

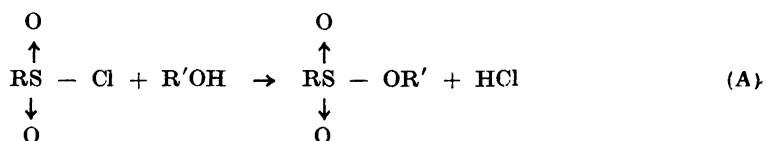
The Alcoholysis of Some Aromatic Sulphonyl Chlorides

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The work of Tommila and (Miss) Lindholm¹ has shown that for the solvolysis of ethyl benzenesulphonate the activation energies are within experimental error constant and that the differences in reaction velocities are entirely due to different frequency factors. The present paper is an attempt to elucidate the alcoholysis of sulphonyl chlorides. The hydrolysis of sulphonyl chlorides has been investigated by Berger and Olivier², and Hedlund³.

On account of the practical importance of the alkyl esters of aromatic sulphonic acids as alkylating agents and because of the difficulties in the other preparation methods, the reactions between the different sulphonyl chlorides and alcohols are, concerning the sort and quantities of the products, cleared up fairly extensively. The reaction



is rather slow at and below room temperature⁴, but the alcoholysis of the ester formed,



obtains first at high temperatures a velocity¹ to disturb the kinetic investigation of the first reaction.

Probably only Goubau⁵ has kinetically investigated the alcoholysis of sulphonyl chlorides.

EXPERIMENTAL

Materials. — Benzenesulphonyl chloride: A product prepared according to *Organic Syntheses*, Part XV, was distilled twice in an all-glas apparatus at reduced pressure; b. p. 105°/6.5 mm.

p-Chlorobenzenesulphonyl chloride, prepared according to Ullmann und Korselt⁶ and crystallised several times from light petroleum (b. p. 40–50°), had after some days' staying in a vacuum desiccator with solid KOH m. p. 53.8–53.9°.

p-Toluenesulphonyl chloride: Schering's specimen "reinst für wissenschaftliche Zwecke", was crystallised twice from light petroleum and had after some days' staying in a vacuum desiccator m. p. 69.1°.

The alcohols were commercial products, purified by the method of Lund and Bjerrum as described before¹.

Acetone: A commercial product of high purity was dried over potassium carbonate and then slowly distilled through a Widmer column.

Rate measurement. — The proceeding of the reaction (A) was followed by measuring after appropriate time intervals the amount of HCl formed. The experiments were conducted in reaction vessels described before¹. About 100 mg (or 200 mg) of sulphonyl chloride were accurately weighed into the side tube and by means of a burette a calculated amount of alcohol (between 6 and 30 ml) was measured into the bulb, so that the initial concentration of the chloride was 0.05 mole/liter (in some series 0.1 or 0.2 mole/l). The reaction vessels were kept in the thermostat until the reactants had acquired its temperature (at 0° about 30 mins., at 15° and 25°, to avoid the attack of alcohol vapour upon the chloride, only 5 mins.) and the reaction was started by shaking the tube. The chloride always dissolved at once.

Of the analytical methods of which several were proved, the best results were obtained by a slight modification of the procedure described by Goubau⁵. The reaction was stopped by sudden pouring of the reaction mixture into 50 ml of acetone which was pre-cooled to 0° C and the reaction vessel rinsed with 20 ml of 0° acetone. Then the acid was quickly titrated with *N*/50 baryta solution, cresol red as indicator. All titrations were carried to a standard tint. The acetone always required a few tenths of ml of *N*/50 alkali, which were taken into account in the calculations. The presence of a large excess of acetone and the low temperature make the reaction with alcohol and water so slow that titration is possible. However, it is necessary to operate very quickly and the titration is to be stopped at once when the standard tint is reached, owing to the extremely rapid decomposition caused by an excess of alkali.

The reaction velocities were determined at 25°, 15° and 0°. For 25° and 15° the thermostat could be regulated to within 0.01°. Experiments at 0° were carried out in a well-isolated vessel which contained crushed ice and water. All thermometers were checked against standard thermometers.

