

On the Alkaline Alcoholysis of Benzenesulphonyl Chloride

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In a previous paper¹, in connection with the analytical procedure, attention was paid to the fact that the hydroxyl ion considerably accelerates the solvolysis of sulphonyl chlorides. This observation is not a new one. In the preparation of sulphonic esters, bases have generally been used to make the alcoholysis of sulphonyl chlorides more rapid. In general, the process has been carried out according to the Schotten-Baumann reaction by using alcohol and sulphonyl chloride in equimolar proportions in the presence of sodium methoxide, trimethyl amine, pyridine, or a concentrated aqueous solution of sodium hydroxide². After a gradual mixing of the reagents, often in the presence of an indifferent liquid, the reaction mixture has been left to stay, during which period, if needed, it has been shaken. The reaction time has varied from ten minutes to several months. High yields of esters have thus been obtained at temperatures in the 0—15° range. Menalda³ has investigated the influence of temperature and of the water content of the alcohol upon the yield of ester and the corresponding acid in Schotten-Baumann reaction. In this connection also the reaction with benzenesulphonyl chloride has been studied.

Since the alkaline alcoholysis of sulphonyl chlorides is of great importance as a method of preparation of sulphonic esters, and as on the other hand it influences in a special way the following of the course of the alcoholysis by acid-base titration, we have carried out some experiments on the velocity of the alcoholysis of benzenesulphonyl chloride in the presence of bases. The preparation and purification of the materials and the experimental method are, in their main features, described in the previous paper. Reactions conducted in the presence of sodium hydroxide, sodium ethoxide, or sodium acetate were stopped by a to 0° C precooled mixture of 70 ml of acetone and of a slight excess of 0.02 *N* aqueous hydrochloric acid. As an indicator in the titration of solutions containing acetate bromothymol blue was used, and

cresol red in all the other cases. The degree of advancement of reaction was calculated to give the percentage of the number of moles acid formed in the reaction compared with the number of moles sulphonyl chloride in the beginning of the reaction.

EXPERIMENTS

Experiment 1. Benzenesulphonyl chloride was weighed in the side tube of the reaction vessel ⁴, and sodium hydroxide solution in absolute methanol was placed in the bulb, and thermostated. After mixing the concentrations of both reactants were 0.05 moles/liter. Temperature 25.00° C.

	Time	Advancement of reaction
a.	960 sec.	98.9 per cent
b.	60	97.2
c.	17	98.1

Experiment 2. Solvent absolute methanol. Concentrations after mixing: benzenesulphonyl chloride 0.025, NaOH 0.05 moles/liter. Temperature 25.00° C

Time	Advancement of reaction
30 sec.	105.2 per cent

Experiment 3. Solvent absolute ethanol. Concentrations after mixing: benzenesulphonyl chloride 0.0394, sodium ethoxide 0.0394 moles/liter. Temperature 25.00° C

Time	Advancement of reaction
21 sec.	99.0 per cent

Experiment 4. Abs. ethanol. Concentrations: benzenesulphonyl chloride 0.0166, sodium ethoxide 0.0394 moles/liter. Temperature 25.00° C

Time	Advancement of reaction
25 sec.	105.0 per cent

Experiment 5. Benzenesulphonyl chloride 0.05 moles/liter, pure ethanol containing water 0.05 moles/liter. Temperature 25.00° C.

Time	Advancement of reaction
300 sec.	0.67 per cent

Table 1. Benzenesulphonyl chloride 0.05 moles/liter, Na-acetate 0.05 moles/liter in absolute methanol, t = time in minutes, p = percentage change, k_1 in sec.^{-1} calculated from the first order and k_2 in $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec.}^{-1}$ calculated from the second order formula.

t	25.00° C			17.00° C		0.00° C	
	p	$k_1 \cdot 10^4$	$k_2 \cdot 10^3$	t	p	t	p
5	15.5	5.60	12.2	8	12.5	60	14.7
10	21.2	3.97	8.99	30	25.5	168	25.8
21	33.8	3.28	8.12	32	28.4	260	33.1
30	40.4	2.88	7.54	61	37.9	391	39.3
51	51.5	2.37	6.95	91	46.9	985	61.7
60	56.1	2.29	7.09	120	52.9	1374	70.7
90	66.1	2.00	7.21	406	72.6		
122	72.7	1.77	7.27				

Table 2. Benzenesulphonyl chloride 0.05 moles/liter, Na-acetate 0.05 moles/liter in absolute ethanol, t = time in minutes, p = percentage change, k_1 in sec.^{-1} calculated from the first order formula and k_2 in $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec.}^{-1}$ calculated from the second order formula.

