KINETICS AND MECHANISM OF THE REACTION OF BENZOYL CHLORIDE WITH 4-(4'-N,N-DIMETHYLAMINOSTYRYL)PYRIDINE-N-OXIDE IN TOLUENE

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The reaction of benzoyl chloride with 4-(4'-N,N-dimethylaminostyryl)pyridine-N-oxide in toluene proceeds according to an addition–elimination mechanism. The rate and equilibrium constants of the individual steps were determined. An inhibiting effect of the substrate was detected.

It was shown earlier [1] that the reaction of benzoyl chloride (BC) with 4-(4'-N,N-dimethylaminostyryl)pyridine-N-oxide [Nu, R = -CH=CH-C6H4N(CH3)2] in toluene proceeds in an equilibrium manner with the formation of 1-benzoyloxy-4-(4'-N,N-dimethylaminostyryl)pyridinium chloride:

\[
\text{C}_6\text{H}_5\text{C} = \text{O} \rightarrow \text{N} \quad \rightarrow \text{R} \quad \xrightleftharpoons{\text{k}_+}{\text{k}_-} \quad \text{C}_6\text{H}_5\text{C}-\text{O} \rightarrow \text{N} \quad \rightarrow \text{R} \cdot \text{Cl}^-
\]

The rate constant of formation of theonium salt (k+) and the rate constant of its monomolecular decomposition (k−) increase with increasing dielectric permeability of the medium (\(\varepsilon\)). The following constants were found in toluene: \(k_+ = 0.058\) liter/mole-sec, \(k_- = 1.78 \times 10^{-5}\) sec\(^{-1}\), and \(k_+/k_- = K_{eq} = 3 \times 10^3\) liters/mole [2].

To demonstrate the stepwise mechanism of nucleophilic substitution at the carbonyl carbon atom in a medium of low polarity we studied the kinetics of reaction (1) at high benzoyl chloride concentrations under pseudomonomolecular conditions with respect to the substrate [\(\text{CX}, 10^{-2} - 10^{-1}\) M] >> [\(\text{Nu}, 1.4 \times 10^{-5}\) M] in toluene at 298 K.

The dependence of the observed rate constant (\(k_0\), sec\(^{-1}\)) on the benzoyl chloride concentration takes the form of a curve with a maximum (Fig. 1a), which is transformed in a plot of \(k_0\) versus \(\log[\text{CX}]\) into a symmetrical bell-shaped curve (Fig. 1b). These functions indicate (cf. [3]) that the investigated reaction proceeds in multiple steps and, in addition to the intermediate product, an inactive complex is accumulated as the benzoyl chloride concentration is increased.

Taking the data obtained into account, the nucleophilic substitution reaction (1) can be represented in the form of the following scheme:

\[
\text{CX} + \text{Nu} \xrightarrow{K_1} (\text{CX})^-\text{Nu}^+ \xrightarrow{k_2 \text{slow}} (\text{CX})_2^+\text{Nu}^+
\]

The intermediate product (\(\text{CX})^-\text{Nu}^+\) slowly breaks down to the ion pair of the onium salt CNu\(^+\)X\(^-\) and forms an inactive complex with the substrate, (\(\text{CX})_2^+\text{Nu}^+\).

Let us present methods of determining the rate and equilibrium constants of individual steps of the reaction under investigation.
Fig. 1. \( k_0 \) (sec\(^{-1}\)) as a function of the benzoyl chloride concentration (a) and the logarithm of its concentration (b) in the reaction with 4-(4'-N,N-dimethylaminostyryl)pyridine-N-oxide in toluene at 298 K.

The data for the rising branch of the observed function (Fig. 1a) were treated according to the equation

\[
\frac{1}{k_0} = \frac{1}{k_2} + \frac{1}{K_1k_2}[CX_I].
\]

(3)

The calculated values of the equilibrium constant of formation of the intermediate product and the rate constant of its monomolecular breakdown to the ion pair were equal to \( K_1 = 3.0 \pm 0.5 \text{ M} \) and \( k_2 = 0.16 \pm 0.04 \text{ sec}^{-1} \), respectively.

The data of the falling branch of the function were treated according to the equation

\[
\frac{1}{k_o} = \frac{1}{k_2} + K_3[CX_I]/k_2.
\]

(4)

The equilibrium constant of formation of an inactive complex \( K_3 = 18.7 \pm 0.5 \text{ M} \) and the rate constant \( k_2 = 0.18 \pm 0.02 \text{ sec}^{-1} \) were calculated. The satisfactory agreement of the values of the rate constant \( k_2 \) found according to Eqs. (3) and (4) confirms the correctness of the proposed scheme (2) of the reaction under investigation.

The values found for the rate and equilibrium constants of individual steps of the investigated reaction [scheme (2)] are comparable with the effective constants obtained under conditions of steady-state kinetics [scheme (1)]. The constants cited are interrelated by the following functions: \( k_+ = K_1k_2 \), \( K_{eq} = k_+/k_- = K_1k_2 = K_1k_2/k_- \), where \( K_2 \) is the equilibrium constant of the conversion of the intermediate product to an ion pair.

The value of \( k_+ \) calculated in the form of the product of the constants obtained, \( K_1k_2 (0.16 - 3 = 0.48 \text{ liter/mole-sec}) \), is an order of magnitude greater than that found in toluene \( (k_+ = 0.058 \text{ liter/mole-sec}, \epsilon = 2.2) \). The increase in the rate constant \( k_+ \) can be explained by an increase in \( \epsilon \) of the medium, due to the high benzoyl chloride concentrations (up to \( \text{4-10}^{-1} \text{ M} \)) in this experiment. The bimolecular rate constant of the reaction \( 0.48 \text{ liter/mole-sec}, \) on the basis of the Kirkwood function [2], corresponds to a medium with \( \epsilon = 3.2 \). In such a medium the effective equilibrium constant \( K_{eq} \) is equal to 5800 liters/mole. Considering the expression for \( K_{eq} \), we find \( k_- = 1.1 \times 10^{-4} \text{ sec}^{-1} \) and \( K_2 = 1430 \). The product of the equilibrium constants found, \( K_1K_2 = 4300 \text{ liters/mole} \), is in satisfactory agreement with the effective equilibrium constant found under conditions of steady-state formation of the intermediate product.

Consequently, the reaction of benzoyl chloride with 4-(4'-N,N-dimethylaminostyryl)pyridine-N-oxide, which proceeds with the formation of an onium salt, is a multistep equilibrium in a medium with low polarity; it proceeds through a fast step of formation of the intermediate product, the slow breakdown of which to the ion pair limits the rate.

The most probable structure of the active intermediate product is a zwitterion-type intermediate

\[
\begin{array}{c}
\text{N}^+ \text{O}^- \\
\text{C} \text{Cl}
\end{array}
\]

with a negative charge on the oxygen atom. The equilibrium reaction of addition of a substrate molecule to the active intermediate product leads to the formation of an inactive salt-like complex.