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Acetyl Exchange between Pyridine *N*-Oxides in Acetonitrile Solutions: An Attempt to Apply the Marcus Equation to Acetyl Transfer

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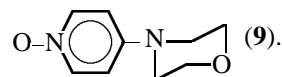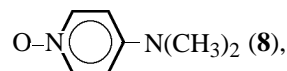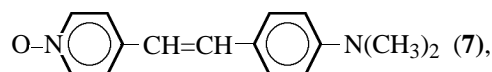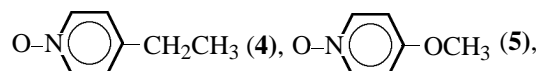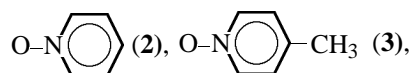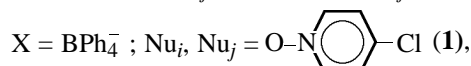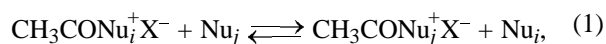**Abstract** — Forty-three (including eight identical) reactions of acetyl transfer from *N*-acetyloxypyridinium salts to pyridine *N*-oxides in acetonitrile solutions were studied. The rate constants k_2 vary in the range 10^7–10^{-1} l mol^{-1} s^{-1}; the equilibrium constants K, in the range 10^7–10^{-7}; the activation enthalpy $\Delta H^{\neq}$, in the range 17–30 kJ mol^{-1}; the activation entropy $-\Delta S^{\neq}$, in the range 60–85 J mol^{-1} K^{-1}; and the heat of reaction $-\Delta H^0$, within ±50 kJ mol^{-1}. All reactions occur in a single stage by the concerted S$_N$2 mechanism with a low degree of bond cleavage in the transition state. The rate and equilibrium of the acetyl exchange are satisfactorily described by the Brønsted equation. The quality of predicting the reactivity is substantially improved by introducing into the correlation equation a second parameter, the rates of identical reactions.

Nucleophilic substitutions at the carbonyl center are actively studied because of particular significance of carbonyl compounds in chemistry and biology [1]. At the same time, the problem of predicting their reactivity is still urgent [2, 3]; many questions remain to be answered, especially concerning determination of the reaction mechanism and choice of the analytical procedure [3, 4]. Examples demonstrating the step (A$_N$ + D$_N$) mechanism of acyl transfer are well known [5]. However, in aprotic solvents acyl transfer occurs most frequently in a single stage as a classical S$_N$2 reaction by the concerted (A$_N$D$_N$) or induced concerted (A$_N$·D$_N$) mechanism [6]. This is the case, e.g., for transfer of the methoxycarbonyl group from acylonium salts to *N*- and *O*-nucleophiles [7, 8].
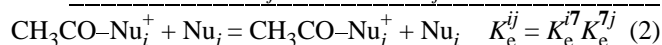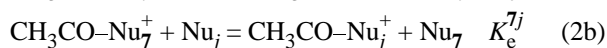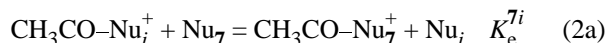
In the majority of studies devoted to nucleophilic substitution at the carbonyl group [3, 5, 6], the reactivity is analyzed in terms of the linear free energy relationship. At the same time, recently in the field of nucleophilic reactivity active efforts have been made to develop and adapt new, physically more substantiated models such as the Marcus equation [9] or the method of crossing parabolas [10], the Shaik–Pross approach [11], cubic reaction diagrams [12], etc., but examples of their practical use for interpreting the experimental data on acyl transfer are few, and for indentical reactions such examples are lacking at all.

The goal of this work was to determine the equilibrium and kinetic parameters of acetyl transfer (1)

between the acetyloxypyridinium salts and pyridine *N*-oxides in acetonitrile solutions, including identical reactions (Nu$_i$ = Nu$_j$), to elucidate the reaction mechanism, to reveal correlations between the reaction rates and equilibria, and to examine the possibility and assess the result of using the "internal" activation barrier as the reactivity parameter.

