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Rate and Equilibrium Constants of Dimethylcarbamoyl Transfer between Pyridine *N*-Oxides

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Abstract — Dimethylcarbamoyl transfer from *N*-acyloxypyridinium salts to pyridine *N*-oxides in acetonitrile occurs in one stage by the forced concerted SN2 mechanism. The rate and equilibrium of the reaction are fairly described by the Brønsted equation. The Marcus equation provides a much higher quality of reactivity predictions.

Reactivity analysis and prediction is one of the most actual problems of organic and bioorganic chemistry [1, 2]. Over the past years new rigorously physically substantiated theoretical concepts have been developed [3], which have found wide application (in particular, Marcus equation [4]) in analysis of reactions whose mechanism is proved or casts no doubts. They include hydrogen [5], methyl [6], proton [7], or hydride transfer [8], etc. The situation with nucleophilic substitution reactions which may involve formation of intermediate compounds and are not *a priori* one-stage, like those with carboxylic acid derivatives [2, 9], is more intricate. A question arises whether the analytical technique, especially new, is suitable for a proposed mechanism which in itself is most commonly to be diagnosed [3, 10]. At present, no verified lines of approaching this problem are available, which necessitates recourse to traditional methods based, in particular, on the Brønsted equation [2, 10]. Another impediment to wide use of the Marcus equation in organic chemistry is the shortage or, more frequently, lack of rate and equilibrium data for identity reactions.

It the present work we set ourselves the task to obtain kinetic and equilibrium characteristics of dimethylcarbamoyl transfer reactions [scheme (1)] in acetonitrile between acyloxypyridinium salts and pyridine *N*-oxides (Nu), including identity (Nu$_i$ = Nu$_j$), and also to establish the mechanism of these reactions, to correlate their rates and equilibria, and to find out the use of the Marcus equation for data treatment.

All measured and calculated logarithms of the rate and equilibrium (1) constats in acetonitrile are listed

$$Me_2NCONu_i^+ \ BPh_4^- + Nu_j$$
$$\rightleftharpoons Me_2NCONu_j^+ \ BPh_4^- + Nu_i, \qquad (1)$$
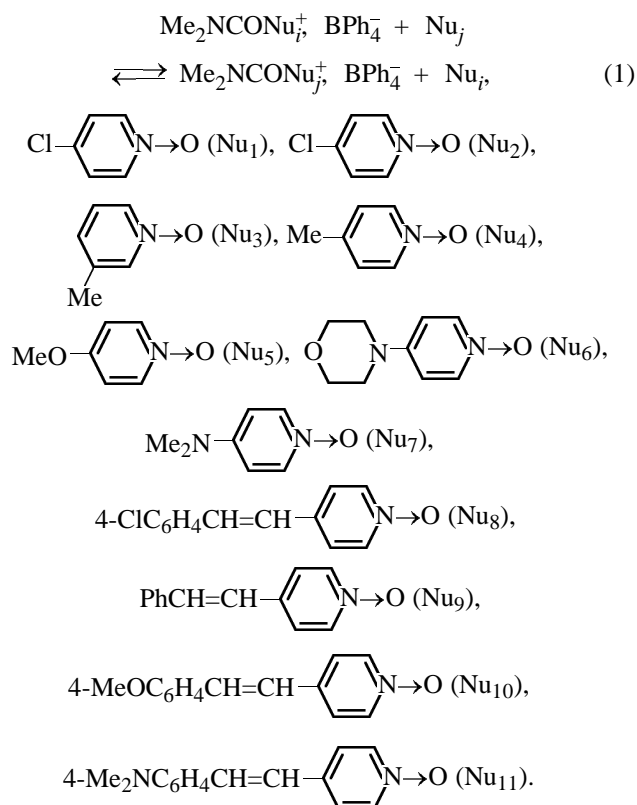
in Table 1, together with the "intrinsic" barriers $\{1/2(\log k_{ii} + \log k_{jj})\}$ to the corresponding reactions and the basicity constants of the leaving group and nucleophile in water. With reaction nos. 1–29 ($i \neq j$), kinetic measurements were performed under pseudo-first-order conditions in one of the reagents. Reaction progress was followed by UV spectroscopy at optimal wavelengths. Therewith, the rate constants of slow reactions (nos. 8–11) were determined by the initial