Calculation of rate constants. — The course of the reaction is expressed by the usual first order formula $dx/dt = k_1(a-x)$; this may be exemplified by the following typical series, obtained for benzenesulphonyl chloride in absolute ethanol at 25° C, the initial concentration being 0.05 mol/liter:

Time mins.	75	129	135	195	220	318	420	669	947	1470
Percentage change	9.2	13.7	15.8	20.6	23.8	32.3	39.6	55.5	68.2	85.3
$10^5 \cdot k_1 \text{ sec.}^{-1}$	2.13	1.89	2.12	1.97	2.06	2.05	2.00	2.01	2.02	2.17

In every case at least six, but usually more measurements were made at each temperature.

RESULTS AND DISCUSSION

Rate constant and concentration. — Goubau⁵ found that the first order formula does not give constant values for k , but the velocity constant increases with the time. He therefore concluded that the hydrogen ion formed catalytically accelerates the reaction, and, in fact, he got higher values for k when HCl was added to the reaction mixture. Hedlund, on the contrary, came to the result that HCl somewhat *decreases* the rate of *hydrolysis* of sulphonyl chlorides, but the influence is of the same order of magnitude as that of neutral salts. To reinvestigate any influence of hydrogen ion upon the alcoholysis we carried out experiments with benzenesulphonyl chloride in absolute ethanol using different concentrations. Our results are given in Table 1.

Table 1. The alcoholysis of benzenesulphonyl chloride in absolute ethanol at 25°, initial concentration a . (The values of k are means of about eight observations.)

a mole/liter	0.01	0.05	0.1	0.2
$10^5 \cdot k_1$ sec. ⁻¹	2.028	2.045	2.137	2.172

We see that k_1 increases a little with the initial concentration of the sulphonyl chloride, but the effect is a very feeble one. In the measuring series carried out with the same initial concentration it can be neglected, as shown by the example given above. On the ground of these results there is no evidence of hydrogen-ion catalysis in the alcoholysis of sulphonyl chlorides. The feeble increase of k_1 with the initial concentration can be explained by relating the rate constant to that in very dilute solution by using activity coefficients.

Influence of light. — Two series of experiments were carried out with *p*-chlorobenzenesulphonyl chloride in ethanol at 25.0° C, the one series in bright sun light, the other in dark. The values for k_1 were $2.40 \cdot 10^{-5}$ in the sun light and $2.38 \cdot 10^{-5}$ in dark; thus no influence of light was noted.

Rate constants and parameters of the Arrhenius equation. — The first order rate constants k_1 , as mean values of the measuring series, are given in Table 2. The Table also includes the values of activation energy E and frequency factor A , according to the simple equation of Arrhenius,

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

calculated from the k_1 -values at different temperatures by the method of least squares. The plot of experimental values of $\log k_1$ against $1/T$ showed that the Arrhenius equation was followed within the experimental error in every case.

Table 2. The values of k_1 , E and $\log A$. In all cases the initial concentration of the sulphonyl chloride $a = 0.05$ mole/liter.

	Temp., °C	$10^6 \cdot k_1$ sec. ⁻¹	E cal	$\log_{10} A$
C ₆ H ₅ SO ₂ Cl, methanol	0.0	7.79	16 670	8.23
	15.0	37.5		
	25.0	103		
C ₆ H ₅ SO ₂ Cl, ethanol	0.0	1.47	16 980	7.76
	15.0	7.26		
	25.0	20.5		
C ₆ H ₅ SO ₂ Cl, <i>n</i> -propanol	0.0	0.888	17 090	7.63
	15.0	4.60		
	25.0	12.5		
<i>p</i> -Cl · C ₆ H ₄ SO ₂ Cl, ethanol	0.0	1.58	17 530	8.23
	15.0	8.49		
	25.0	23.7		
<i>p</i> -CH ₃ · C ₆ H ₄ SO ₂ Cl, ethanol	0.0	1.27	17 770	8.32
	15.0	6.85		
	25.0	19.8		