$$CH_3CONu_i^+X^- + Nu_j \rightleftharpoons CH_3CONu_j^+X^- + Nu_i, \quad (1)$$

$$X = BPh_4^- ; Nu_i, Nu_j = O-N\bigcirc -Cl \ (\mathbf{1}),$$

$$O-N\bigcirc \ (\mathbf{2}), \ O-N\bigcirc -CH_3 \ (\mathbf{3}),$$

$$O-N\bigcirc -CH_2CH_3 \ (\mathbf{4}), \ O-N\bigcirc -OCH_3 \ (\mathbf{5}),$$

$$O-N\bigcirc -CH=CH-\bigcirc \ (\mathbf{6}),$$

$$O-N\bigcirc -CH=CH-\bigcirc -N(CH_3)_2 \ (\mathbf{7}),$$

$$O-N\bigcirc -N(CH_3)_2 \ (\mathbf{8}),$$

$$O-N\bigcirc -N\diagup\diagdown_O \ (\mathbf{9}).$$
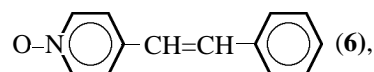
The kinetic and equilibrium characteristics of reaction (1) are listed in the table. The equilibrium constants ($\log K_e^{ij}$) of reaction nos. 1–6 and 9–16 in the table were determined by UV spectroscopy in CH_3CN at 298 K. The reagents in these reactions, 4-(4'-*N,N*-dimethylaminostyryl)pyridine *N*-oxide (Nu_7, λ_{max} 395 nm) and its *O*-acetyl salt (λ_{max} 510 nm), have long-wave absorption bands which do not overlap with each other and with the absorption bands of the other reactants and are very strong (ε 36 000 and 50 000 l mol^{-1} cm^{-1}, respectively). This fact allowed spectrophotometric monitoring of two equilibrium concentrations simultaneously, which considerably improved the accuracy and reliability of determination of the constants. This is particularly important, because, by summing in pairs reactions (2a) and (2b), we were able to calculate the constants of reaction nos. 17–34 in the table for which $i, j \neq$ **7**.

$$CH_3CO–Nu_i^+ + Nu_7 = CH_3CO–Nu_7^+ + Nu_i \quad K_e^{7i} \quad (2a)$$

$$CH_3CO–Nu_7^+ + Nu_j = CH_3CO–Nu_j^+ + Nu_7 \quad K_e^{7j} \quad (2b)$$

$$CH_3CO–Nu_i^+ + Nu_j = CH_3CO–Nu_j^+ + Nu_i \quad K_e^{ij} = K_e^{i7}K_e^{7j} \quad (2)$$

The optical properties of the species participating in these reactions are so similar that reliable determination of the equilibrium concentrations is difficult. For reaction nos. 7 and 8, the equilibrium constant was calculated from the kinetic data: $\log K_e^{ij} = \log k^{ij} - \log k^{ji}$. The constants for reaction nos. 3–6, 9, and 10 can be determined similarly. It can be readily seen that the $\log K_e^{ij}$ values calculated by Eq. (2) agree within the measurement error with the constants determined from the reaction rates.

The rate constants ($\log k^{ij}$) of reaction nos. 4, 6–8, 10, 12, 14, and 16–19 were determined for the first time in this work in CH_3CN solutions by the stopped-flow procedure. The values for reaction nos. 1, 3, 5, 9, 23, 24, 27, and 28 were obtained similarly [13], and those for reaction nos. 25 and 26 were determined previously in [13] and remeasured in this work. The other values for the reactions with $i \neq j$ were calculated as $\log k^{ij} = \log K_e^{ij} + \log k^{ji}$. The constants for the identical ($i = j$) reaction nos. 35–38 and 41–43 were determined by dynamic NMR, and for reaction no. 39 the constant was determined similarly in [14].
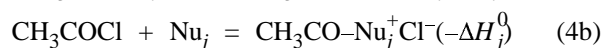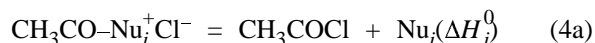
All the experimentally studied reactions (1) follow second-order kinetics. The constants of the non-identical reactions were determined by Eq. (3) under pseudo-first-order conditions at a 10-fold and larger excess of one of the reactants for its 3–6 analytical concentrations.

$$k_{obs} = k_f + k_2[Ac—Nu_i^+X^-], \quad (3)$$

or $k_{obs} = k_f + k_2[Nu_j]$.