Table 1. Kinetic [log k_{ij}, 1/2(log k_{ii} + log k_{jj})] and thermodynamic (log K_{ij}) characteristics of reaction (1)

Reaction no.	Nu_i	Nu_j	log k_{ij}	log K_{ij}	1/2(log k_{ii} + log k_{jj})	$pK_{BH^+}(Nu_i)$[a]	$pK_{BH^+}(Nu_j)$
1	11	1	–3.83			1.43	0.33
2	11	2	–3.31	–1.99[b]	–2.26	1.43	0.79
3	11	3	–2.88	–1.30, –1.28[b]	–2.31	1.43	1.03
4	11	4	–2.34	–0.51, –0.51[b]	–2.15	1.43	1.29
5	11	5	–1.06	1.57, 1.62[b]	–2.03	1.43	2.05
6	11	6	0.63		–1.39	1.43	3.25
7	11	7	1.21		–1.20	1.43	3.88
8	2	11	–1.32	1.99[b]	–2.26	0.79	1.43
9	3	11	–1.60	1.30, 1.28[b]	–2.31	1.03	1.43
10	4	11	–1.83	0.51, 0.51[b]	–2.15	1.29	1.43
11	5	11	–2.68	–1.57, –1.62[b]	–2.03	2.05	1.43
12	10	2	–2.88	–1.34[c]	–2.22	1.25	0.79
13	10	3	–2.62	–0.64[c]	–2.26	1.25	1.03
14	10	4	–1.96	0.12[c]	–2.10	1.25	1.29
15	10	5	–0.72	2.33[c]	–1.99	1.25	2.05
16	10	6	0.84		–1.35	1.25	3.25
17	10	7	1.30		–1.16	1.25	3.88
18	9	2	–2.74	–0.90[c]	–2.26	1.10	0.79
19	9	3	–2.50	–0.20[c]	–2.30	1.10	1.03
20	9	4	–1.78	0.55[c]	–2.14	1.10	1.29
21	9	5	–0.62	2.77[c]	–2.03	1.10	2.05
22	9	6	0.87		–1.39	1.10	3.25
23	9	7	1.45		–1.20	1.10	3.88
24	8	2	–2.67	–0.76[c]	–2.26	1.05	0.79
25	8	3	–2.43	–0.06[c]	–2.3	1.05	1.03
26	8	4	–1.73	0.70[c]	–2.14	1.05	1.29
27	8	5	–0.53	2.92[c]	–2.03	1.05	2.05
28	8	6	0.90		–1.39	1.05	3.25
29	8	7	1.52		–1.20	1.05	3.88
30	2	2	–2.31, –2.22[c]	0		0.79	0.79
31	3	3	–2.40[c]	0		1.03	1.03
32	4	4	–2.08[c]	0		1.29	1.29
33	5	5	–1.85[c]	0		2.05	2.05
34	6	6	–0.57[c]	0		3.25	3.25
35	7	7	–0.19, –0.79[c]	0		3.88	3.88
36	8	8	–2.20[c]	0		1.05	1.05
37	9	9	–2.20[c]	0		1.10	1.10
38	10	10	–2.12[c]	0		1.25	1.25
39	11	11	–2.21[c]	0		1.43	1.43
40	2	10	–1.74[d]	1.34[c]	–2.22	0.79	1.25
41	3	10	–2.16[d]	0.64[c]	–2.26	1.03	1.25
42	4	10	–2.24[d]	–0.12[c]	–2.10	1.29	1.25
43	5	10	–3.14[d]	–2.33[c]	–1.99	2.05	1.25
44	2	9	–2.03[d]	0.90[c]	–2.26	0.79	1.10
45	3	9	–2.54[d]	0.20[c]	–2.3	1.03	1.10
46	4	9	–2.48[d]	–0.55[c]	–2.14	1.29	1.10
47	5	9	–3.46[d]	–2.77[c]	–2.03	2.05	1.10
48	2	8	–2.10[d]	0.76[c]	–2.26	0.79	1.05
49	3	8	–2.54[d]	0.06[c]	–2.3	1.03	1.05
50	4	8	–2.57[d]	–0.70[c]	–2.14	1.29	1.05
51	5	8	–3.51[d]	–2.92[c]	–2.03	2.05	1.05

[a] Taken from [10]. [b] Obtained from the equation $K_{ij} = k_{ij}/k_{ji}$. [c] Obtained from correlation equations. [d] Obtained from $k_{ij} = K_{ij}k_{ji}$.

