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Acylation of Piperidine and Morpholine with Phenyl Benzoates in the Mixtures Water–2-Propanol and Water–Dioxane

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Abstract—Kinetics of acylation of piperidine and morpholine with 4-nitro- and 2,6-dinitrophenyl benzoates was studied in binary systems water–2-propanol and water–dioxane. Structural and energy characteristics of solvate complexes of morpholine and piperidine with the components of the mixed solvents were calculated. Kinetic regularities of acylation are considered from the viewpoint of specific solvation of amines.

Keywords: piperidine, morpholine, esters, acylation, specific solvation, solvate complexes

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The interest to reactivity of heterocyclic amines in the reactions of N-acylation is due to their wide application in the synthesis of practically valuable compounds, first of all – biologically active compounds, like drugs, inhibitors of enzymes, pesticides. It is known that piperidine and morpholine derivatives are low-toxic analgesics and anesthetics, the piperidine ring is a constituent of a large number of natural and synthetic alkaloids, morpholine acts as a building block in the synthesis of antibiotics and anticancer drugs [1–3].

Kinetic studies on model reactions aiming at elucidation of the influence of the reagents structure and effects of medium on the rate of the process are important for optimization of the synthesis conditions of the morpholine and piperidine acyl derivatives. Nowadays, as one of such models, the reaction of amines of different types with esters in solutions or microemulsions is considered [4–7]. In the industrial synthesis of amides, water–organic media are widely used [8, 9], which allows to substantially vary the rate of the target reaction and the simultaneously occurring hydrolysis of the acylation agent [7]. However, no systematic studies of the influence of the composition of water-organic media on the reactions of amide formation with participation of heterocyclic amines were performed so far.

The present work consists in the experimental and theoretical studies of the reactivity of piperidine and morpholine in the reaction with 4-nitrophenyl benzoate **I** and 2,6-dinitrophenyl benzoate **II** in binary mixtures water–2-propanol and water–dioxane.

The processes occurring in the system are represented by Eqs. (1) and (2) by the example of the piperidine reaction with compound **I**. Along with aminolysis [Eq. (1)], in water-organic medium the hydrolysis of the ester [Eq. (2)] can proceed.

$$\mathrm{NH(CH_2)_5 + PhCOOC_6H_4NO_2 \xrightarrow{k} PhCON(CH_2)_5 + HOC_6H_4NO_2,} \quad (1)$$

$$\mathrm{PhCOOC_6H_4NO_2 + H_2O \xrightarrow{k_{hydr}} PhCOOH + HOC_6H_4NO_2.} \quad (2)$$

The rate of concentration variation of the acylation agent under the condition $c_0 >> c_{\mathrm{eff}}$ is determined by Eq. (3).

$$-\frac{dc_{\mathrm{eff}}}{d\tau} = (k_{\mathrm{hydr}} + kc_0)c_{\mathrm{eff}}. \quad (3)$$

Here, c_{eff} denotes the concentration of ester at time τ, c_0 is the initial concentration of amine, k and k_{hydr} denote the rate constants of reactions (1) and (2).

Our previous studies have shown that in water-organic media at pH = 9–10 the rates of reactions (1) and (2) are comparable, but at pH < 9 the rate of hydrolysis of the esters decreases and becomes negligible with respect to the rate of acylation [7, 10].

To create the required pH value, a predetermined amount of HCl was added to the solution of amine. The concentration of the nonprotonated amine (c_0) was determined as the difference between its initial concentration in the solution and the concentration of HCI. The observed rate constant k_{obs} taking into account k_{hydr} is defined by Eq. (4).

$$k_{\text{obs}} = k_{\text{hydr}} + kc_0. \tag{4}$$

In the absence of hydrolysis ($k_{\text{hydr}} \approx 0$) the value of k can be calculated by Eq. (5).

$$k = k_{\text{obs}}/c_0. \tag{5}$$

If $k_{\text{hydr}} << kc_0$, the rate constant k, calculated by Eq. (5), should be constant within experimental error with varying c_0. Substantial deviations in the values of k determined at different c_0 are indicative of a considerable contribution of k_{hydr} into the observed rate constant k_{obs}. In this case, k can be determined by Eq. (4) describing the dependence of k_{obs} on c_0.

The obtained kinetic data are presented in Tables 1, 2. They show that at 298 K and at the molar fraction of water in the mixture $x_1 < 0.77$ the contribution of hydrolysis into the rates of the reactions under consideration is small, so the rate constant for reaction (1) was calculated as the arithmetic mean of k values determined from Eq. (5). With the increase of temperature and concentration of water in the solution the contribution of hydrolysis is increased resulting in substantial variations of k. In this case, the value of k was calculated by Eq. (4) using the root-mean-square method (Tables 1, 2).