t	25.00° C			17.00° C		0.00° C	
	p	$k_1 \cdot 10^4$	$k_2 \cdot 10^3$	t	p	t	p
8	14.6	2.89	7.10	10	9.8	143	16.8
15	20.8	2.59	5.82	16	12.1	173	18.6
20	24.0	2.28	5.26	22	15.0	282	25.5
40	35.6	1.83	4.60	36	21.6	472	31.9
59	41.6	1.52	4.02	62	34.0	1129	47.2
81	47.2	1.32	3.68	120	40.1	2496	58.4
93	50.2	1.25	3.61	174	46.0	3952	58.7
121	53.6	1.06	3.18	312	54.9		
165	58.7	0.89	2.87	354	53.7		
245	62.5	0.67	2.27				

Experiments 6 and 7. Solvent acetone-water containing 50 volume per cent acetone. Concentration of benzenesulphonyl chloride 0.05 moles/liter. Temperature 0.00° C. 6. Pure solvent. 7. Sodium hydroxide, 0.05 moles/liter.

	Time	Advancement of reaction
6.	180 sec.	0.19 per cent
7.	180 »	50.12 »

Table 3. Benzenesulphonyl chloride 0.05 moles/liter, Na-acetate 0.032 moles/liter in absolute n-propanol. t = time in minutes, p = percentage change.

25.00 °C		17.00 °C		0.00 °C	
t	p	t	p	t	p
10	13.2	31	15.3	156	14.8
23	20.2	78	28.0	314	21.4
40	28.2	119	34.1	513	28.0
79	41.6	217	45.2	1395	48.2
133	50.8	363	54.4	1411	48.6
315	66.1	472	58.8		
		590	63.2		

DISCUSSION

The acidity of the reaction mixture, except in cases where acetate was used, may be changed by the following over-all reactions:

- (a) $\text{RSO}_2\text{Cl} + \text{R}'\text{OH} \rightarrow \text{RSO}_2\text{OR}' + \text{HCl}$
- (b) $\text{RSO}_2\text{Cl} + \text{R}'\text{OH} \rightarrow \text{RSO}_2\text{OH} + \text{R}'\text{Cl}$
- (c) $\text{RSO}_2\text{OR}' + \text{R}'\text{OH} \rightarrow \text{RSO}_2\text{OH} + \text{R}'\text{OR}'$
- (d) $\text{RSO}_2\text{OR}' + \text{HOH} \rightarrow \text{RSO}_2\text{OH} + \text{R}'\text{OH}$
- (e) $\text{RSO}_2\text{Cl} + 2\text{NaOH} \rightarrow \text{RSO}_2\text{ONa} + \text{NaCl} + \text{H}_2\text{O}$
- (f) $\text{RSO}_2\text{Cl} + \text{R}'\text{ONa} \rightarrow \text{RSO}_2\text{OR}' + \text{NaCl}$
- (g) $\text{RSO}_2\text{OR}' + \text{NaOH} \rightarrow \text{RSO}_2\text{ONa} + \text{R}'\text{OH}$
- (h) $\text{RSO}_2\text{OR}' + \text{R}'\text{ONa} \rightarrow \text{RSO}_2\text{ONa} + \text{R}'\text{OR}'$
- (i) $\text{R}'\text{Cl} + \text{NaOH} \rightarrow \text{R}'\text{OH} + \text{NaCl}$

In the absence of alkali the solvolysis (reactions (a) and (b)) at the temperatures used is slow¹. Preparative experiments show that in the absence⁵ as well as in the presence* of a base the reaction (b) has hardly any significance. Hence, the reactions of the alkyl chloride may be neglected. Thus, in pure alcohol practically only the reaction (a) occurs, and the velocity experimentally measured is that of this reaction. In the presence of sodium hydroxide or sodium ethoxide the solvolysis of the sulphonyl chloride is so fast that the reactions (b), (c), (d), (g), (h), and (i) may be neglected⁴.

* *E. g.*, we dropped rapidly a cooled 5 per cent solution of sodium methoxide in abs. methanol in an equivalent amount of benzenesulphonyl chloride which was cooled by keeping the vessel in ice-water mixture. The temperature was not allowed to rise above 20° C. Methanol was immediately evaporated in a vacuum, water added to the mixture, and the ester taken in ether. After drying with anhydrous sodium sulphate the ester was distilled at reduced pressure. The yield was about 95 per cent of theoretical (*Cf.*¹¹).