The constants k_r were usually close to zero, with the condition $k_f \ll k_2$ always fulfilled. The concentration of the acetyloxypyridinium salts in the kinetic experiments at $i \neq j$ did not exceed 3×10^{-3} M. In the kinetic studies of the identical reactions, under conditions of stoichiometric equivalence, the salt concentrations were an order of magnitude higher. However, even under these conditions, as shown in [15], tetraphenylborates of the alkoxypyridinium salts are practically fully dissociated ($\alpha \geq 0.8$). The plots for Eq. (3) were always linear, i.e., the effects of ionic association or hydrolysis were not manifested. The characteristics of the transition states $\Delta H_{ij}^{\neq}$ and $\Delta S_{ij}^{\neq}$ (see table) were determined from the k^{ij} values at three temperatures in the 30°C range.

The heats of the acetyl transfer between Nu_i and Nu_j (see table) were calculated from the thermochemical cycle (4a) + (4b).

$$CH_3CO–Nu_i^+Cl^- = CH_3COCl + Nu_i(\Delta H_i^0) \quad (4a)$$

$$CH_3COCl + Nu_j = CH_3CO–Nu_j^+Cl^-(-\Delta H_j^0) \quad (4b)$$

$$CH_3CO–Nu_i^+Cl^- + Nu_j = CH_3CO–Nu_j^+Cl^- + Nu_i \quad (-\Delta H_{ij}^0) \quad (4)$$

The required heats of formation of chlorides of acetyloxypyridinium cations from the neutral species [reaction (4b)] in $CHCl_3$ solutions (see table) were determined by calorimetric titration. The values for $j = 1–3$ and 8 were taken from [16], and for $j = 7$ the heat of formation of the acetyloxypyridinium salt was measured similarly in this work.

Nu_j	**1**	**2**	**3**	**7**	**8**
ΔH_j^0, kJ/mol	50±3	60±3	78±3	66±2	109±2

As seen from the table, the constants of equilibrium (1) vary within 14 orders of magnitude, and the rate constants, within 7 orders of magnitude, depending on structural features of the reactants. The equilibrium constants and the heats of reactions show a satisfactory linear correlation (5) (Fig. 1):

$$-\Delta H^0 = (0.00\pm2.53) - (7.48\pm0.69)\log K_e^{ij}; \quad (5)$$

$$n\ 14, \ r\ 0.952, \ S_0\ 0.48.$$

The fact that an isothermodynamic relationship of type (5) is obeyed indicates [2] that the transition states are similar for all the members of the reaction series, i.e., the reaction mechanism is the same. The activation parameters of reaction (1) are typical of spontaneous (noncatalytic) bimolecular nucleophilic

Kinetic ($\log k_{ij}$, $\Delta H_{ij}^{\neq}$, $-\Delta S_{ij}^{\neq}$) and thermodynamic ($\log K_{e}^{ij}$, $-\Delta H_{e}^{ij}$) characteristics of reaction (1)

