ON THE NATURE OF THE INTERACTION OF ARYLSULFONYL CHLORIDES WITH PRIMARY ALKYLAMINES IN BENZENE SOLUTION

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L. M. LITVINENKO, A. F. POPOV

ON THE NATURE OF THE INTERACTION OF ARYLSULFONYL CHLORIDES WITH PRIMARY ALKYLAMINES IN BENZENE SOLUTION

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The widely occurring reaction of formation of arylsulfonamides has been little investigated from the kinetic standpoint. In a work (^{1}) devoted to a quantitative study of the interaction of arylsulfonyl chlorides with a secondary amine (diethylamine) in benzene, we found that the rate of this reaction is described by a second-order equation and is markedly subject to the catalytic influence of polar impurities (for example, small amounts of water or of amine hydrochloride formed in the course of the reaction).

Continuing investigations in the indicated direction, we undertook a study of the kinetics of the reaction of arylsulfonyl chlorides with primary amines. Here the reaction of *n*-butylamine with 2,4-dinitrobenzenesulfonyl chloride will be considered; its interaction, unlike that of other arylsulfonohalides (^{1}), is practically not complicated by the influence of the salt formed in the course of the process.

In the course of the work* it was found that, despite the stoichiometry usual for such reactions and following from the scheme

$$\mathrm{ArSO_2Cl + H_2NR \rightarrow ArSO_2NHR + HCl} \quad \text{(slow)}, \tag{1}$$

$$\mathrm{HCl + H_2NR \rightarrow RNH_3^+Cl^-} \quad \text{(fast)} \tag{2}$$

or, in total,

$$\mathrm{ArSO_2Cl + 2H_2NR \rightarrow ArSO_2NHR + RNH_3^+Cl^-}, \tag{3}$$

Table 1

$a = 0.001$; $b = 0.002$

Time, min	Yield, %	Y''	Y'''
10	11.6	0.110	58.4
20	20.3	0.106	59.7
35	30.5	0.104	63.6
50	38.0	0.102	66.8
85	49.1	0.094	70.0
125	56.0	0.088	72.5
200	65.2	0.078	75.8

the kinetics of the process with participation of a primary amine, in contrast to the previously investigated case ([1]), is distinguished by greater peculiarity. Thus, the current second-order rate constants, denoted here as Y'' ($\text{l/mol} \cdot \text{sec}$), decrease appreciably in the course of the process, whereas the third-order rate constants Y''' ($\text{l}^2/\text{mol}^2 \cdot \text{sec}$) increase (Table 1)**. The latter indicates that the reaction order is intermediate between second and third. Its determination for the example illustrated in Table 1 ([2]) gave a value equal to 2.6.

* The previous method for measuring the rate was used ([1]).
** The data presented in Tables 1, 2, and 3 refer to 25°.

On the basis of the results obtained, it may be assumed that the reaction proceeds along two parallel paths; the rate of one of them is described by a second-order equation (first order in sulfonyl chloride and first order in amine), and the other by a third-order equation (first order in sulfonyl chloride and second order in amine). In the latter case the second amine molecule acts as a catalyst. Therefore, the expression for the overall rate of the process is written as

$$\frac{dx}{dt} = k_2(a-x)(b-2x) + k_3(a-x)(b-2x)^2, \tag{4}$$

where a and b are, respectively, the initial concentrations of arylsulfonyl chloride and amine in mol/l; x is the current concentration of the arylsulfonamide formed; t is the time in sec; k_2, in $\text{l/mol} \cdot \text{sec}$, and k_3, in $\text{l}^2/\text{mol}^2 \cdot \text{sec}$, are, respectively, the rate constants of the second and third order.

