, since no double bond exists and consequently the electron displacements around the central atom are impossible, the hydroxyl ion can not be attached to the sulphur and the reaction takes place by another mechanism. The positive charge of the sulphur atom causes electrons in the chain to be drawn towards the sulphur: $S \leftarrow O \leftarrow C$, which renders the carbon atom of the alkyl group weakly positive. Therefore, the hydroxyl ion adds at this atom. Because, however, the attraction between the negative ion and the carbon atom is small, *i. e.*, the repulsion large, the activation energy is large. Reactions (C) and (D) may accordingly be represented^{cf. 11,9,12}



where X^- is OH^- or $\text{C}_2\text{H}_5\text{O}^-$ (or any nucleophilic reagent). Thus here the etheral oxygen with the bond electrons follows the acid side and this radical comes off as an ion. The experiment carried out in the presence of KCl shows that the reaction with Cl^- is extremely slow^{cf. 6}.

If the standard state is taken as corresponding to a concentration of 1 mole per liter, we obtain by the formula

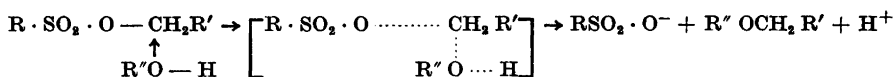
$$A = e \frac{kT}{h} e^{\Delta S^\ddagger/R}$$

for the reaction (C) at 300° K from $A = 5.0 \times 10^{12}$ for the standard entropy of activation $\Delta S^\ddagger = -2.44 \text{ cal deg.}^{-1} \text{ mole}^{-1}$, whereas the value $A = 2.8 \times 10^{11}$, which equals the theoretical collision frequency Z , gives $\Delta S^\ddagger = -8.2 \text{ cal deg.}^{-1} \text{ mole}^{-1}$. For the reaction (D) we obtain from the experimental result $A = 7.4 \times 10^{11}$ $\Delta S^\ddagger = -6.6 \text{ cal deg.}^{-1} \text{ mole}^{-1}$. These values of ΔS^\ddagger indicate that the transition state in reactions (C) and (D) has a loose structure¹³, the bond between the etheral oxygen and the alkyl carbon being largely stretched. For the alkaline hydrolysis of ethyl benzoate in water

the entropy of activation has the very negative value $\Delta S^\ddagger = -24.9$ cal. deg.⁻¹ mole⁻¹, which is most easily understood in terms of the electromeric displacement and of the change in solvation in the formation of the transition state.

As stated above, the usual mode of alkaline hydrolysis of carboxylic esters involves a bimolecular attack of carbonyl carbon by hydroxyl ion and acyl-oxygen fission. However, recent work by Kenyon, Balfe, and their collaborators¹⁴ shows that in some cases in alkaline hydrolysis of carboxylic esters the mechanism which involves alkyl-oxygen fission, as in the hydrolysis of sulphonic esters, is operating.

For the solvolysis a corresponding mechanism can be presented:



R'' is a hydrogen atom or an alkyl group. Here it is the uncharged R''OH which attacks the carbon atom of the CH₂R' group, and since the electrostatic attraction between this carbon atom and the dipole is less than between this carbon and a negative ion, the experimental result that for the solvolysis the activation energy is somewhat greater than for the reactions (C) and (D), is readily understandable. It is also natural that, on the one hand, the activation energy is nearly the same for (C) and (D), and the near-constancy of *E* for the solvolytic reactions on the other hand. In a solvolytic reaction there is a considerable re-arrangement of energy among the various degrees of freedom to accompany the formation of the activated complex, *i. e.*, a small probability of formation of the activated complex, and, therefore, the entropy of activation is appreciably negative, the more the more complicated is the reagent molecule. Thus, the standard state being a concentration of 1 mole per liter, we obtain from the bimolecularly calculated log *A* values for the solvolysis of ethyl benzenesulphonate with water, methanol, or ethanol for ΔS^\ddagger the values -17.6 , -22.8 or 23.6 cal deg.⁻¹ mole⁻¹.

Acetone reduces remarkably the rate of the reaction, as is seen from the following values concerning the solvolysis of ethyl benzenesulphonate with water:

water (k_2) _{50°} = 29.0 · 10 ⁻⁷	<i>E</i> = 22 030 cal	log <i>A</i> = 9.68
56 per cent acetone 3.89 · 10 ⁻⁷	21 730	8.29

Here k_2 is the bimolecular rate constant of reaction (A), calculated from the Arrhenius equation and log *A* also refers to the bimolecular reaction. The retarding effect is wholly in the *A* term, with *E* remaining unchanged or

rather decreasing a little. The decrease of A , or a more negative value of the entropy of activation, is probably explained in terms of the solvation entropy¹³. The dipole moment of acetone (2.72 D) is much larger than that of water (1.84 D), and thus the acetone dipoles compete successfully with water dipoles in the solvation of reagents and activated complex, and this might make the entropy of activation more negative, since it is possible that it renders the rearrangement of the energy in the formation of transition state more complex. The eventual small decrease of E might be explained by an increase of attraction between $R''OH$ and CH_2R' as the dielectric constant of the medium decreases.