Run no.	Nu_i	Nu_j	$\log k_{ij}$	$\log K_e^{ij}$	$-\Delta H_e^{ij}$, kJ mol^{-1}	$\Delta H_{ij}^{\neq}$, kJ mol^{-1}	$-\Delta S_{ij}^{\neq}$, J mol^{-1}K^{-1}	$\log (k_{ii} k_{jj})$	pK_i	pK_j
1	1	7	4.31	2.72	16			6.59	0.38	1.43
2	7	1	1.59^a	−2.72	−16			6.59	1.43	0.38
3	2	7	4.14	1.76	6	30	62	6.85	0.79	1.43
4	7	2	2.24	−1.76	−6	17	83	6.85	1.43	0.79
5	3	7	3.46	0.48	−12	29	82	7.15	1.29	1.43
6	7	3	3.00	−0.48	12			7.15	1.43	1.29
7	4	7	3.35	0.30^b				7.16	1.34	1.43
8	7	4	3.05	−0.30^b				7.16	1.43	1.34
9	5	7	3.24	−1.35		17	81	7.61	2.05	1.43
10	7	5	4.13	1.35				7.61	1.43	2.05
11	6	7	3.4^a	0.86				7.02	1.10	1.43
12	7	6	2.54	−0.86				7.02	1.43	1.10
13	8	7	1.3^a	−5.26	−43			8.31	3.88	1.43
14	7	8	6.53	5.26	43			8.31	1.43	3.88
15	9	7	1.61^a	−3.80				8.09	3.25	1.43
16	7	9	5.41	3.80				8.09	1.43	3.25
17	3	9	5.97	4.28^c				7.92	1.29	3.25
18	4	9	6.07	4.1^c				7.93	1.34	3.25
19	5	9	5.81	2.45^c				8.38	2.05	3.25
20	9	3	1.69^a	−4.28^c				7.92	3.25	1.29
21	9	4	1.97^a	−4.1^c				7.93	3.25	1.34
22	9	5	3.36^a	−2.45^c				8.38	3.25	2.05
23	2	8	7.5	7.0^c	49			7.84	0.79	3.88
24	2	5	5.31	3.1^c				7.14	0.79	2.05
25	3	5	4.46	1.83^c				7.44	1.29	2.05
26	4	5	4.89	1.65^c		25.5	66.2	7.45	1.34	2.05
27	1	3	4.40	2.2^c	28			6.42	0.38	1.29
28	2	3	4.13	1.3^c	18			6.68	0.79	1.29
29	8	2	0.5^a	−7.0^c	−49			7.84	3.88	0.79
30	5	2	2.2^a	−3.1^c				7.14	2.05	0.79
31	5	3	2.63^a	−1.83^c				7.44	2.05	1.29
32	5	4	3.24	−1.65^c				7.45	2.05	1.34
33	3	1	2.2^a	−2.2^c	−28			6.42	1.29	0.38
34	3	2	2.8^a	−1.3^c	−18			6.68	1.29	0.79
35	1	1	2.93	0					0.38	0.38
36	2	2	3.19	0					0.79	0.79
37	3	3	3.49	0					1.29	1.29
38	4	4	3.5	0					1.34	1.34
39	5	5	3.95	0					2.05	2.05
40	6	6	3.36^d	0					1.10	1.10
41	7	7	3.66	0					1.43	1.43
42	8	8	4.65	0		22	82		3.88	3.88
43	9	9	4.43	0					3.25	3.25

^{a} Calculated from $k^{ij} = K^{ij} k^{ji}$. ^{b} Determined from $K^{ij} = k^{ij}/k^{ji}$. ^{c} Determined by summation of two reactions ($K^{ij} = K^{i7} K^{7j}$). ^{d} Calculated by Eq. (9).
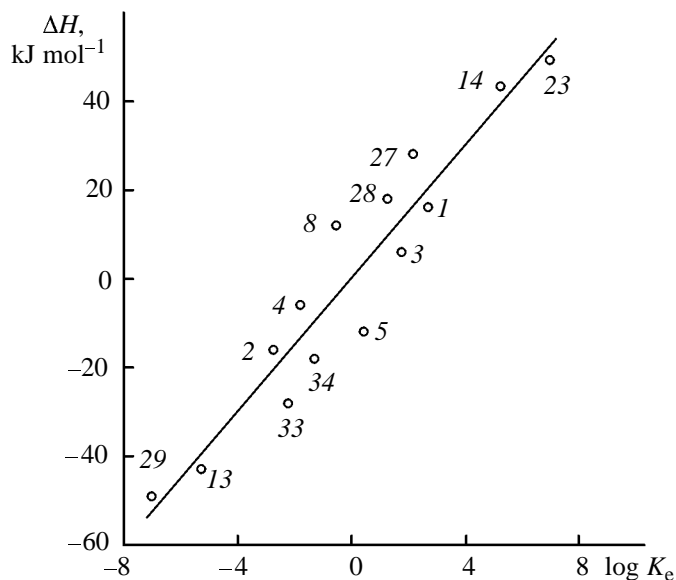
Fig. 1. Correlation between the thermal effect of reaction (1) and the equilibrium constant. The reaction numbering is the same as in the table; the same for Figs. 2–5.

Fig. 2. Correlation between the rate of the acetyl exchange and basicity of the (a) nucleophile and (b) leaving group.

substitutions [17]. The low activation enthalpies $\Delta H^{\neq}$ (17–30 kJ mol^{-1}) and entropies $\Delta S^{\neq}$ (from –60 to –82 J mol^{-1} K^{-1}) suggest an associative transition state with a low extent of cleavage of the bond with the leaving group [11]. As shown in [18], nucleophilic substitutions proceeding via stable tetrahedral intermediates are usually characterized by negative activation enthalpies. Therefore, our values of $\Delta H^{\neq}$ can be considered as evidence in favor of a concerted, rather than a multistage, reaction mechanism.

