# Kinetics and Mechanism of the Reaction of Benzoyl Chloride with 4-(4′-*N,N*-Dimethylaminostyryl)pyridine *N*-Oxide in Acetonitrile

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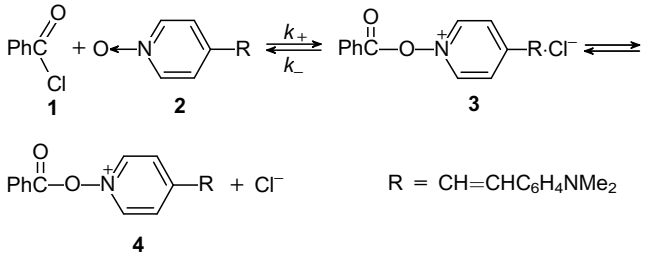
The rate and equilibrium constants for the individual steps in the reaction of benzoyl chloride with 4-(4′-*N,N*-dimethylaminostyryl)pyridine *N*-oxide in acetonitrile to afford 1-benzoyloxy-4-(4′-*N,N*-dimethylaminostyryl)pyridinium chloride have been determined; the slow step of the reaction involves decomposition of a tetrahedral intermediate.

Oxygen-nucleophilic catalysis by pyridine *N*-oxides has been found in the acylation of arylamines.[1] The phenomenon of catalysis results from the formation of an acylonium salt, which has high acylating ability, from an acyl halide and a catalyst.

It has been shown previously[2] that the reaction of benzoyl chloride **1** with 4-(4′-*N,N*-dimethylaminostyryl)pyridine *N*-oxide **2** leads to equilibrium formation of 1-benzoyloxy-4-(4′-*N,N*-dimethylaminostyryl)pyridinium chloride **3** which rapidly dissociates to ions in acetonitrile, according to Scheme 1.




**Scheme 1**

Kinetic studies of the reaction revealed a linear dependence of the observed rate constant ($k_{obs}$, $s^{-1}$) on the concentration of 4-(4′-*N,N*-dimethylaminostyryl)pyridine *N*-oxide ($b$, mol $dm^{-3}$).

$$k_{obs} = k_- + k_+ b \qquad (1)$$

Relation (1) indicates the equilibrium formation of salt **3** with a bimolecular rate constant ($k_+ = 6000$ $dm^3$ $mol^{-1}$ $s^{-1}$) of its formation and a monomolecular rate constant of its decomposition to the starting reagents ($k_- = 0.012$ $s^{-1}$).

The present work reports studies on the kinetics of the reaction (Scheme 1) over a wide range of benzoyl chloride concentrations ($a$, mol $dm^{-3}$) with the purpose of proving experimentally the multi-step mechanism of formation of the acylonium salt. At low concentrations of benzoyl chloride ($10^{-5}$–$10^{-4}$ mol $dm^{-3}$, method i) the reaction was studied by monitoring the decrease in the concentration of the starting pyridine *N*-oxide (λ 400 nm) and by the accumulation of cation **4** (λ 515 nm). Fast reactions ($10^{-4}$–$10^{-2}$ mol $dm^{-3}$ of benzoyl chloride, method ii) were studied by observing the accumulation of the cation using a flow spectrophotometer.

The observed rate constants obey a linear relation of type (1) (Table 1, method i). We obtained numerical equation (2):

$$k_{obs} = (0.02 \pm 0.01) + (5500 \pm 400)a \qquad (2)$$
$$N = 12,\ S_0 = 0.21,\ R = 0.970$$

The calculated rate constants $k_+$ and $k_-$, which are equal to 5500 $dm^3$ $mol^{-1}$ $s^{-1}$ and 0.02 $s^{-1}$, respectively, coincide with the previously determined values obtained with an excess of the nucleophilic reagent. At equal concentrations of the reagents ($a = b = 1.5 \times 10^{-5}$ mol $dm^{-3}$) the bimolecular rate constant ($k_+ = 5700 \pm 100$) is consistent with the values obtained with a pseudo-monomolecular ratio of the reagents.