Table 2. Parameters of Brønsted equations for reaction (1)[a]

Reaction no.	$\log k_{ij} = f(pK_{BH}^+)$		β		Int	r	S_0	n	τ
	Nu_i	Nu_j	Nu	Lg					
1	8–11	2		-1.64 ± 0.25	-0.92 ± 0.31	0.977	0.07	4	0.88
2	8–11	3		-1.15 ± 0.10	-1.22 ± 0.13	0.992	0.03	4	1.21
3	8–11	4		-1.60 ± 0.18	-0.02 ± 0.22	0.989	0.05	4	0.90
4	8–11	5		-1.33 ± 0.20	0.87 ± 0.24	0.979	0.06	4	1.09
5	8–11	6		-0.68 ± 0.16	1.63 ± 0.20	0.946	0.05	4	1.53
6	8–11	7		-0.81 ± 0.11	2.35 ± 0.14	0.981	0.03	4	1.45
7	8	2–7	1.37 ± 0.07		-3.64 ± 0.18	0.994	0.22	6	0.94
8	9	2–7	1.38 ± 0.08		-3.72 ± 0.18	0.994	0.22	6	0.95
9	10	2–7	1.40 ± 0.09		-3.87 ± 0.20	0.993	0.24	6	0.96
10	11	1–7	1.48 ± 0.05		-4.32 ± 0.11	0.997	0.17	7	1.01
11	2–5	11		-1.07 ± 0.03	-0.47 ± 0.04	0.999	0.03	4	1.26

[a] β is slope in nucleophile (Nu) or leaving group (Lg) and Int is intercept.

concentration technique [11] at c_1 ~0.1 and c_2 ~0.0001 (c_1 and c_2 are the initial concentrations of the reagents. In the other cases, c_1/c_2 ~10–100, and the apparent first-order rate constants (k_{app}) were calculated by the Guggenheim method as described in [12]. Fast reactions (nos. 6, 7, 16,17, 22, 23, 28, and 29) were studied by the stopped-flow technique. The second-order rate constants (k_2) were calculated by the least-squares method from the dependence of k_{app} on the analytical concentration of excess reagent (3–6 points) [Eq. (2)].

$$k_{app} = k_{rev} + k_2[Ac\text{–}Nu_i^+, X^-] \text{ or } k_{app} = k_{rev} + k_2[Nu_j]. \quad (2)$$

The k_{rev} values relating to reverse reactions always met the condition $k_{rev} \ll k_2$ and were not considered. The concentrations of acyloxypyridinium salts in the kinetic experiments were no higher than 2×10^{-2} M. As shown in [13], under these considitions the salts are almost completely dissociated into ions (electrolytic dissociation degree $\alpha \geq 0.8$). The plots constructed by Eqs. (2) were linear and beared no signs of ionic dissociation and(or) hydrolysis.

The rate constants of reaction nos. 8, 11, and 30 were determined earlier [9, 14] and refined for the latter two reactions in the present work. The rate constants of reaction nos. 40–51 were obtained from correlation (3).

$$\log k_{ij} = \log K_{ij} + \log k_{ji}. \quad (3)$$

The equilibrium constants of the same reactions, required for the calculations, were determined from correlation (4).

$$\log K_{ij} = (0 \pm 0.06) + (2.92 \pm 0.13)\Delta pK_{BH^+}; \quad (4)$$
$$r\ 0.994, \ S_0\ 0.18, \ n\ 8.$$

Here $\Delta pK_{BH^+} = pK_{BH^+}(Nu_i) - pK_{BH^+}(Nu_j)$.