The experiments 1 and 3 show that even within the shortest times possible in the measurements sodium hydroxide or sodium ethoxide has been entirely used. In the presence of an excess of either of these reagents (experiments 2 and 4) it may be said that processes (a) and (f) go in a few moments into completion. That the degree of advancement of the over-all reaction, as defined above, in both cases is a little over 100 per cent, is due to reactions ⁴ (g) and (h). If in experiments 1 and 2 as a fast step were the reaction (e), the degree of advancement of the over-all reaction must have been about 200 per cent instead of about 100 per cent. Thus the fastest step, even in the presence of sodium hydroxide, is the formation of ester. From experiment 5 we see that the great increase in reaction velocity is not due to water formed in the reaction $R'OH + NaOH \rightleftharpoons R'ONa + H_2O$. Experiment 6 shows that in acetone-water the reaction between sulphonyl chloride and water is so slow at 0° C that it does not appreciably occur during the titration of reaction mixtures in which the reaction is stopped by diluting with acetone precooled to 0° C¹. Experiment 7 shows that sodium hydroxide accelerates greatly also the hydrolysis of sulphonyl chloride.

The experiments referred to above showed that in the presence of sodium hydroxide, or sodium alkoxide the alcoholysis of benzenesulphonyl chloride is so fast that it was not possible to follow the reaction by the method used. Therefore, the influence of sodium acetate was investigated, the reaction now proceeding with a measurable velocity. The results are given in Tables 1—3. The first order or the second order equation does not give a constancy for k (Tables 1 and 2, columns 3 and 4). Assuming that besides the pure alcoholysis, which is of the first order¹, a bimolecular reaction takes place between sulphonyl chloride and acetate ion (j), we should obtain:

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)(b-x) \quad (1)$$

Table 4. Benzenesulphonyl chloride 0.05 moles/liter, Na-acetate 0.05 moles/liter in absolute methanol, or in absolute ethanol, p = percentage change from curves, dx/dt = the slope of the tangent in mole · l⁻¹ · sec.⁻¹ k_2 = second order rate constant in equation (1) in l · mole⁻¹ sec.⁻¹, 25.00° C.

p	Methanol		Ethanol	
	$dx/dt \cdot 10^5$	$k_2 \cdot 10^3$	$dx/dt \cdot 10^5$	$k_2 \cdot 10^3$
10	2.03	8.48	1.02	5.49
20	1.21	4.49	0.702	3.88
30	0.828	3.53	0.438	2.99
40	0.548	3.05	0.268	2.29
50	0.387	2.65	0.149	1.40

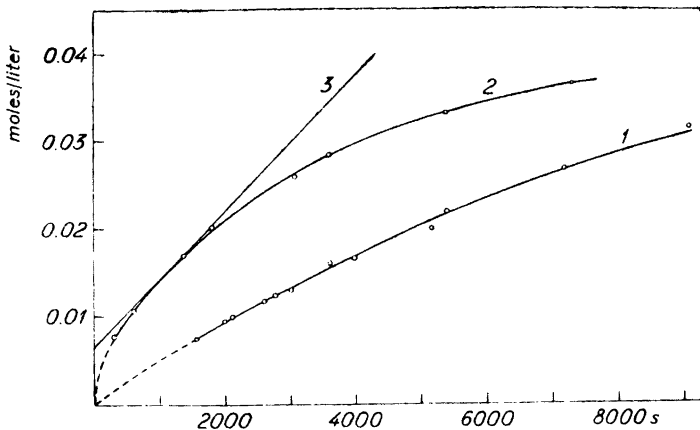


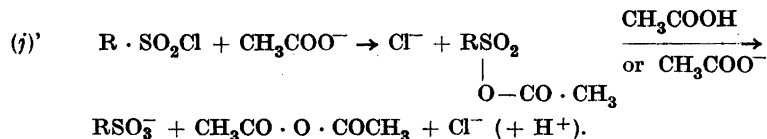
Fig. 1. 1. Benzenesulphonyl chloride (0.05 moles/liter) in pure methanol, 25° C. Data taken from the previous work (Ref. 1).
 2. Benzenesulphonyl chloride (0.05 moles/liter) + sodium acetate (0.05 moles/liter) in methanol, 25° C.
 3. Tangent drawn to curve 2. Its slope represents dx/dt at 30 per cent change.

The value of k_1 is known from the previous work¹. For the calculation of k_2 , the integral of this equation is very complicated. By the graphical method, from the slope of the tangents drawn to the curve which represents x as a function of time (Fig. 1), however, dx/dt may be roughly evaluated at different times and k_2 so obtained as a function of time. Table 4 shows that no constancy for k_2 is thus obtained. This shows that the change of the composition of the reaction mixture is not governed only by these two reactions, or by one of them. The esterification of acetic acid formed in the reaction influences the acidity of the mixture, too, but this reaction is very slow⁶, especially in the beginning, when the concentration of the acetic acid is small, and is, therefore, in the above consideration and in all following considerations neglected.

