

## Rate and Equilibrium Constants of Benzoyl Group Transfer between Pyridine N-Oxides

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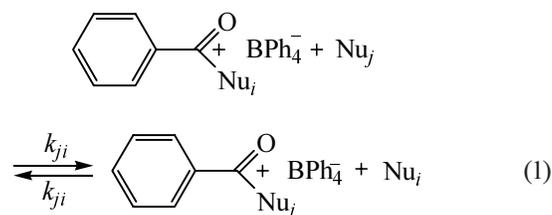
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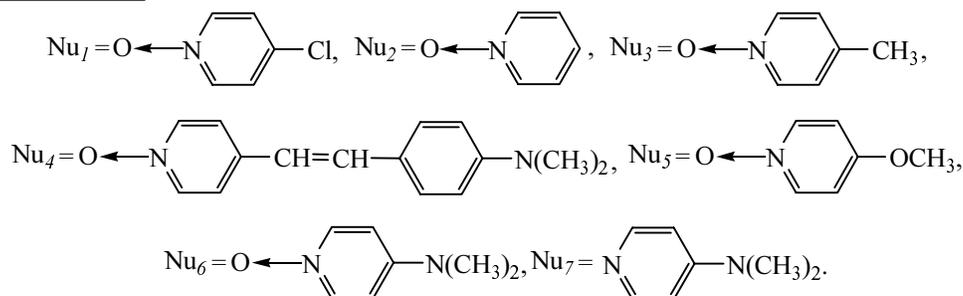
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**Abstract**—Kinetic characteristics of 19 transfer reactions of benzoyl group from N-benzoyloxypyridinium salts to pyridine N-oxides and 4-dimethylaminopyridine were studied in acetonitrile by the stopped-flow method. The rate of an identical reaction for 4-methoxypyridine was measured by dynamic NMR spectroscopy. For 5 other identical reactions the rates were estimated from Brønsted correlations. Equilibrium constants were estimated with the use of UV spectrophotometry (6), IR spectroscopy (2), from kinetic data ( $K_{ij} = k_{ij}/k_{ji}$ ) (2), and in one case as  $\log K_{i-x} = \log K_{j-x} - \log K_{j-x}$ . The second order rate constants ( $k_{ij}$ ) varied in the range  $10^2$ – $10^5$  l mol<sup>-1</sup> s<sup>-1</sup>, the equilibrium constants ( $K_{ij}$ ) in the range  $10^2$ – $10^{-2}$ ; the activation parameters ( $\Delta H^\ddagger$ ) were within 15–50 kJ mol<sup>-1</sup>, ( $-\Delta S^\ddagger$ ) –20–110 J mol<sup>-1</sup> K<sup>-1</sup>. The reactions under study occur in a single stage following the concerted S<sub>N</sub>2 mechanism through an early associative transition state. The benzoyl groups exchange rate and equilibrium are well described by simplified Marcus equation (omitting the quadratic term).

Benzoylation is considerably accelerated in the presence of pyridine N-oxides, highly basic pyridines, and azoles [1, 2]. This fact is rationalized as formation on the reaction coordinate of the corresponding acylium salt [3]. We formerly investigated the structure of some benzoylonium salts [4, 5] and estimated the kinetic and thermodynamic characteristics of formation reactions for a series of N-benzoyloxypyridinium and N-benzoylpyridinium salts [5, 6]. The present study concerns the reactivity of these compounds in the exchange processes of the type (1).



Kinetic and in some cases also equilibrium data were measured in acetonitrile solutions for reaction series where as nucleophiles and/or departing groups ( $\text{Nu}_i, \text{Nu}_j$ ) operated the following compounds:



The experimentally determined rates of reactions (1) follow the second order kinetics. The measurements were carried out by the stopped-flow method under pseudofirst order conditions where ( $C_{\text{Nu}}/C_{\text{AOC}} > 10$ ). The acylium

salt concentration ( $c_{\text{AOC}}$ ) in the kinetic experiments did not exceed  $3 \times 10^{-4}$  mol l<sup>-1</sup> thus excluding the ion association effects on the measured magnitudes [7]. The second order rate constants ( $k_{ij}$ ) were calculated by the least-

**Table 1.** Kinetic ( $\log k_{ij}$ ,  $\Delta H_{ij}^\ddagger$ ,  $-\Delta S_{ij}^\ddagger$ ) and thermodynamic ( $\log K_{ij}$ ) characteristics of reaction (1) ( $\text{CH}_3\text{CN}$ , 298 K)

