

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

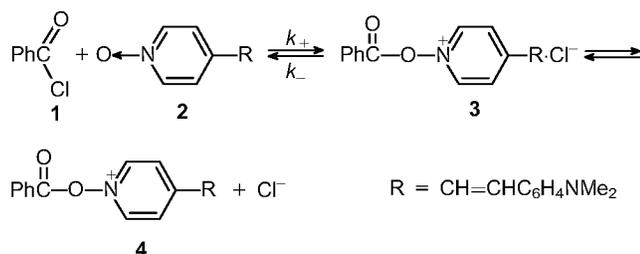
Gennadii D. Titskii,\* Mariya K. Turovskaya and Aleksandr A. Yakovets

*L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of the Ukraine, 340117 Donetsk, Ukraine. Fax: +7 0622 553 542*

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.<sup>1</sup> 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<sup>2</sup> 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 ( $k_{\text{obs}}$ , s<sup>-1</sup>) on the concentration of 4-(4'-*N,N*-dimethylaminostyryl)pyridine *N*-oxide ( $b$ , mol dm<sup>-3</sup>).

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

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

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

$$k_{\text{obs}} = (0.02 \pm 0.01) + (5500 \pm 400)a \quad (2)$$

$N = 12, S_0 = 0.21, R = 0.970$

The calculated rate constants  $k_+$  and  $k_-$ , which are equal to  $5500 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $0.02 \text{ s}^{-1}$ , respectively, coincide with the previously determined values obtained with an excess of the nucleophilic reagent. At equal concentrations of the reagents ( $a = b = 1.5 \times 10^{-5} \text{ mol dm}^{-3}$ ) 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  $k_{\text{obs}}$  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.<sup>3</sup>

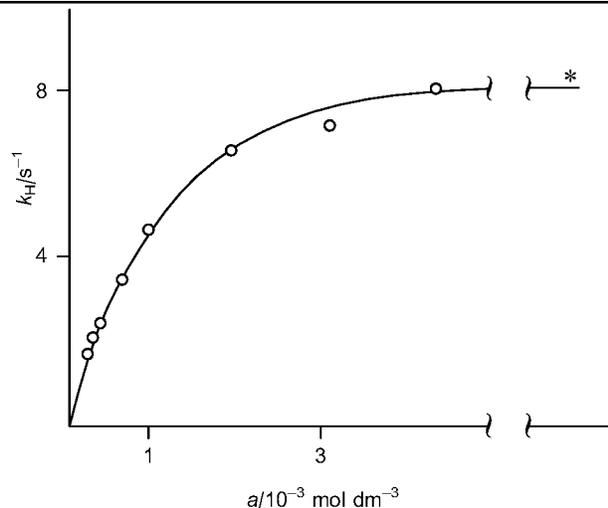


Fig. 1 Dependence of  $k_{\text{obs}}$  on  $a$  for the reaction of **1** with **2** in acetonitrile at 298 K (\* is the value at  $a = 2.8 \times 10^{-2} \text{ mol dm}^{-3}$ ).

The dependence observed obeys equation (3):

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

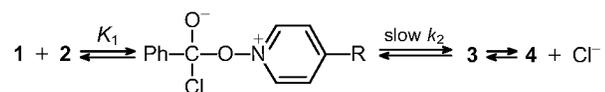
where  $K_1/\text{dm}^3 \text{ mol}^{-1}$  is the equilibrium constant of intermediate formation, and  $k_2/\text{s}^{-1}$  is the rate constant of intermediate decomposition. According to equation (3), the plots in the coordinates  $1/k_{\text{obs}}$  versus  $1/a$  gave the values  $K_1 = 840 \pm 50$  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.

$a/10^{-5} \text{ mol dm}^{-3}$	$k_{\text{obs}}/10^2 \text{ s}^{-1}$
$\lambda$ 515 nm, $b$ $1 \times 10^{-6} \text{ mol dm}^{-3}$ , $l^a$ 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	$16.9 \pm 0.3$
$\lambda$ 515 nm, $b$ $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ , $l^a$ 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	$31.0 \pm 0.5$
$\lambda$ 400 nm, $b$ $2.2 \times 10^{-6} \text{ mol dm}^{-3}$ , $l^a$ 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	$29.0 \pm 0.3$

<sup>a</sup>  $l$  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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