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Abstract

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On the Kinetics of the Interaction of Acid Chlorides with Amines

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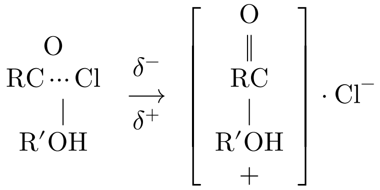
The question of the mechanism of the interaction of acid chlorides with amines has again become topical in connection with the appearance of a new promising method for the synthesis of polyamides by polycondensation of diacid chlorides with diamines. These reactions proceed at very high rates, for which only rough estimates are available in the literature (^{1}). The mechanism of the interaction of acid chlorides with amines has been considered in the literature by several authors ($^{2-4}$); however, the lack of experimental data does not make it possible to accept any one of the mechanisms definitively. Common to all the schemes described is the assumption that the reaction of an acid chloride with an amine proceeds in stages. In the first stage an intermediate product is formed, which then is converted into the final reaction product—an amide. However, experimental evidence for the stepwise nature of this reaction is lacking in the literature. The structure of the intermediate product and of the activated complexes in both stages is a subject of discussion. In the case of hydrolysis of acid chlorides, the presence of isotopic exchange in oxygen (^{5}) argues in favor of the formation of intermediate products of addition of water at the C=O bond. But even in alcoholysis, the structure of the activated complex, which is highly polar, can be understood if one assumes as the intermediate compound an ion pair consisting of a protonated ester and a chloride ion (^{6}):



$$\begin{matrix} \mathrm{O} \\ \mathrm{RC}\cdots\mathrm{Cl} \\ | \\ \mathrm{R'OH}\end{matrix} \xrightarrow[\delta^+]{\delta^-} \left[\begin{matrix}\mathrm{O}\\ \| \\ \mathrm{RC} \\ | \\ \mathrm{R'OH} \\ + \end{matrix}\right]\cdot \mathrm{Cl}^- \qquad \text{(I)}$$

The absence of retardation of the reaction when hydrogen in aniline is replaced by deuterium (^{2}) in its reaction with benzoyl chloride indicates that in the rate-determining step there is no rupture of the N–H bond, i.e., the amine does not add to the carbonyl of the acid chloride at the C=O bond.

It is natural to assume, in accordance with (^{2,3}), that in the reaction of an acid

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

chloride with an amine, in the first stage a complex is formed through interaction of the nitrogen of the amine with the carbon of the acid chloride, which possesses acceptor properties. Such an intermediate complex probably has a structure of the type of complex (I) and is a highly polar molecule or ion pair (2,6), while the intermediate product is an ion pair in which one of the ions is a protonated amide. Such a structure should be preferred over the product of addition of the amine to the acid chloride at the C=O bond, as assumed by Bender (4). Another very probable possibility for the course of the first stage is interaction of the acid chloride and the amine with formation of a charge-transfer complex, which subsequently is converted into the final reaction product. This is all the more plausible because amines are known as good electron donors (7), and acid chlorides as good acceptors (8) in reactions forming charge-transfer complexes. Depending on the strength of the donor and acceptor, the properties of the charge-transfer complex will be substan-

substantially: from a complex bound by weak exchange interaction, through the appearance of triplet states, to an ion pair consisting of two ion-radicals. Accordingly, the manifestations of the complexes will also change in the region of optical spectra, in EPR spectra, and in changes in the electrical conductivity and polarity of the system. However, it should be noted in advance that the presence of features characteristic of the existence of charge-transfer complexes in these systems is not yet proof of their participation in the reaction as intermediates. Formation of complexes may occur in a side reaction.

Fig. 1. Example of a recording of the kinetic curve for the reaction of benzoyl chloride with piperidine

All kinetic studies available in the literature concern reactions of acid chlorides with aromatic amines, mainly with aniline derivatives (9–12). The high rate of acylation of primary and secondary aliphatic and heterocyclic amines until recently made it impossible to observe the kinetics of such reactions (13). Reports on studies of the true kinetics of the interaction of bifunctional acid chlorides with diamines are altogether absent.