The adequacy of the two methods of calculation of k values is proved by the data of Table 1, in which k values for the reaction of piperidine with ester **I** in aqueous 2-propanol ($x_1 = 0.83$, 308 K) calculated by Eq. (5) are given. The mean value of $k = 1.1\pm 0.1$ L mol^{-1} s^{-1}. The value of k calculated by Eq. (4) using the same kinetic data is 1.12 ± 0.06 L mol^{-1} s^{-1} with the coefficient of correlation 0.994. A similar approach was realized for investigation of the kinetics of the reaction of morpholine with compound **II** (Table 2).

The data of Tables 1, 2 show that with the increase of water content in 2-propanol the rate constants of acylation k increase, the dependences of k and ln k on x_1 being nonlinear (Tables 1, 2; Fig. 1). The dependence of ln k on the Kirkwood function is also nonlinear (Fig. 2), which is indicative of an important role of specific solvation of amines and transition states of the reaction of acylation. The solvation of the acylation reagents in the reaction of the acyl group transfer, according to the available data [7, 10–13], plays a subordinate role.

Table 3 presents the results of the kinetic study of the reactions of piperidine and morpholine with compounds **I** and **II** in the system water (40 wt %)–dioxane. The discrepancies between the rate constants k determined at various initial concentrations of amines in aqueous dioxane are small, allowing to neglect the contribution of the ester hydrolysis to k_{obs}. For equal amounts of water in the system the values of k for all studied reactions in the mixture water–dioxane are considerably larger than the k values for the same reactions in aqueous 2-propanol (Tables 1–3). The accelerating effect of aqueous dioxane as compared to aqueous 2-propanol on the rate constants of N-acylation was observed also in other reactions, for example, in the reactions of ammonia, aliphatic amines and α-amino acids with esters and sulfonyl chlorides [7, 10–13].

In Table 4, the activation parameters of the studied reactions are presented as determined from the temperature dependence of the rate constants. The energy of activation is substantially decreased with increase of water content in 2-propanol. Thus, for variation of x_1 from 0.69 to 0.87 the value of E_a for the reaction of compound **II** with morpholine is decreased by 18 kJ/mol, and for the reaction of compound **I** with piperidine, by 24 kJ/mol, and the value of $\Delta S^{\neq}$ becomes more negative. The value of E_a for the reaction of compound **II** with morpholine in the mixture water (40 wt %)–dioxane is lower, and the $\Delta S^{\neq}$ value is more negative than for the same reaction in aqueous 2-propanol having the same water fraction, which is consistent with a higher value of k in aqueous dioxane.

For the reactions proceeding in aqueous 2-propanol, the compensation effect is observed, which is characterized by Eq. (6) (**I** + piperidine) and Eq. (7) (**II** + morpholine):

$$\Delta H^{\neq} = (94220\pm1770) - (393\pm11)\Delta S^{\neq},\ n = 6,\ r = 0.999, \tag{6}$$

$$\Delta H^{\neq} = (89336\pm2791) - (372\pm18)\Delta S^{\neq},\ n = 5,\ r = 0.997. \tag{7}$$

The isokinetic temperature (T_{iso}) for the two reactions is close to the solvent boiling temperature or exceeds it. These values are consistent with the values of T_{iso} for the reactions of diethylamine and dibutylamine with compound **I** in aqueous 2-propanol [7]. The value of T_{iso} is in the range typical for the reactions of nucleophilic substitution at the carbonyl

Table 1. Rate constants k_{obs} and k for the reaction of piperidine with 4-nitrophenyl benzoate **I** in the system water–2-propanol[a]