Run no.	Nu <sub>i</sub> , <i>i</i> =	Nu <sub>j</sub> , <i>j</i> =	$\log k_{ij}$ , l (mol·s) <sup>-1</sup>	$\Delta H_{ij}^\ddagger$ , kJ mol <sup>-1</sup>	$-\Delta S_{ij}^\ddagger$ , J (mol·K) <sup>-1</sup>	$\log K_{ij}$	$\text{p}K_{\text{BH}}^+$		$\nu_{\text{C=O}}$ , cm <sup>-1</sup> of reactant	$\nu_{\text{C=O}}$ , cm <sup>-1</sup> of product
							Nu <sub>i</sub>	Nu <sub>j</sub>		
1	1	2	3.04	–	–	–	0.33	0.79	1803	1817, 1793
2	1	3	4.05	19	103	–	0.33	1.29	1803	1800
3	1	4	4.3	–	–	–	0.33	1.43	1803	1798
4	1	5	5.17	31	41	–	0.33	2.05	1803	1804, 1786
5	1	6	5.47	50	–20	–	0.33	3.88	1803	1826, 1789
6	2	3	3.26	20	109	1.02	0.79	1.29	1817, 1793	1800
7	2	4	3.7	–	–	1.76	0.79	1.43	1817, 1793	1798
8	2	5	4.67	15	106	2.0 <sup>a</sup>	0.79	2.05	1817, 1793	1804, 1786
9	2	6	5.32	22	72	–	0.79	3.88	1817, 1793	1826, 1789
10	3	2	2.58	–	–	–1.02	1.29	0.79	1800	1817, 1793
11	3	4	3.3	–	–	0.42	1.29	1.43	1800	1798
12	3	5	4.31	24	84	1.43 <sup>b</sup>	1.29	2.05	1800	1804, 1786
13	3	6	5.15	31	46	–	1.29	3.88	1800	1826, 1789
14	4	3	2.7	–	–	–0.42	1.43	1.29	1798	1800
15	4	5	3.87	17	114	1.24	1.43	2.05	1798	1804, 1786
16	4	6	4.97	17	95	–	1.43	3.88	1798	1826, 1789
17	5	3	2.88	–	–	–1.43 <sup>b</sup>	2.05	1.29	1804, 1786	1800
18	5	6	4.90	15	102	–	2.05	3.88	1804, 1786	1826, 1789
19	4	7	4.86	20	84	–	1.43	9.65	1798	1734

<sup>a</sup>  $\log K_{2-5} = \log K_{2-4} - \log K_{3-4}$ ; <sup>b</sup>  $\log K_{3-5} = \log (k_{3-3}/k_{5-3})$ .

squares procedure from the relation of  $k_{\text{app}}$  to three or four analytical concentrations of the nucleophile by equation (2).

$$k_{\text{app}} = k_{ji} + k_{ij}[\text{Nu}_j] \quad (2)$$

The thermodynamic parameters of the transition state were calculated from  $k_{ij}$  values obtained at three temperatures in the range 298–308 K. The equilibrium constants ( $K_{ij}$ ) for reactions of Nu<sub>4</sub> were evaluated from UV spectrophotometric measurements as in [8] (for Nu<sub>4</sub>  $\lambda_{\text{max}}$  395 nm,  $\epsilon$  36000 l mol<sup>-1</sup> cm<sup>-1</sup>, in *N*-oxybenzoyl salt of this nucleophile  $\lambda_{\text{max}}$  510 nm,  $\epsilon$  59000 l mol<sup>-1</sup> cm<sup>-1</sup>). The equilibrium constants  $K_{23}$ ,  $K_{32}$  were measured in CH<sub>3</sub>CN with the use of IR spectroscopy. Here as an analytical band was chosen that of the stretching vibrations of the heterocyclic ring skeleton  $\nu_{8a}$  of the 1-benzoyloxy-4-methylpyridinium tetraphenylborate ( $\nu_{8a}$  1628.0 cm<sup>-1</sup>,  $\epsilon$  185 l mol<sup>-1</sup> cm<sup>-1</sup>). This absorption band considerably overlapped with the corresponding absorption band of the 1-benzoyloxy pyridinium tetraphenylborate ( $\nu_{8a}$  1613.5 cm<sup>-1</sup> [4]) hampering the precise evaluation of the equilibrium concentrations. Therefore in these experiments we applied perdeuterated in the heterocyclic ring analog of the 1-benzoyloxy pyridinium tetraphenylborate where  $\nu_{8a}$  was 1570 cm<sup>-1</sup>. The values  $K_{53}$ ,

$K_{35}$  were obtained as the ratio of the rate constants  $k_{53}$  and  $k_{35}$ . In event  $i = 2$  and  $j = 5$  the equilibrium constant was found as  $K_{2-5} = K_{2-4}/K_{5-4}$ .