To determine the constants k_2 and k_3, the integral method discussed earlier ([3]) was used. In this case two methods of integrating (4) are possible. According to one of them, the left-hand side gives Y'':

$$Y'' = \frac{2.303}{t(b-2a)} \lg \frac{a(b-2x)}{(a-x)b} = k_2 + k_3 b - 2k_3 \frac{1}{t} \int_0^t x\, dt, \tag{5}$$

according to the other, Y''':

$$Y''' = \frac{2.303}{t(b-2a)^2} \lg \frac{a(b-2x)}{(a-x)b} - \frac{2x}{t(b-2a)(b-2x)b} = k_3 + k_2 \frac{1}{t} \int_0^t \frac{dt}{b-2x}. \quad (6)$$

On the basis of the linear dependence of Y'' and Y''' on their corresponding integral quantities in (5) and (6), divided by t (the integrals were determined by numerical integration (^{3})), two sets of constants k_2 and k_3 can be obtained from one kinetic curve. Processing the data presented in Table 1 according to (5) gives the values $k_2 = 0.0402$ l/mol·sec and $k_3 = 38.1$ $\mathrm{l^2/mol^2}$·sec; and according to (6), respectively, 0.0375 l/mol·sec and 39.9 $\mathrm{l^2/mol^2}$·sec. Within the errors of experiment and calculation, constants of the same order must agree with one another. To reduce the error, both methods were used, and the averaged values are given below.

Table 2

a	b	Y_0''	k_2	k_3
0.0005	0.00164	0.105	0.0411	39.1
0.0010	0.00200	0.116	0.0388	39.0
0.0010	0.00315	0.162	0.0350	41.9
0.0010	0.00726	0.320	–	43.4
$k_2 = 0.0407;\ k_3 = 38.5$			0.0383	40.8

Table 3

$a = 0.0010;\ b = 0.00726$

Time, min	Yield, %	$Y''' = k_3$
2	22.9	44.1
4	38.7	43.7
7	54.4	42.7
12	71.5	43.0

The satisfactory agreement of the constants k_2 and k_3, calculated by the indicated method for kinetic curves at different initial concentrations of the reactants (Table 2), with the constants calculated from the same data on the basis of the linear relation

$$Y_0'' = k_2 + k_3 b, \quad (7)$$

which follows from (5) (Table 2, left-hand side of the lower row), serves as important evidence for the correctness of the assumption that the reaction under consideration proceeds along noncatalytic and catalytic paths.

Fig. 1

Figure 1: Fig. 1

Y_0'' in (7) is the limiting value of Y'' under the condition that $\frac{1}{t}\int_0^t x\,dt$ becomes zero when $x = 0$ and $t = 0$.

From (4) and (7) it is clear that, by changing the initial concentrations of the reagents, especially of the amine, one can arrive at a situation in which some one of the parallel reactions will begin to predominate substantially over the other, and the observed rate will be determined by the dominant process. This is well illustrated by the example presented in Table 3 (cf. Table 1).

Table 4

Temp., °C	k_2	k_3	Y_0''	k_2/Y_0''	Temp., °C	k_2	k_3	Y_0''	k_2/Y_0''
6		53.4			35	0.0842	30.7	0.207	0.41
10		53.4			45	0.1320	20.0	0.189	0.70
15	0.0311	46.2	0.216	0.14	50	0.1440	19.2	0.205	0.70
20	0.0219	46.3	0.166	0.13	55	0.2115		0.213	0.99
25	0.0395	39.6	0.162	0.24	70	0.3114		0.300	1.04
30	0.0551	37.1	0.172	0.32					

Thus, it may be considered proven that in the present case the reaction proceeds by two parallel paths, in contrast to analogous reactions of arylsulfonyl chlorides with secondary amines, whose rate is described by the usual second-order equation (first order with respect to sulfonyl chloride and first order with respect to amine) (^{1}).

Fig. 1

It is of interest to follow the influence of temperature on the rate of the reaction under consideration (see Table 4). Whereas the constant k_2 changes normally with temperature and this change is described by the Arrhenius equation (Fig. 1), the constant k_3 decreases with increasing temperature. The energy parameters of the reaction characterized by k_2 ($E_A = 8.9$ kcal/mole, $\lg A = 5.22$, $\Delta S^{\neq} = -36.7$ cal/deg$\cdot$mole) are close to those for related reactions studied earlier (^{1}).