Recently there has been a considerable progress in identification of concerted mechanisms of organic reactions [19]. Figure 2 shows the correlations between the rate constants and basicities of the nucleophile and leaving group for the reactions in which Nu$_7$ is either a nucleophile or a leaving group. The corresponding correlation equations are as follows:

$$\log k^{7j} = (1.15\pm0.08) + (1.37\pm0.04)pK^{j}_{BH^+}; \quad (6)$$

$$n\ 8,\ r\ 0.997,\ S_0\ 0.13.$$

$$\log k^{i7} = (4.64\pm0.15) - (0.87\pm0.07)pK^{i}_{BH^+}; \quad (7)$$

$$n\ 8,\ r\ 0.980,\ S_0\ 0.23.$$

As seen, in both cases there are good linear correlations. It should be noted that for 4-(4'-*N,N*-dimethylaminostyryl)pyridine *N*-oxide (Nu$_7$) it is impossible to evaluate experimentally the basicity of the *N*-oxide group, since the nitrogen atom of the dimethylamino
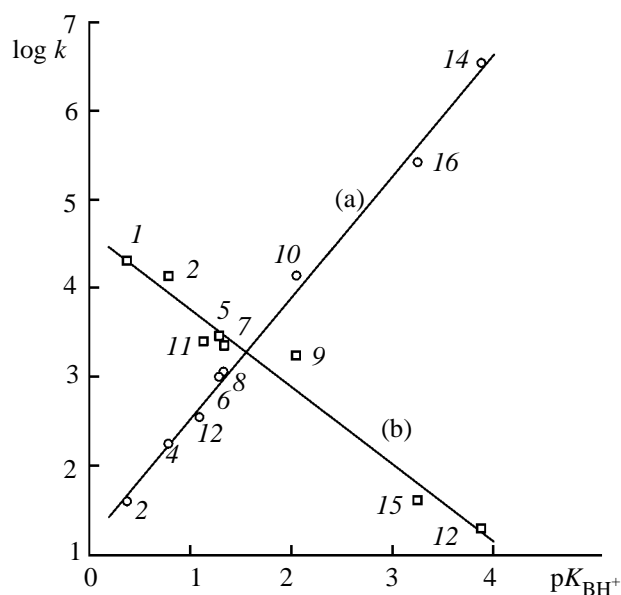
group is protonated first, $pK_{BH^+}[N(CH_3)_2] = 4.30$ [20]. However, the basicity can be estimated from the correlation between $\log K_e$ and pK_{BH^+}.

$$\log K_e = (3.92\pm0.14) - (2.74\pm0.06)pK_{BH^+}; \quad (8)$$

$$r\ 0.998,\ n\ 7,\ S_0\ 0.21.$$

Then for Nu$_7$ $\log K_e = 0$ and $pK_{BH^+}(N{\to}O)$ is, correspondingly, 1.43. According to [6, 19], the lack of a break in the point for the identical reaction (in the vicinity of pK_{BH^+} 1.43 in Fig. 2) is a necessary condition and evidence of the concerted mechanism.

The coefficients of Eqs. (6) and (7) ($\rho_{Nu} = 1.37$ and $-\rho_{log} = 0.87$) are higher than those for the similar reaction series studied previously [17, 21], i.e., exchange of the CH$_3$CO group between pyridine *N*-oxides is, apparently, one of the most structure-sensitive acetyl transfer reactions. Comparison of the coefficients of Eqs. (6) and (7) shows that the nucleophilic substitution at the carbonyl group is more sensitive to structural changes in the nucleophile as compared to the leaving group. This result can be checked.