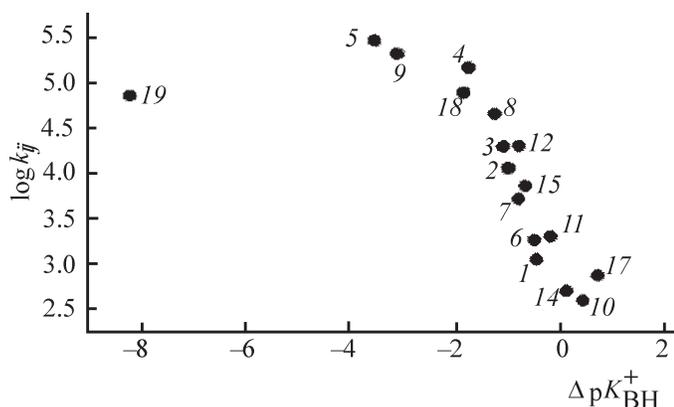
The rate and equilibrium constants logarithms, and also values  $\Delta H^\ddagger$  and  $-\Delta S^\ddagger$  of reaction (1) at  $T$  298 K are compiled in Table 1. Here are also given the  $\text{p}K_{\text{BH}}^+$  values of bases in water at  $T$  298 K, and the stretching vibration frequencies of the benzoyl group AOC in acetonitrile solutions measured in [5, 9].

As seen from Table 1, the variation in rate and equilibrium constants of reaction (1) depending on structural factors reaches ~3–4 orders of magnitude. In the series of reactions under study an isokinetic relation is valid:

$$\Delta H_{ij}^\ddagger = (42.8 \pm 1.7) + (0.25 \pm 0.02)\Delta S_{ij}^\ddagger, \quad (3)$$

$$n \ 12, r \ 0.970, S_0 \ 2.52,$$

evidencing that the process occurs along a single-type mechanism [10]. The activation parameters of reaction (1) are typical of spontaneous (noncatalyzed) bimolecular reactions of nucleophilic substitution [1, 11]. Inasmuch as in all cases the  $\Delta H^\ddagger$  values are positive the mechanism of the reaction in question should be concerted [12] and not stepwise [13]. The proper values of the activation enthalpy  $\Delta H^\ddagger$  (~15–50 kJ mol<sup>-1</sup>) and entropy  $\Delta S^\ddagger$



The rate constants of benzoyl transfer as a function of the difference between basicity of nucleophile and departing group (the numeration same as that presented in Table 1).

( $\sim -20$ – $110 \text{ J mol}^{-1} \text{ K}^{-1}$ ) suggest an early associative transition state where the extent of rupture and formation of bonds is small. In such cases the variations of reactivity usually follow well the structural characteristics of the reagents [14].

We measured for all reactions studied the frequencies of the stretching vibrations of C=O group in reactants and products of reaction (1), and basicity constants of the nucleophile ( $\text{Nu}_j$ ) and the departing group ( $\text{Nu}_i$ ). As seen from Table 1 the vibration bands  $\nu_{\text{C=O}}$  are split for a number of salts apparently due to the interaction between the vibrations [15], and the overall pattern of their changes is poorly interpretable. As a result we did not find any correlations between  $\log k_{ij}$  and  $\nu_{\text{C=O}}$ .

The correlation in the coordinates of Brønsted equation is achieved better using simultaneously both  $\text{p}K_{\text{BH}^+}$  values of the nucleophile and the departing group. The relationship between  $\log k_{ij}$  and values  $\text{p}K_{\text{BH}^+} = \text{p}K(\text{Nu}_j) - \text{p}K(\text{Nu}_i)$  is presented on the figure. The great scatter of the points on this correlation should be indicated, especially the deviation of the point 19, namely, when the nucleophile and the departing group are of different nature. This phenomenon we frequently observed investigating, for instance, transfer of acetyl [16] and dimethylcarbamoyl moieties [17]. This is caused by the failure of agreement between the basicity and the nucleophilicity at the change of the nucleophile [6]. However even without point 19 the quality of correlation (4) cannot be regarded as fair.

$$\log k_{ij} = (3.16 \pm 0.23) - (0.67 \pm 0.16)\text{p}K_i + (0.76 \pm 0.08)\text{p}K_j, \quad (4)$$

$n 18, r 0.853, S_0 0.370$

The other way to analyze the reactivity in one-step reactions of nucleophilic substitution is the use of rela-

tions between the reaction rate and equilibrium [17, 18]. The comparison of rate and equilibrium constants we measured gives a correlation of the same statistical validity as (4).

$$\log k_{ij} = (3.19 \pm 0.14) + (0.51 \pm 0.11)\log K_{ij}, \quad (5)$$

$n 9, r 0.873, S_0 0.370$

We believe that the low predictability of the reactivity in reaction (1) by applying equations (4) and (5) is due to the fact that the fixed term in these equations is not really constant.