The equilibrium constants of reaction nos. 6, 7, 16, 17, 22, 23, 28, and 29 fall far beyond the experimental $\log K_{ij}$ range (reaction nos. 2–5, 8–11) and are not given in Table 1 because of the poor reliability of predicted values. The rate constants of identity ($i = j$) reactions (nos. 30 and 35) were determined in CD_3CN by IR spectroscopy using deuterated analog of N-oxides, by the procedure described in [15]. Reaction progress was followed by the absorbance at the hetero-ring skeletal stretching frequency [15] (1614 and 1642 cm^{-1} for reaction nos. 30 and 35, respectively) of the consumed salt. The rate constants of other identity reactions (nos. 31–34 and 36–39), as well as those of reaction nos. 30 and 35 (for the sake of comparison) were estimated from the Brønsted correlations $\log k_{ij} = f(pK_{BH^+})$. Parameters of the corresponding equations are listed in Table 2. As seen from data in Table 1, the rate constants of identity reactions, obtained from the correlations, fairly fit experimental, thus attesting the calculated values.
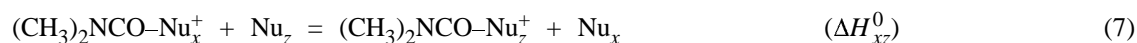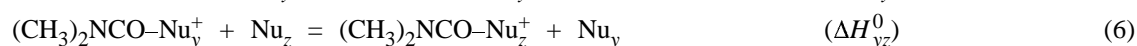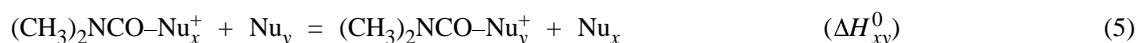
The equilibrium constants $\log K_{ij}$ of reaction nos. 2–5 and 8–11 (Table 1) were determined by UV spectroscopy in acetonitrile at 298 K. The components of these equilibria, [4-(4-dimethylaminostyryl)pyridine N-oxide (Nu_{11}) (λ_{max} 395 nm) and its O-dimethyl-carbamoyl salt (λ_{max} 510 nm)], have long-wave absorption bands which do not overlap with each other and with bands of other reagents and are very strong [ε 36000 and 50300 l mol^{-1} cm^{-1}, respectively]. For this reason, we could measure simulta-

neously two equilibrium concentrations and thus obtain more accurate and reliable constants. It will be emphasized that the reliability of our kinetic and thermodynamic results is confirmed by the fact that the $\log K_{ij}$ values estimated from the correlation $\log K_{ij} = \log k_{ij} - \log k_{ji}$ nicely fit experimental (reaction nos. 3–5 and 9–11; Table 1). In all the other cases, equilibrium constants were difficult to measure for two reasons: close spectral characteristics of the reactants and(or) long equilibration time and, a result, uncontrolled effects of side reactions.

The activation characteristics $\Delta H_{ij}^{\neq}$ and $\Delta S_{ij}^{\neq}$ of the carbamoyl-transfer reaction were determined from k_{ij}

at three temperatures within the range 298–318 K. The following values were obtained: $\Delta H^{\neq}$ 56.7$\pm$3.0 kJ/mol, $\Delta S^{\neq}$ 42.6$\pm$5.0 J mol^{-1} K^{-1} (reaction no. 6); $\Delta H^{\neq}$ 56.4$\pm$4.2 kJ/mol, $\Delta S^{\neq}$ 81$\pm$14 J mol^{-1} K^{-1} (reaction no. 8); and $\Delta H^{\neq}$ 65.6$\pm$3.6 kJ/mol, $\Delta S^{\neq}$ 67$\pm$12 J mol^{-1} K^{-1} (reaction no. 11).

The heats of carbamoyl exchange-reactions between pyridine *N*-oxides in acetonitrile were measured earlier [16] by calorimetric titration (Table 3, reaction nos. 1–3). The other values in Table 3 were calculated from the thermochemical cycle by pair summation [schemes (5)–(7)].

$$(CH_3)_2NCO-Nu_x^+ + Nu_y = (CH_3)_2NCO-Nu_y^+ + Nu_x \qquad (\Delta H_{xy}^0) \qquad (5)$$

$$(CH_3)_2NCO-Nu_y^+ + Nu_z = (CH_3)_2NCO-Nu_z^+ + Nu_y \qquad (\Delta H_{yz}^0) \qquad (6)$$

$$(CH_3)_2NCO-Nu_x^+ + Nu_z = (CH_3)_2NCO-Nu_z^+ + Nu_x \qquad (\Delta H_{xz}^0) \qquad (7)$$

As seen from data in Table 1, in response to structural factors, the equilibrium (1) constants vary 5 orders of magnitude and the rate constants, up to 7 orders of magnitude. Note for comparison that acetyl transfer in similar conditions [9] is much faster (rate constants are 5–7 orders of magnitude higher), but the equilibrium constants almost coincide with those in Table 1 for the same Nu_i–Nu_j pairs, i.e. they are independent of the nature of the acyl fragment in the acyloxypyridinium salt. To explain this fact is our immediate task. The experimental rate constants of reaction (1) correlate well with the difference in the basicities of the nucleophile and leaving group [identity reactions were not included in correlation (8)].

$$\log k_{ij} = (-2.16\pm0.04) + (1.40\pm0.03)\Delta pK_{BH^+}; \quad (8)$$

$$r \ 0.993, \ S_0 \ 0.20, \ n \ 29.$$

A similar linear correlation was obtained for the heat of reaction (1) [Eq. (9)].