Figure 3 illustrates the dependence of the rate on the basicity of the nucleophile and/or leaving group for a set of identical reaction; the corresponding equation is the first example of such correlations for acyl transfer:

$$\log k^{ii} = (2.83\pm0.05) + (0.49\pm0.02)pK^{i}_{BH^+}; \quad (9)$$

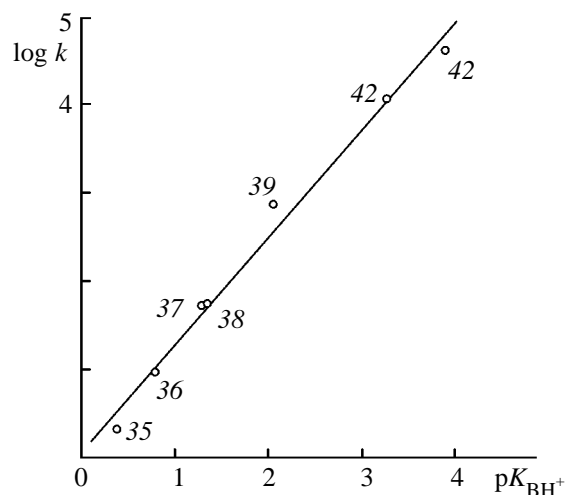$$n\ 7,\ r\ 0.994,\ S_0\ 0.08.$$

Fig. 3. Correlation between the rate constants of the identical acetyl transfer reactions and the basicity of the nucleophile.

Using Eq. (9), we can estimate, in particular, the rate constant of the identical reaction for $i, j = $ **6**, $\log k^{66} = 3.36$, which was difficult to determine experimentally because of large errors in analysis of the

dynamic NMR spectra. However, another fact is very important. It can be readily shown [22] that within a reaction series the coefficients of the correlation equations are related as follows:

$$\rho_{ij} = 1/2\rho_{ii} + 1/2\rho_e, \qquad (10)$$

$$\rho_{ji} = 1/2\rho_{ii} - 1/2\rho_e, \qquad (11)$$

$$\rho_{ij} + \rho_{ji} = \rho_{ii}. \qquad (12)$$

Summation of the coefficients in Eqs. (6) and (7) $(1.37 - 0.87 = 0.50)$ leads to a result that excellently agrees with a slope of 0.49 in the identical series; this fact proves the reliability of the coefficients in Eqs. (6) and (7).

Figure 4 shows the correlation between the rate and equilibrium [Eq. (1)] constants, which is described by the equation

$$\log k_{ij} = (3.62 \pm 0.07) + (0.499 \pm 0.025)\log K_4^{ij}; \quad (13)$$

$$n\ 43,\ r\ 0.950,\ S_0\ 0.47.$$

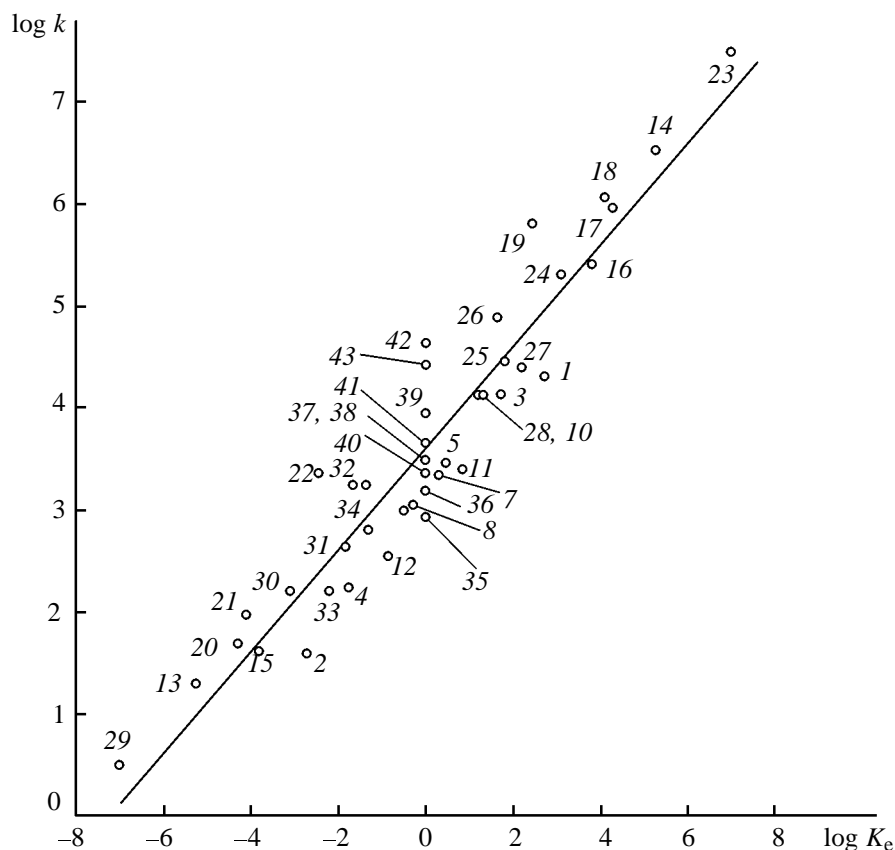This equation satisfactorily reproduces the correlation between the kinetic and equilibrium characteris-