The modern interpretation of Brønsted and Evans–Polanyi [19] equations regards this as the kinetic characteristic (barrier) of the identical reaction. We showed however experimentally [16, 20] that the rate of identical ( $\text{Nu}_i = \text{Nu}_j$ ) acyl transfer reactions depended both on the character of the acyl group and on the structure of the nucleophile (departing group). Actually the measuring of rates of identical reactions is a labor-consuming and not always soluble problem. To a certain extent this statement is also valid for the identical reactions of benzoyl transfer. However we have a possibility to estimate the  $\log k_{ii}$  values from the Brønsted correlations for the reaction series (1) where either  $\text{Nu}_i = \text{const}$  or  $\text{Nu}_j = \text{const}$ . The parameters of equations obtained are presented in Table 2. Here the correlation factors are mainly considerably higher than for equations (4) and (5). The predicted rate constants of identical benzoyl transfer reactions are given in Table 3. In the case of 4-methoxypyridine N-oxide the experimental value of identical transfer rate constant is also presented. The latter finding was obtained in the acetonitrile solution by dynamic NMR spectroscopy [19, 20]. Therewith as indicator signals were chosen the proton signals from the methoxy group of the 4-methoxypyridine N-oxide ( $\delta 3.81 \text{ ppm}$ ) and of 1-benzoyloxy-4-methoxypyridinium tetraphenylborate ( $\delta 4.12 \text{ ppm}$ ). The close values of experimental  $\log k_{55}$  and that obtained from the correlation permit a conclusion that the  $\log k_{ii}$  found from the correlation actually represent the experimental values. Another argument supporting the above statement is the nonlinearity of the  $\log k_{ii}$  (Table 3) relation to  $\text{p}K_{\text{BH}^+}$  in keeping with the theoretical predictions [21]. Note that in the transfer reaction of dimethylcarbamoyl group [17] the values  $\log k_{ii}$  and  $\text{p}K_{\text{BH}^+}$  well fit to a parabola.

Now let us test the possibility to apply  $\log k_{ij}$  for the analysis of reactivity in reactions (1). In an explicit form these values enter the Marcus equation [22], that for the rate and equilibrium can be written [22] as expression (6).

**Table 2.** Parameters of Brønsted equation for the benzoyl transfer (1) in CH<sub>3</sub>CN

Correlation no.	$Y = a + bX$	$a$	$b$	$n$	$r$	$S_0$
1	$\log k_{1-j} = f(pK_a \text{Nu}_j)$	$2.97 \pm 0.41$	$0.67 \pm 0.19$	4	0.93	0.45
2	$\log k_{2-j} = f(pK_a \text{Nu}_j)$	$2.69 \pm 0.53$	$0.72 \pm 0.22$	4	0.92	0.45
3	$\log k_{3-j} = f(pK_a \text{Nu}_j)$	$2.18 \pm 0.40$	$0.81 \pm 0.17$	4	0.96	0.39
4	$\log k_{4-j} = f(pK_a \text{Nu}_j)$	$1.86 \pm 0.56$	$0.83 \pm 0.21$	3	0.97	0.400
5	$\log k_{i-3} = f(pK_a \text{Nu}_i)$	$4.00 \pm 0.39$	$-(0.68 \pm 0.29)$	4	0.9	0.39
6	$\log k_{i-4} = f(pK_a \text{Nu}_i)$	$4.60 \pm 0.13$	$-(1.04 \pm 0.15)$	3	0.99	0.10
7	$\log k_{i-5} = f(pK_a \text{Nu}_i)$	$5.53 \pm 0.18$	$-(1.07 \pm 0.17)$	4	0.98	0.15
8	$\log k_{i-6} = f(pK_a \text{Nu}_i)$	$5.56 \pm 0.07$	$-(0.34 \pm 0.05)$	5	0.97	0.07

$$\log k_{ij} = 1/2(\log k_{ii} + \log k_{jj}) + 1/2 \log K_{ij} - (\log K_{ij})^2/8(\log k_{ii} + \log k_{jj}) \quad (6)$$