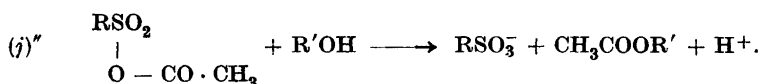
That the acetate ion reacts with the sulphonyl chloride has previously been shown⁷ by heating solid sodium acetate with benzenesulphonyl chloride.

As a further test we carried out the following experiment. 10 g of benzenesulphonyl chloride were dissolved in 50 g of acetic acid made free from water and acetic anhydride according to Kilpi⁸, and 10 g of dry sodium acetate (an excess) were mixed to this solution, a part of the salt remaining undissolved. After five days' staying at room temperature, a considerable amount of solid sodium chloride was formed. A quantitative determination of the chloride ion showed that about 70 per cent of the sulphonyl chloride had reacted. The filtered solution was distilled at reduced pressure. The distillate contained, besides acetic acid, acetic anhydride, and the solid residue (10 g) was composed of sodium acetate and a large amount of sodium benzenesulphonate.

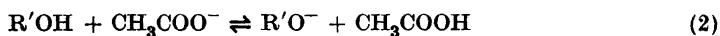
According to the general scheme¹ the mechanism of the reaction may be supposed to be:



In an alcohol the second step (fast) involves alcohol molecule instead of acetic acid or acetate ion:



In the alcohol solution, the equilibrium



produces a small concentration of alkoxide ions the concentration of which in course of the reaction is given by the (approximate) formula

$$[\text{R}'\text{O}^-] = \frac{K_{\text{alc.}}}{K_{\text{HAc}}} \cdot \frac{b-x}{x} \quad (3)$$

where b is the initial concentration of the added acetate and x the concentration of the acid liberated. $K_{\text{alc.}}$ is the ionic product of the alcohol, and K_{HAc} the acid constant of acetic acid in the alcohol used. Since the reaction (f) is very fast, as stated above, even the small concentration of $\text{R}'\text{O}^-$ produced by (2) must influence the measured over-all velocity.

If all the three reactions (a), (f), and (j) are taken into the consideration the rate equation will be

$$\frac{dx}{dt} = k_1 (a-x) + k_2 (a-x) (b-x) + k' \frac{(b-x)}{x} (a-x). \quad (4)$$

As given above, k_1 is known from the previous work. The values of k_2 and k' could be obtained by evaluating dx/dt graphically at two points corresponding to different change percentages p_1 and p_2 , and by resolving the system of the two equations. However, the possible errors in the drawing of the curves and their tangents are so large that the dispersion of the values of k' is too great to allow any accurate results of their constancy. Thus only very rough values may be obtained. In methanol solution, *e.g.*, at 25°C $k_2 \approx 1 \cdot 10^{-3}$, $k' \approx 3 \cdot 10^{-5}$. By using the values of the ionic product of methanol², $K_{\text{MeOH}} =$

2.2×10^{-17} , and the acid constant of acetic acid in methanol¹⁰, $K_{\text{HAc}} = 2.24 \cdot 10^{-10}$, at 25° C, we obtain by means of the equation (3) for the bimolecular rate constant of the reaction (f) $k_t = \frac{K_{\text{HAc}}}{K_{\text{alc}}} \cdot k' \approx 300$. For the reaction with ethoxide ion, the rate constant is roughly of the same order.

From preparative and analytical viewpoints, on the ground of the above results the following general conclusions can be made:

1. The formation of ester in systems formed by mixing benzenesulphonyl chloride, an aliphatic alcohol, and sodium hydroxide, or sodium alkoxide, judged on the ground of the formation of hydrochloric acid, is too rapid to be measured by means of the method used here. In the presence of sodium acetate the speed of the reaction is measurable, but the total reaction is complicated, and thus only rough evaluations of the rate of the reaction between benzenesulphonyl chloride and alkoxide ion are possible.

2. In preparations of sulphonic esters from benzenesulphonyl chloride and alcohols in presence of bases much shorter reaction times could be used than has been customary until now.

3. The proceeding of the reaction between sulphonyl chlorides and alcohols can be followed by the method used in the previous work¹.

SUMMARY

The alkaline alcoholysis of benzenesulphonyl chloride has been investigated and reactions possible in the system discussed.

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