In the present work, a study was undertaken of the kinetics of reactions of secondary mono- and diamines with mono- and diacid chlorides, using as examples the interaction of piperidine (P) and piperazine ( ), on the one hand,

Fig. 2. Kinetic curves (1) and their semilogarithmic transforms (2) for the reaction of phthalyl chloride with piperazine: **a** –stage I, **b** –stage II

with benzoyl chloride ( ), phthalyl chloride ( ), and terephthalyl chloride ( ), on the other. *n*-Heptane was used as the solvent. In order to make it possible to study the kinetics of fast reactions, the experiments were carried out with very low reagent concentrations (10^{-6}—10^{-5} mol/l), and, to follow the reaction, a spectrophotometric method was used with automatic recording of the change in optical density over time.

Figure 1 presents a recording of a typical kinetic curve for the interaction of benzoyl chloride with piperidine. Two branches are clearly visible, corresponding to two stages of the process. The time from the beginning of the reaction to the minimum is ~ 15 sec.

In general form the reaction can be written as

$$A + B \xrightarrow{k^{I}} AB \xrightarrow{k^{II}} C, \qquad (II)$$

where k^{I} and k^{II} are the rate constants of the first and second stages.

Figure 2 presents typical kinetic curves and their semilogarithmic anamorphoses for the first and second stages of the reaction of phthaloyl chloride with piperazine. In all the reactions studied, two stages were found, and the first- and second-order constants k_1^{I} and k_2^{I} for the first stage and the first-order constant k_1^{II} for the second stage were determined.

The values of these constants at definite initial concentrations C_{XA} of the acid chloride and C_A of the amine are presented in Table 1. As is seen from the data

Table 1

Reaction	Temp., °C	$C_{XA} \cdot 10^6$, mol/l	$C_A \cdot 10^5$, mol/l	I stage K_1^{I}, 1/sec	I stage K_2^{I}, l/(mol·sec)	II stage K_1^{II}, 1/sec	λ, mμ	Character of the extremum on the kinetic curve
+	20	$2 \cdot 10$	5,40	$5{,}2 \cdot 10^{-1}$	$9{,}5 \cdot 10^{4}$	$6{,}8 \cdot 10^{-2}$	230	min.
+	20	4,72	1,77	$9{,}9 \cdot 10^{-1}$	$5{,}6 \cdot 10^{4}$	$3{,}5 \cdot 10^{-3}$	229,6	min.
+	20	2,20	2,88	$9{,}2 \cdot 10^{-3}$	$3{,}2 \cdot 10^{2}$	$1{,}1 \cdot 10^{-4}$	228	max.
+	18,8	5,85	2,06	$6{,}7 \cdot 10^{-2}$	$3{,}3 \cdot 10^{3}$	$6{,}8 \cdot 10^{-4}$	228	max.

in Table 1, the acylation reactions of secondary heterocyclic amines by acid chlorides are characterized by high rates. For example, the half-conversion time for the reaction of with is ~ 0.003 sec at an initial reagent concentration of 0.1 mol/l, usually employed in polymer synthesis.

The fact is noteworthy that the stagewise character in the reactions of and with is not due to the bifunctionality of the reagents, since two stages are also found in the interaction of with .

The identity of the kinetic picture in the reactions of with monobasic and dibasic is connected with the fact that the experiments were carried out with a deficiency of acid chloride, and only one of the two amino groups of entered into the reaction. A substantial difference in the reactivity of the amino groups in should be expected from their strongly differing basicities. Thus, the basicity constants are $K_1 = 9.0 \cdot 10^{-5}$ and $K_2 = 5.7 \cdot 10^{-9}$ ([14]).

Apparently, in the case of dichloroanhydrides one can observe only the reaction of the second acid-chloride group, when the first has already been converted into an amide. This explains the lower rates observed for reactions with and , as compared with . The rate of reaction of the first acid-chloride group, due to the presence in the ring of such an electron-withdrawing substituent as the second COCl group, is so high that it cannot be detected using the present method.