Table 3. Heats of dimethylcarbamoyl transfer in CH$_3$CN at 298 K

Reaction no.	Nu$_i$	Nu$_j$	$-\Delta H_{ij}^0$, kJ/mol
1	2	7	30.5$\pm$2.0
2	4	7	29.0$\pm$1.5
3	5	7	22.4$\pm$2.5
4	2	5	8
5	4	5	7
6	2	4	2

$$-\Delta H^0 = (-3.1\pm2.7) + (11.7\pm1.4)\Delta pK_{BH^+}; \quad (9)$$

$$r \ 0.972, \ S_0 \ 3.2, \ n \ 6.$$

The equilibrium rate constants [see Eq. (4)], too, are linearly related to ΔpK_{BH^+}. This all gives us grounds to believe that we deal here with an isothermodynamic reaction series; and this, in turn, suggests [10] identical transition states for all members of the series and a uniform reaction mechanism. The activation parameters of reaction (1) are typical of noncatalytic bimolecular nucleophilic substitution reactions [2, 3]. Such reactions involve stable tetrahedral transition states and feature negative activation enthalpies [17]. Therefore, our $\Delta H^{\neq}$ values argue in favor of a concerted rather than a step mechanism of the reaction in study [1]. At the same time, the low activation enthalpies $\Delta H^{\neq}$ (~50 kJ/mol) and entropies $-\Delta S^{\neq}$ [~60 J mol^{-1} K^{-1}] are indicative of an associative transition state [3, 9] with a low degree of bond fission with the leaving group.

Let us now consider identical reactions (Table 1, reaction nos. 30–39). As seen, their rate varies with structure up to 2 orders of magnitude, which much exceeds the experimental accuracy ($\pm$0.05 log. units) and confidence of the correlation prognosis ($\pm$0.4 log. units). This finding gives us grounds to state that the reaction characteristics of the identity carbamoyl transfer are structure-dependent. The mechanism and transition state of these reactions were analyzed in terms of the More O''Ferrall–Jencks diagram [18]

(Fig. 1), whose application to nucleophilic substitution reactions has been considered in detail in [1, 2]. It has therewith been shown that the position of the transition state on the perpendicular diagonal of the diagram (bond lengthening/contraction) for identity reactions is determined by the β_{Nu}/β_{eq} and(or) β_{Lg}/β_{eq} (Leffler α parameter [19], where β_{Nu}, β_{Lg}, and β_{eq} are the sensitivities in nucleophile, leaving group, and equilibrium, respectively). The quality of our β values (Table 2) can be tested. There are linear β_{Nu}–$pK^j_{BH^+}$ and β_{Lg}–$pK^j_{BH^+}$ correlations [Eqs. (10) and (11), respectively].

$$\beta_{Nu} = (0.28 \pm 0.05)\Delta pK^i_{BH^+} + (1.07 \pm 0.07); \quad (10)$$

$$r\ 0.964,\ S_0\ 0.02,\ n\ 4.$$

$$\beta_{Lg} = (0.25 \pm 0.08)\Delta pK^i_{BH^+} - (1.67 \pm 0.19); \quad (11)$$

$$r\ 0.800,\ S_0\ 0.24,\ n\ 7.$$

In terms of the linear free energy approximation, for the reaction series $\beta_{eq} = \beta_{Nu} - \beta_{Lg}$. From this by Eqs. (10) and (11) we obtain $\beta_{eq} = 2.74 \pm 0.26$[1]. The latter value is nicely consistent with an analogous but independently obtained parameter (2.92 ± 0.13) in Eq. (4). On the perpendicular diagonal of the More O'Ferrall–Jencks diagram (Fig. 1) we placed points for the reactions studied. As seen, the points locate between the $(Lg - Acyl - Nu)^+$ and $(Lg + Acyl^+ + Nu)$ corners, i.e. the identity carbamoyl transfer between pyridine N-oxides occurs by a concerted mechanism as an S_N2 reaction. For numerical characterization of transition-state structures of identity reactions, Kreevoy and Lee [8] proposed the tightness parameter τ [Eq. (12)] which was defined as a sum of the forming and cleaving bond orders.