Mechanism of the reaction. — It is seen from Table 2 that chlorine as a substituent in the aromatic nucleus somewhat enhances and the methyl group somewhat reduces the reaction velocity. However, the activation energy E is clearly higher for the *p*-CH₃ and *p*-Cl compounds than for the unsubstituted chloride. The introduction of an electron-attracting substituent *e. g.* chlorine into the sulphonyl chloride molecule will (a) decrease the electron density at the S-atom, and (b) strengthen S-atom's hold on the S—Cl bond electrons, or decrease the ionic character of this bond. These two effects act in opposite directions. The first effect, because of lowering of the repulsion of an approaching alcohol molecule, tends to decrease the activation energy, whereas the second one tends to increase it. An electron-repelling substituent (*e. g.* methyl group) acts in opposite direction. The above-mentioned experimental results show that in the alcoholysis of *p*-chloro benzenesulphonyl chloride the effect of the substituent on E is governed mainly by the strength of the S—Cl bond, whereas in the alcoholysis of *p*-toluenesulphonyl chloride the repulsion energy is the most important factor. This indicates that in the alcoholysis of unsubstituted benzenesulphonyl chloride the S—Cl bond strength and the repulsion energy contribute nearly equally to the activation energy.

In both the cases the substituent also causes an increase of the parameter A of the Arrhenius equation, and therefore the reaction velocity, despite the increase of activation energy, is either only a little decreased (*p*-toluenesulphonyl chloride) or is increased (*p*-chlorobenzenesulphonyl chloride). This increase of A denotes, according to the theory of absolute reaction rates, that the entropy of activation is less negative than in the alcoholysis of the unsubstituted compound.

As to the dependence of the reaction velocity on the alcohol, the table shows that the rate of the alcoholysis in the temperature range investigated changes in the order: methanol > ethanol > propanol. This is partly due to changes in E , partly to changes in A , both influencing in the same direction. As usual in bimolecular reactions, the frequency factors are smaller or the entropies of activation more negative for reactions involving more complex molecules having a large number of degrees of freedom⁷. The differences in the activation energies are probably due to different repulsion energies between the reactants.

A comparison of our results with the work of Hedlund³ concerning the hydrolysis of sulphonyl chlorides, from which some data are taken into Table 3, shows that the hydrolysis in pure water is much faster than the alcoholysis in pure alcohols.

Table 3. Hydrolysis of sulphonyl chlorides (Hedlund), 25° C.

RSO ₂ Cl	Water			42 per cent acetone		
	k_1 sec. ⁻¹	E	log A	k_1 sec. ⁻¹	E	log A
<i>p</i> -CH ₃ · C ₆ H ₄ -	0.00385	17 690	12.35	0.000233	14 270	8.62
C ₆ H ₅ -	0.00307	17 420	12.07	0.000303	14 430	8.85
<i>p</i> -O ₂ N · C ₆ H ₄ -	0.00272	18 060	12.46	0.00174	12 870	8.46
<i>m</i> -O ₂ N · C ₆ H ₄ -	0.00144	18 810	12.74	0.000717	13 780	8.83

Methyl substitution increases, whereas the electron-attracting nitro group decreases the rate of hydrolysis in pure water, but in 42 per cent acetone the effect is reversed. Accordingly, in pure water, the substituent influences are contrary to those in the alcoholysis in pure alcohols. Concerning the activation energies, however, the effects act in same direction.

For the hydrolysis in water the activation energy is probably a little higher than for the alcoholysis in pure alcohols, but the frequency factors are much higher. Accordingly, the entropies of activation are much more negative for

the alcoholysis than for the hydrolysis. This is in harmony with general experience. In the first case one of the reactants is more complex, and in such cases there is a considerable rearrangement of energy among the degrees of freedom, which causes the formation of the activated complex to be followed by a large decrease in the entropy and a decrease in the reaction rate.

The mechanism proposed above is the S_N2 mechanism of Ingold and Hughes⁸. However, because an electron-repelling substituent (methyl group) increases and an electron-attracting substituent (nitro group, halogen) decreases the velocity of reaction in water³, it is possible that the hydrolysis in water proceeds, at least partly, by a S_N1 mechanism, or is a two-stage reaction



The suffix *s* means that the component is solvated. It is reasonable to assume that water has a more powerful affinity for chloride ion than alcohol and so facilitates ionisation of the sulphonyl chloride.

SUMMARY

The alcoholysis of some sulphonyl chlorides has been kinetically investigated. The reaction mechanism is discussed.

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