The increase in the scatter of points on the Arrhenius plot (Fig. 1) in the region of low temperatures is explained by the corresponding decrease in the accuracy of determining k_2, since, as the temperature decreases, the fraction of this process—which at the initial moment of the reaction may be characterized by the ratio k_2/Y_0'' (Table 4)*—in the overall rate decreases. Thus, at temperatures of 6–10° it is no longer possible to determine the value of k_2, since the entire process proceeds practically by the catalytic mechanism characterized by the constant k_3, which now coincides with Y'''. Statistical treatment ([4]) does indeed show that in this case there is no systematic shift in the values of Y''' over the course of the reaction. Conversely, at temperatures above 50° the noncatalytic process substantially predominates (k_2/Y''_0 approaches unity), as a result of which the value of k_3 can no longer be determined.

* Since, depending on the ratio of a and b, the value of k_2/Y''_0 will change somewhat at one and the same temperature, Table 4 gives the data obtained when the initial amine concentration was approximately three times higher than the sulfonyl chloride concentration, which in these experiments was within the range 0.01 mole/liter.

The unusual temperature dependence of the constants k_3 most likely indicates that the reaction described by this constant proceeds in several stages. Therefore the quantity k_3 is complex and includes both kinetic and thermodynamic constants. For the overall acylation process described by equation (4), as a first approximation one may adopt a scheme according to which there is rapid and equilibrium formation of the addition product of the sulfochloride to the amine

$$\mathrm{ArSO_2Cl} + \mathrm{H_2NR} \overset{\mathrm{K}}{\rightleftarrows} \mathrm{ArSO_2Cl \cdot NH_2R} \qquad (8)$$

with its subsequent decomposition into the final substances either spontaneously (9a), or under the catalytic action of a second molecule of amine (9b)

$$\mathrm{ArSO_2Cl \cdot NH_2R} \begin{cases} \xrightarrow{k_1^0} \mathrm{ArSO_2NHR} + \mathrm{HCl} & (9a) \\ \xrightarrow[+\mathrm{H_2NR}]{k_2^0} \mathrm{ArSO_2NHR} + \mathrm{HCl} + \mathrm{H_2NR} & (9b) \end{cases}$$

It follows from what has been said that both k_2 and k_3 (in the general case k_n) must be determined by the product: $k_n = k^0_{n-1}K$, where k^0_{n-1} is the rate constant of any decomposition process of $\mathrm{ArSO_2Cl \cdot NH_2R}$. Then the dependence of k_n on temperature will be expressed by the equation:

$$\frac{d \ln k_n}{dT} = \frac{d \ln k^0_{n-1} + d \ln K}{dT} = \frac{E_A - \bar{Q}_v}{RT}, \qquad (10)$$

where E_A is the activation energy of the process according to Arrhenius, the rate of which is characterized by the constant k^0_{n-1}; $\bar{Q}_v$ is the heat effect of the equilibrium determined by the constant K. Depending on the ratio of E_A and $\bar{Q}_v$, the observed reaction rate constant k_n will have different temperature behavior. Since the activation energy of catalytic processes is considerably lower than for noncatalytic ones, it is natural that in the case of reaction (9a) $E_A - \bar{Q}_v > 0$, and the constants k_2 satisfactorily obey the Arrhenius equation (Fig. 1). For the catalytic process, however, this difference is negative, as a result of which the constants k_3 decrease with increasing temperature (Table 4). A temperature dependence of third-order rate constants of this kind, and even more complex, is also observed for some other reactions (see, e.g., (^{5})).

Everything that has been said about the acylation of *n*-butylamine by 2,4-dinitrobenzenesulfonyl chloride was fully confirmed in the reaction of other primary alkylamines with various acid chlorides of arylsulfonic acids. Thus, it may be considered established that primary and secondary amines behave differently in reactions with arylsulfohalides. Possibly this is connected with an increase in steric hindrance in the case of reactions of secondary amines. We hope to report further refinement of the mechanism of the indicated reactions after obtaining additional experimental data.

Kharkov State
University

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