It is necessary to dwell especially on the question of spectrophotometric observation of the kinetics of consecutive reactions. It is not difficult to show that the form of the kinetic curve is a consequence of the ratio of the absorption coefficients of the substances participating in both stages of the reaction. Thus, if ε_{A}, ε_{B}, $\varepsilon_{\mathrm{AB}}$, ε_{C} are the absorption coefficients of substances A, B, AB, C (see Eq. (II)) at $\lambda = \mathrm{const}$ and

$$\varepsilon_{\mathrm{B}} \ll \varepsilon_{\mathrm{A}}, \qquad \varepsilon_{\mathrm{B}} \ll \varepsilon_{\mathrm{AB}}, \qquad \varepsilon_{\mathrm{B}} \ll \varepsilon_{\mathrm{C}}, \tag{III}$$

then the optical density D_1 during the course of the first stage of the reaction is

$$D_1 = \varepsilon_{\mathrm{A}}(a_0 - x_1 - y_1) + \varepsilon_{\mathrm{B}}(b_0 - x_1 - y_1) + \varepsilon_{\mathrm{AB}} x_1 + \varepsilon_{\mathrm{C}} y_1,$$

where a_0 and b_0 are the initial concentrations of reagents A and B, and x_1 and y_1 are the concentrations of AB and C.

When condition (III) is fulfilled and when $y_1 \ll x_1$,

$$\frac{dD_1}{dt} = (\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{A}})\frac{dx}{dt} = \alpha\frac{dx}{dt},$$

where

$$\alpha = \varepsilon_{AB} - \varepsilon_{A}.$$

Then, for $\varepsilon_{AB} > \varepsilon_{A}$, $\alpha > 0$ (increase of D), and for $\varepsilon_{AB} < \varepsilon_{A}$, $\alpha < 0$ (decrease of D).

The optical density during the course of the second stage is

$$D_2 = \varepsilon_B(b_0 - a_0) + \varepsilon_{AB}x_2 + \varepsilon_{Cy}2,$$

where x_2 and y_2 are the concentrations of AB and C.

Then, for $\varepsilon_{AB} > \varepsilon_{C}$, a decrease in the optical density is observed, and for $\varepsilon_{C} > \varepsilon_{AB}$, an increase.

The results of the analysis are presented in Table 2. From the data of Table 2 it is seen that, depending on the ratio of the absorption coefficients of substances A, AB, C, the kinetic curve may have a maximum, a minimum, or no extremum at all. The character of the extremum of the kinetic curves of the reactions studied is shown in Table 1.

Table 2

Type of kinetic curve	Ratio of absorption coefficients
D vs. t: curve rises to a maximum and then falls	$\varepsilon_{AB} > \varepsilon_{A}\varepsilon_{AB} > \varepsilon_{C}$
D vs. t: curve falls to a minimum and then rises	$\varepsilon_{AB} < \varepsilon_{A}\varepsilon_{AB} < \varepsilon_{C}$
D vs. t: monotonically rising curve	$\varepsilon_{AB} > \varepsilon_{A}\varepsilon_{AB} < \varepsilon_{C}$
D vs. t: monotonically falling curve	$\varepsilon_{AB} < \varepsilon_{A}\varepsilon_{AB} > \varepsilon_{C}$

Note: $\lambda = \text{const}$; $\varepsilon_B \ll \varepsilon_A$; $\varepsilon_B \ll \varepsilon_{AB}$; $\varepsilon_B \ll \varepsilon_C$.

Experimental Part

The reactions were carried out in an all-soldered quartz cell 5 cm long, placed in a thermostated cell holder. The temperature in the cell was maintained with an accuracy of $\pm 0.5°$. Measurements were made on a quartz single-beam SF-4 spectrophotometer. The change in optical density with time was recorded on an EPP-09 instrument connected in parallel to the output milliammeter of the spectrophotometer. Into the working cell was introduced a solution of the acid chloride in heptane, conc. $\sim 10^{-6}$ mole/liter. The reaction began after instantaneous injection into the cell of the amine solution (the concentration of amine in the cell was $\sim 10^{-5}$ mole/liter). The amount of each component of the reaction mixture was determined by weighing.

Thus, the study revealed the presence of two stages in the reactions of acid chlorides with secondary amines, and the order of the reactions was found and the rate constants in both stages were measured.

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