$$\tau = 2\beta_{eq}/\beta_{Nu} \text{ or } \tau = 2\beta_{Lg}/\beta_{eq} + 2. \quad (12)$$

The τ values, as seen from data in Table 2, vary from 1.53 for the most electron-donor substituent in the reactants to 0.88 for the most electron-acceptor substituent in the reaction series. Consequently, as the basicity of the nucleophile and leaving group increases, the transition state of reaction (1) shifts to the $(Lg - Acyl - Nu)^+$ corner of the diagram (A$_N$ + D$_N$ mechanism), and as the basicity of the nucleophile and leaving group decreases, to the $(Lg + Acyl^+ + Nu)$ corner (D$_N$ + A$_N$ mechanism). Furthemore, taking into account that $\tau = 1 + \beta_{ii}/\beta_{eq} = 1 + 2(apK^i_{BH^+} + bB)/\beta_{eq}$ [20] we have the following equation for characterization of the transition state of identity carbamoyl transfer between pyridine N-oxides [Eq. (13)].

[1] The slopes of dependences (10) and (11) are considered equal to each other.
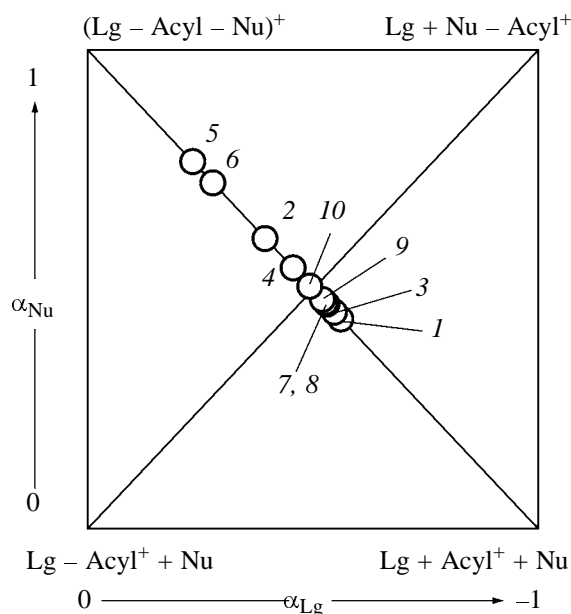
Fig. 1. More O'Ferrall–Jencks diagram for dimethyl-carbamoyl transfer between pyridine N-oxides (for reaction numbering, see Table 2).

$$\tau = 0.19 pK^i_{BH^+} + 0.59. \quad (13)$$

Substituting $\tau = 2$, 1, and 0 into Eq. (13) we obtain $pK^i_{BH^+}$ 7.4, 2.1, and –3.1. These values characterize conditions for realization of the associative (A$_N$ + D$_N$), concerted (A$_N$D$_N$), and dissociative (D$_N$ + A$_N$) mechanisms of the dimethylcarbamoyl transfer. The $pK^i_{BH^+}$ values of 7.4 and –3.1 may belong to hypothetical N-oxides only, and, therefore, reactions (1) all should occur by the forced concerted mechanism (A$_N$–D$_N$). The concerted mechanism (A$_N$D$_N$) could only be diagnosed for the identity transfer between Nu$_{i5}$ (Table 1, reaction no. 33). It is interesting to correlate the transition-state properties of reaction (1), revealed in the present work and reported in the literature. The shift of the transition state along the perpendicular diagonal of the diagram as the $pK^i_{BH^+}$ of nucleophile/leaving group charges by unit is determined as $d = d\tau/dpK^i_{BH^+} = 2a/\beta_{eq}$. For reaction (1) we have d 0.19, which is close to d 0.21, obtained in [20] for acetyl transfer between phenolate anions.