The dependence of $k_{obs}$ on the concentration of benzoyl chloride (method ii) is a curved line (see Fig. 1), whose shape allows us to propose the accumulation of an intermediate.[3]

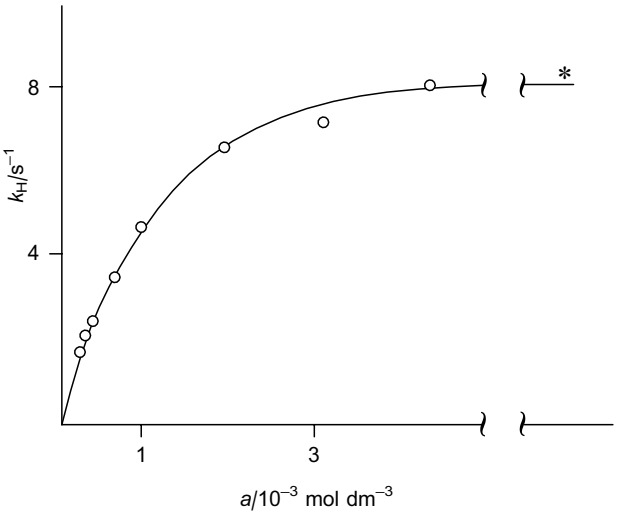



**Fig. 1** Dependence of $k_{obs}$ on $a$ for the reaction of **1** with **2** in acetonitrile at 298 K (* is the value at $a = 2.8 \times 10^{-2}$ mol $dm^{-3}$).

The dependence observed obeys equation (3):

$$k_{obs} = K_1 k_2 / (1 + K_1 a) \qquad (3)$$

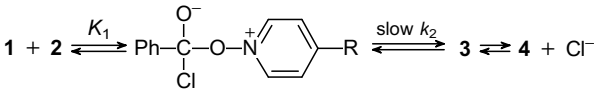
where $K_1$/$dm^3$ $mol^{-1}$ is the equilibrium constant of intermediate formation, and $k_2$/$s^{-1}$ is the rate constant of intermediate decomposition. According to equation (3), the plots in the coordinates $1/k_{obs}$ *versus* $1/a$ gave the values $K_1 = 840 \pm 50$ and $k_2 = 9.80 \pm 0.50$. The product of the constants, $K_1 k_2$, is equal to the value of the bimolecular constant $k_+$ determined under the stationary conditions of intermediate formation. The

**Table 1** Observed rate constants for the reaction of benzoyl chloride with 4-(4′-*N,N*-dimethylaminostyryl)pyridine *N*-oxide in acetonitrile at 298 K.

| $a/10^{-5}$ mol $dm^{-3}$ | $k_{obs}/10^2$ $s^{-1}$ |
|---|---|
| λ 515 nm, $b$ $1 \times 10^{-6}$ mol $dm^{-3}$, $l$[a] 3 cm | |
| 0.4 | $1.75 \pm 0.01$ |
| 1.2 | $9.70 \pm 0.01$ |
| 1.5 | $13.4 \pm 0.1$ |
| 2.4 | $16.9 \pm 0.3$ |
| λ 515 nm, $b$ $2.5 \times 10^{-6}$ mol $dm^{-3}$, $l$[a] 1 cm | |
| 3.0 | $18.0 \pm 0.1$ |
| 3.5 | $23.5 \pm 0.4$ |
| 4.0 | $25.0 \pm 0.2$ |
| 4.7 | $31.0 \pm 0.5$ |
| λ 400 nm, $b$ $2.2 \times 10^{-6}$ mol $dm^{-3}$, $l$[a] 3 cm | |
| 2.0 | $13.7 \pm 0.2$ |
| 3.0 | $20.5 \pm 0.2$ |
| 4.2 | $22.0 \pm 0.2$ |
| 5.2 | $29.0 \pm 0.3$ |

[a] $l$ is the optical cell path length.

intermediate is proposed to have a betaine structure with an $sp^3$-hybridized carbon atom. The improved scheme of the reaction can be presented as:




**Scheme 2**

Thus, the reaction studied for the formation of acylonium salt is a multi-step equilibrium reaction that proceeds through formation of a tetrahedral intermediate, whose decomposition is the slow step of the reaction.

## References


1 L. M. Litvinenko and G. D. Titskii, *Dokl. Akad. Nauk SSSR*, 1967, **177**, 127 [*Dokl. Chem. (Engl. Transl.)*, 1967, **177**, 990].

2 G. D. Titskii and M. K. Turovskaya, *Zh. Org. Khim.,* 1992, **28**, 1911 (*Russ. J. Org. Chem*., 1992, **28**, 1531).

3 I. V. Berezin and A. A. Klesov, *Prakticheskii kurs khimicheskoi i fermentativnoi kinetiki (Practical course of chemical and enzyme kinetics)*, Izd. Mosk. Univ., Moscow, 1976 (in Russian).



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