The data from Tables 1 and 3 show that the value of the “quadratic” term in equation (6) is less than 0.1 logarithmic unit. Therefore we do not go beyond the two first terms in equation (6) as has been done for methyl [22], acetyl [16], and dimethylcarbamoyl transfer [17]. The correlation processing of the data from Tables 1 and 3 afforded the equation:

$$\log k_{ij} = (0.987 \pm 0.030)(\log k_{ii} + \log k_{jj}) + (0.964 \pm 0.152) \log K_{ij}, \quad n 9, r 0.994, S_0 0.266 \quad (7)$$

As compared to equation (5) equation (7) significantly refines the quality of prediction for benzoyl transfer reactions (1). Hence the benzoyl transfer like the other acyl transfer reactions of type (1) we have previously investigated [16, 17] is governed alongside the thermodynamic factor,  $\log K_{ij}$ , also by a purely kinetic,  $1/2(\log k_{ii} + \log k_{jj})$ , internal barrier [22, 23]. It may be concluded in general that the characteristic of identical reaction is a useful and indispensable part of the analysis and prediction of nucleophilic substitution reactions at the carbonyl center.

## EXPERIMENTAL

All reagents were prepared and purified as described in [1, 2, 4]. Acetonitrile of Acros for HPLC grade was dried before use on molecular sieves 3A. The rates of fast reactions were measured on stopped-flow installation Applied Photophysics equipped with a temperature-control device ( $\pm 0.1$  K). Electronic absorption spectra were registered on a spectrophotometer Specord 200; the optical densities were measured in a cell under temperature control at  $T 298 \pm 0.1$  K. IR spectra were recorded on a spectrophotometer Perkin-Elmer Spectrum BX (resolution  $4 \text{ cm}^{-1}$ , Beer–Norton apodization). <sup>1</sup>H NMR spectra

**Table 3.** Kinetic characteristics of identical ( $i = j$ ) reactions (1)

Nu <sub>i</sub> , $i =$	$pK_{BH}^+$	$\log k_{ii}$
1	0.33	3.20
2	0.79	3.25
3	1.29	3.17 <sup>a</sup>
4	1.43	3.08 <sup>b</sup>
5	2.05	3.34 (3.59 $\pm$ 0.12) <sup>c</sup>
6	3.88	4.00

<sup>a</sup> Average value determined from correlations 3 and 5.

<sup>b</sup> Average value determined from correlations 4 and 6.

<sup>c</sup> Experimental value.

were obtained on a spectrometer Gemini-200 at operation frequency 200 MHz. The concentration values were used in calculation of constants. The reproducibility of rate constants measured by the stopped-flow method was  $\pm 5$ –7%; that of the rate of identical reaction was better than  $\pm 15$ %; that of equilibrium constants was no worse than  $\pm 5$ %.

**1-Benzoyloxy-4-(4'-dimethylaminostyryl)pyridinium tetraphenylborate.** To a dispersion of 0.240 g (1 mmol) of 4-(4'-dimethylaminostyryl)pyridine N-oxide, and 0.342 g (1 mmol) of sodium tetraphenylborate in a small amount of acetonitrile ( $\sim 4$ –5 ml) was slowly added at stirring a solution of 0.281 g (2 mmol) of benzoyl chloride in 1 ml of acetonitrile. The reaction mixture was stirred in the dark for 2 h and then filtered. The filtrate was diluted with  $\sim 100$ –150 ml of dry ethyl ether. In 40–50 min the separated precipitate was filtered off and purified by additional reprecipitation from the acetonitrile solution with anhydrous ethyl ether. Yield 0.53 g (80%), dark-violet crystals. <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 8.75 d [2H, Py( $\alpha$ ),  $J$  7.3 Hz], 8.27 d [2H, P $\sigma$ ( $\beta$ ),  $J$  7.3 Hz], 8.11 d [2H, Bz( $\alpha$ )], 7.97 d (2H, CH=CH,  $J$  16.4 Hz), 7.74 d (2H, Ph,  $J$  7.1 Hz), 7.63 d [1H, Bz( $\gamma$ )], 7.49 t [2H, Bz( $\beta$ )], 7.39 d (2H, CH=CH,  $J$  16.4 Hz), 7.34 m [8H,

BPh<sub>4</sub>(*o*-H)], 7.05 d (2H, Ph, *J* 7.1 Hz), 6.92 m [8H, BPh<sub>4</sub>(*m*-H)], 6.76 m [8H, BPh<sub>4</sub>(*n*-H)], 2.85 c [6H, N(CH<sub>3</sub>)<sub>2</sub>]. Found, %: C 83.5; H 6.3; N 4.1 C<sub>46</sub>H<sub>41</sub>BN<sub>2</sub>O<sub>2</sub>. Calculated, %: C 83.1; H 6.2; N 4.2.

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