According to [21], identity reactions should be described by a quadratic equation like (14), whose coefficients are determined by Eqs. (10) and (11).

$$\log k_{ii} = a(pK^i_{BH^+})^2 + b pK^i_{BH^+} + c. \quad (14)$$
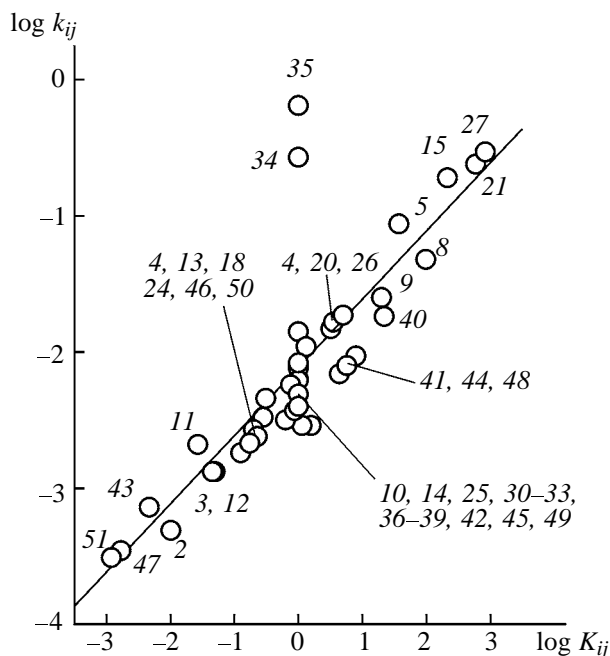
Fig. 2. Rate of dimethylcarbamoyl transfer vs. equilibrium constants (for reaction numbering, see Table 1).

Fig. 3. Rate constants of identity dimethylcarbamoyl transfer vs. nucleophile basicity (for reaction numbering, see Table 1).
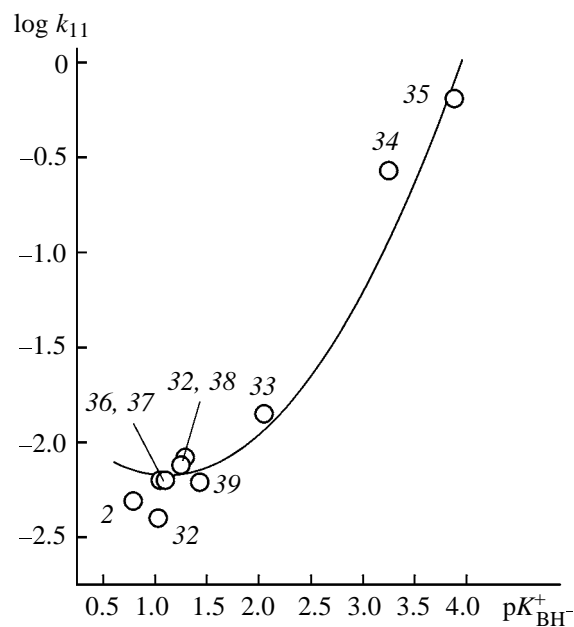
Then in our case we have: $a = (0.28 + 0.25)/2 = 0.27$ and $b = 1.07 - 1.67 = -0.6$. Actually, as seen from Fig. 2, the $\log k_{ii}$ values in Table 1 are readily fitted by a parabola with the above coefficients, but these points can also be fitted by a straight line.

In conclusion let us correlate the rates and equilibria of reaction (1). Treatment of data in Table 1 gave Eq. (15).

$$\log k_{ij} = -(2.12 \pm 0.07) + (0.50 \pm 0.05)\log K_{ij}; \quad (15)$$

$$r\ 0.828,\ S_0\ 0.41,\ n\ 42.$$

As seen from Fig. 3, the points for identity reactions fall out of this dependence, and their variation is far beyond the accuracy limits of the free term in Eq. (15). Consequently, the whole group of reactions cannot formally be described in terms of the Brønsted equation. On the other hand, there are no objective reasons why identical reactions should not be included into correlation (15), the more so that characteristics of such reactions form one of the key prognostic reactivity parameters [3, 4] and a source of information on reaction mechanisms and transition state structures [20, 21]. In an explicit form, $\log k_{ii}$ values are used in the Marcus equation and, in physical sence, should relate to one-stage transformations only. The reaction series studied meets this condition. The corresponding Marcus equation [22] takes form (16).