A comparison of reactions of substituted ethyl benzenesulphonates with ethanol and water (56 per cent acetone) is given in Table 4.

Table 4. The substituent influences.

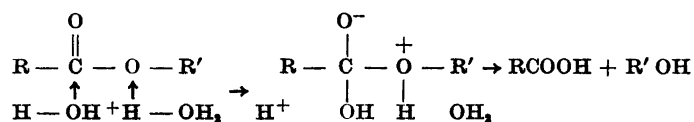
	Ethanol			56 per cent acetone		
	$10^7 (k_2)_{50}^\circ$	E cal	$\log_{10} A$	$10^7 (k_2)_{50}^\circ$	E cal	$\log_{10} A$
<i>p</i> -CH ₃	0.980	22 320	8.09	2.38	21 860	8.24
H	1.58	22 000	8.07	3.89	21 730	8.29
<i>p</i> -Cl	3.43	22 670	8.87	9.76	21 250	8.36

Because the benzene ring which carries the substituents is remote from the seat of reaction, the transmission of the substituent influences must be considerably damped. A substituent which attracts electrons (chlorine) raises, a substituent which repels electrons (methyl group) lowers the velocity of reaction. In acetone water the changes in velocity are principally accounted for by change in the activation energy. In the reaction with ethanol the changes in E and A are irregular.

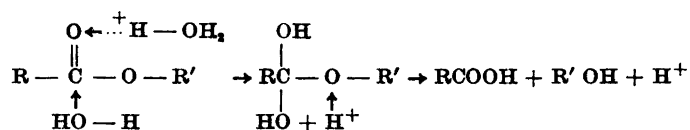
From the alcohol side the substituent influence is, because of the close proximity of the seat of reaction, more powerful, as a comparison of water hydrolysis of methyl and ethyl benzenesulphonates shows. It is true that the rate constants do not differ much, but for the methyl ester E is 1 000 cal lower and A considerably smaller than for the ethyl ester, their changes thus operating in opposite directions. Substitution of a hydrogen atom in CH₃ with CH₃, which repels electrons, makes the C-atom of the former less positive and thus the repulsion of an approaching water molecule larger; accordingly, the activation energy will be increased. On the other hand, the increase of the activation energy causes the dotted bonds in the transition state to be more stretched, whence the entropy of activation in case of the ethyl ester is less negative, *i. e.*, A is larger.

Now the question arises whether in the reactions considered the most important step involves the overcoming of the repulsion of the approaching reagent molecule, or whether the stretching of the bond SO—C, which is to be disrupted, is the controlling step, or, perhaps, whether the reaction proceeds by a compromise between these two mechanisms. Several points discussed above seem to denote that the reaction is of the type in which probably both repulsion energy and bond-stretching energy are of importance. To these facts may be added the small difference in activation energies between reactions (C, D) and (A, B). More general conclusions must, however, be postponed to a further investigation, which is in progress.

A reaction catalyzed by hydrogen ion would take place with another mechanism than that described above for the uncatalyzed solvolysis. A mechanism similar to that in the acid hydrolysis of carboxylic esters would here, too, be the only possible. According to the Lowry mechanism¹⁵, the proton combines with the ethereal oxygen, and the second step involves attachment of hydroxyl ion from water to carbonyl carbon:



However, since the mesomerism of the ester grouping renders carbonyl oxygen fractionally negative and ethereal oxygen fractionally positive, it has also been suggested¹⁶ that the proton is more likely to be attached to the former, and then hydroxyl ion from water is attached to the now very positive carbonyl carbon:



Because, owing to the lack of double bond in a sulphonic ester molecule, the electronic displacements necessary to either of these processes are impossible, the corresponding reaction does not occur, and consequently the hydrogen ion has no catalytic effect on the decomposition of sulphonic esters.

SUMMARY

The reactions of several alkyl benzenesulphonates with water, alcohols, hydroxyl ion, and ethoxyl ion were kinetically investigated. The results and the mechanisms of reactions which are definitely different from that of the hydrolysis of carboxylic esters are discussed.

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