Fig. 4. Correlation between the rates and equilibrium constants of acetyl exchange.
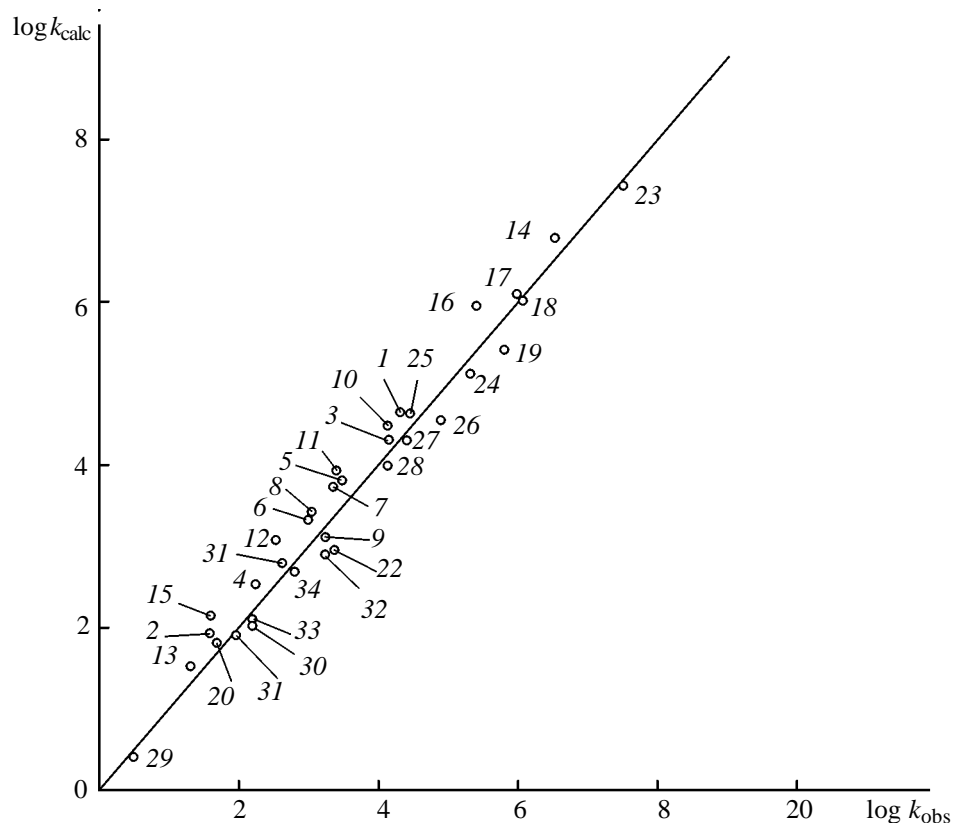
Fig. 5. Experimental ($\log k_{obs}$) and calculated by Eq. (13) ($\log k_{calc}$) rate constants of reaction (1).

tics of reactions (1); Fig. 4 reveals no curvature of the Brønsted plot. However, identical reactions cannot be described in the same coordinates; their rate is variable [Eq. (9)], whereas the position of the "equilibrium" is the same, which determines the location of the corresponding points in Fig. 4.