$$\log k_{ij} = 1/2(\log k_{ii} + \log k_{jj}) + 1/2\log K_{ij}$$
$$- (\log K_{ij})^2/16[\log B - 1/2(\log k_{ii} + \log k_{jj})]. \quad (16)$$

Let us consider Eq. (16) and data in Table 1. According to [22, 23], for symmetrical reactions like (1) in acetonitrile $\log B \approx 12$. Simple calculations show that the maximal "quadratic" deviations in our reaction series at $(\log K_{ij})^2 \sim 12$ and $[16\log B - 8(\log k_{ii} + \log k_{jj})] \sim 200$ should be no larger than 0.06 log. units, which compares with experimental uncertainty and is much smaller than the uncertainty in estimated rate constants. Therefore, we can dwell, like in [22], on the first two terms in Eq. (16). The rate constants of the dimethylcarbamoyl transfer, calculated without inclusion of the quadratic term, well reproduce experimental values [Eq. (17)].

$$\log k_{ij} = (0.05 \pm 0.04) + (1.01 \pm 0.02)\log k_{ij}; \quad (17)$$

$$r\ 0.995,\ S_0\ 0.07,\ n\ 32.$$

Thus, dimethylcarbamoyl transfer between pyridine *N*-oxides is controlled, along with the thermodynamic factor, by the "intrinsic" [4] activation barrier $\lambda = 1/2(\log k_{ii} + \log k_{jj})$. The role and significance of this reactivity parameter in analysis and prognosis of reactions at the carbonyl center are far from understanding [1–3] and may form the subject of further research.

EXPERIMENTAL

All nucleophiles were prepared and purified as described in [9]. Acetonitrile of Acros HPLC grade was kept over molecular sieves (3 Å) before use.

The rate constants of fast reactions were determined on an Applied Photophysics stopped-flow device with a temperature control unit (± 0.1 K). The rates of slow reactions were measured on an SF-26 spectrophotometer. The rates of identical reactions were measured on a Specord IR-75 spectrophotometer.

The equilibrium constants were determined by the optical densities in the electronic absorption spectra of the reagents of reaction (1), measured on an SF-26 spectrophotometer at 298 ± 0.1 K. The constants were calculated with concentration values; activity coefficients were not used in view of the symmetry of scheme (1). The reproducibility of measured equilibrium constants was no worse than $\pm 3\%$, of identity reaction rates, better than $\pm 5\%$, of reaction rates measured by the stopped-flow technique, ± 5–7%, and of the others, ± 0.5–1%.

1-(Dimethylcarbamoyloxy)-4-(4-methoxystyryl)-pyridinium tetraphenylborate. 4-(4-methoxystyryl)-pyridine N-oxide, 1 mmol, and 1 mmol of sodium tetraphenylborate were dissolved in a little acetone ($\sim$4–5 ml). To the resulting yellow solution, a solution of 2 mmol of dimethylcarbamoyl chloride in 1 ml of acetone was slowly added with stirring. The reaction mixture was stirred in the dark for 5 h and then treated with $\sim$15–30 ml of water to a turbid solution. After 40–50 min, the yellow finely crystalline precipitate was filtered off and purified by reprecipitation with diethyl ether from acetonitrile, yield 80%. ^{1}H NMR spectrum (200 MHz, acetone-d_6), δ, ppm (J, Hz): 8.75 d [2H, Py(α), 7.3], 8.13 d [2H, Py(β), 7.3], 7.97 d (2H, CH=CH, 16.4), 7.74 d (2H, Ph, 7.1), 7.39 d (2H, CH=CH, 16.3), 7.34 m [8H, BPh$_4^-$(o-H)], 7.05 d (2H, Ph, 8.7), 6.92 m [8H, BPh$_4^-$(m-H)], 6.76 m [4H, BPh$_4^-$(p-H)], 3.87 s (3H, CH$_3$O), 3.14 s [3H, N(CH$_3$)$_2$], 2.85 s [3H, N(CH$_3$)$_2$]. Found, %: C 79.9; H 6.3; N 4.4. C$_{41}$H$_{39}$BN$_2$O$_3$. Calculated, %: C 79.6; H 6.4; N 4.5.

The other salts were synthesized in a similar way, except for 4-(4-dimethylaminostyryl)-1-(dimethyl-carbamoyl)pyridinium tetraphenylborate that was prepared as described in [14].

All styrene derivatives were isolated from UV light.

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