At the same time, characteristics of identical reactions are key parameters in predicting the reactivity [4, 11]. Therefore, let us analyze our results with the Marcus equation [9]. This equation, when written for the rates and equilibria, has the following form [22]:

$$\log k_{ij} = 1/2(\log k_{ii} + \log k_{jj}) + 1/2\log K_{ij}$$

$$- (\log K_{ij})2/\{16[\log B - 1/2(\log k_{ii} + \log k_{jj})]\}. \quad (14)$$

Here $\log B$ corresponds to the working term in the common notation. In solutions this term is neglected since, on the one hand, it is apparently small [23] and, on the other hand, there are no verified procedures for its determination [24]. The last term in Eq. (14) is responsible for deviations from linearity in the Brønsted coordinates, observed in some cases. Estimation of the maximal values of this term from the available data (see table) shows that at $(\log K_{ij})^2 < 25$ and $s(\log k_{ii} + \log k_{jj}) \approx 50$ the "quadratic" deviations at

the "edges" of reaction series (13) may reach 0.5 log unit, which is comparable with the errors in experimental determination of the rates of fast reactions and with the consequences of neglecting $\log B$ [23]. Therefore, it is appropriate to restrict the consideration to the first two terms in Eq. (14), as it was done, e.g., for methyl transfer reactions [22, 25, 26]. By a two-parameter treatment of the data in the table, we obtained a correlation equation with the coefficients virtually identical to those in Eq. (14):

$$\log k^{ij} = (0.51 \pm 0.02)(\log k^{ii} + \log k^{jj})$$

$$+ (0.50 \pm 0.03)\log K_e^{ij}; \quad (15)$$

$$n \; 34, \; r \; 0.987, \; S_0 \; 0.21.$$

The rate constants calculated by Eq. (14) well reproduce (Fig. 5) the experimental values.

$$\log k_{obs}^{ij} = (1.02 \pm 0.02)\log k_{calc}^{ij}; \; n \; 34, \; r \; 0.983, \; S_0 \; 0.29. \quad (16)$$

As seen, the use of the thermoneutral activation barrier not only considerably improves the quality of the correlation treatment but also offers a way of simple prediction by Eq. (14) of the rates of reactions that have not been studied experimentally. Compari-

son of Eqs. (13) and (15) shows that the acetyl transfer in reaction (1) is controlled not only by the thermodynamic factor as it could be concluded from Eq. (13) considered separately, but also from the "internal" activation barrier $\lambda = 1/2(\log k^{ii} + \log k^{jj})$. This reactivity parameter was introduced for the first time by Marcus in analysis of the simplest one-stage reactions [9], and its role and significance in nucleophilic substitution are only outlined [22, 26], especially for reactions at the carbonyl center [27, 28], and require further study.

EXPERIMENTAL

All the salts were prepared and purified as described in [13, 29]. 4-(4'-*N,N*-Dimethylaminostyryl)-pyridine *N*-oxide was prepared by the procedure given in [30]. The nucleophiles were distilled or recrystallized before use. Acetonitrile of anh grade (Aldrich) was stored over 3 Å molecular sieves before use.

The reaction rate constants were determined with an Applied Photophysics stopped-flow apparatus equipped with a temperature-controlled unit (± 0.1 K). The observed pseudo-first-order rate constants were calculated by the Guggenheim procedure from the time dependence of the UV absorption as described in [8, 31]. The rates of the symmetrical reactions were determined from the dynamic NMR spectra, which were taken on a Gemini-200 spectrometer (200 MHz). As indicator signals we used those of the α-protons of the pyridinium ring in the nucleophile and its acetyl salt; their shifts (δ, ppm) for the Nu_i–AcNu_i^+ pairs were as follows: $i = \mathbf{1}$ (8.05, 8.75), $i = \mathbf{2}$ (8.02, 8.66), $i = \mathbf{3}$ (7.98, 8.58), $i = \mathbf{4}$ (7.97, 8.56), $i = \mathbf{7}$ (7.90, 8.05), $i = \mathbf{8}$ (7.84, 8.00), and $i = \mathbf{9}$ (7.89, 7.98).

The electronic absorption spectra of the participants of reaction (1) were taken on a Specord UV–Vis spectrometer; the optical densities were measured with an SF-26 spectrophotometer in a temperature-controlled cell at 298 ± 0.1 K. When calculating the constants, we used the concentration quantities; the activity coefficients were not introduced because of the symmetry of reaction (1). The reproducibility of the measured equilibrium constants was no worse than $\pm 3\%$; that of the rates of the identical reactions, better than $\pm 15\%$; and that of the rates determined by the stopped-flow procedure, ± 5–7% for fast ($\log k_2 > 5$) and ± 3–5% for the other processes.

Calorimetric measurements were performed at 298 K; solutions of CH_3COCl in chloroform ($c \sim 5 \times 10^{-3}$ M) were titrated with solutions of *N*-oxides of similar concentration.

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