T, K	$c_0 \times 10^2$, mol/L	$k_{obs} \times 10^2$, s^{-1}	k, L mol^{-1} s^{-1}
30 wt % H_2O (x_1 = 0.59)			
298	2.45	0.396±0.001	0.161±0.001
308	2.45	0.647±0.003	0.264±0.002
313	1.22	0.406±0.002	0.333±0.002
	2.45	0.820±0.002	0.335±0.001
	1.22	0.406±0.004	0.332±0.003
	0.815	0.270±0.003	0.331±0.003
35 wt % H_2O (x_1 = 0.64)			
293	2.45	0.405±0.003	0.165±0.002
298	2.45	0.493±0.004	0.201±0.002
	1.22	0.241±0.006	0.198±0.004
303	2.45	0.654±0.005	0.267±0.003
308	2.45	0.796±0.004	0.325±0.002
	1.22	0.388±0.001	0.318±0.001
40 wt % H_2O (x_1 = 0.69)			
293	1.22	0.265±0.001	0.217±0.001
298	1.22	0.326±0.005	0.267±0.004
303	1.22	0.386±0.002	0.316±0.002
308	1.22	0.473±0.003	0.388±0.003
50 wt % H_2O (x_1 = 0.77)			
298	0.294	0.141±0.004	0.40±0.03
	0.306	0.170±0.003	
	0.588	0.261±0.002	
	0.611	0.305±0.001	
	1.22	0.489±0.005	
	1.53	0.67±0.01	
303	0.294	0.189±0.004	0.46±0.02
	0.588	0.400±0.004	
	0.611	0.467±0.004	
	1.18	0.71±0.01	
	1.22	0.719±0.003	
	2.44	1.23±0.01	
308	0.294	0.130±0.004	0.53±0.02
	0.306	0.135±0.005	
	0.588	0.335±0.004	
50 wt % H_2O (x_1 = 0.77)			
308	1.22	0.737±0.003	0.53±0.02
	1.53	0.787±0.005	
	2.45	1.28±0.06	
313	0.385	0.094±0.004	0.64±0.06
	0.538	0.195±0.003	
	0.611	0.330±0.002	
	0.770	0.360±0.001	
	1.22	0.644±0.001	
60 wt % H_2O (x_1 = 0.83)			
298	0.441	0.431±0.003	0.977±0.07
308	0.221	0.245±0.009	1.11±0.04
	0.441	0.478±0.002	1.08±0.01
	0.662	0.685±0.002	1.03±0.01
	0.883	0.990±0.005	1.12±0.01
	1.10	1.30±0.01	1.18±0.01
	1.32	1.41±0.01	1.07±0.01
313	0.221	0.140±0.002	1.56±0.06
	0.441	0.267±0.002	
	0.662	0.769±0.002	
	0.883	1.03±0.03	
70 wt % H_2O (x_1 = 0.89)			
298	0.175	0.305±0.004	1.87±0.09
	0.262	0.405±0.004	
	0.350	0.420±0.004	
	0.430	0.598±0.002	
	0.524	0.866±0.002	
	0.612	1.06±0.04	
	0.699	1.30±0.05	
	0.787	1.34±0.05	
308	0.175	0.062±0.002	2.16±0.08
	0.350	0.391±0.002	
	0.437	0.635±0.005	
	0.612	0.933±0.005	
	0.699	1.21±0.01	

[a] Hereinafter, x_1 is the molar fraction of water.

Table 2. Rate constants k_{obs} and k for the reaction of morpholine with 2,4-dinitrophenyl benzoate **II** in the system water–2-propanol

T, K	$c_0 \times 10^2$, mol/L	$k_{\text{obs}} \times 10^2$, s^{-1}	k, L mol^{-1} s^{-1}	T, K	$c_0 \times 10^2$, mol/L	$k_{\text{obs}} \times 10^2$, s^{-1}	k, L mol^{-1} s^{-1}
$x_1 = 0.69$							
298	1.95	2.54±0.01	0.128±0.001	308	1.95	4.70±0.01	0.241±0.001
298[a]	10.7	5.94±0.01	0.055±0.001	298[b]	0.153	2.35±0.01	1.54±0.01
$x_1 = 0.77$							
298	0.244	0.344±0.001	0.135±0.002	308	0.244	0.564±0.001	0.27±0.02
	0.488	0.679±0.001			0.488	1.07±0.01	
	0.976	1.31±0.01			0.976	2.51±0.01	
318	0.244	0.843±0.002		318	0.976	3.72±0.01	0.363±0.001
	0.488	1.80±0.01					
$x_1 = 0.83$							
298	0.0975	0.227±0.003	0.192±0.003	308	0.195	0.729±0.006	0.291±0.009
	0.244	0.489±0.002			0.244	0.804±0.003	
	0.488	0.962±0.003			0.290	0.941±0.004	
303	0.0975	0.216±0.002	0.24±0.01		0.341	1.07±0.001	
	0.244	0.615±0.003			0.390	1.23±0.001	
	0.488	1.15±0.004			0.439	1.27±0.002	
308	0.0975	0.411±0.03			0.488	1.56±0.002	
$x_1 = 0.89$							
298	0.290	1.04±0.01	0.72±0.04	303	0.680	5.20±0.05	0.89±0.03
	0.390	1.61±0.02		308	0.195	1.00±0.02	0.98±0.05
	0.488	2.27±0.01			0.290	1.70±0.01	
	0.585	3.16±0.04			0.390	2.90±0.02	
303	0.195	0.956±0.001	0.89±0.03		0.487	3.60±0.01	
	0.290	1.68±0.01			0.585	5.12±0.04	
	0.390	2.39±0.01			0.680	5.51±0.04	
	0.580	4.29±0.03					
$x_1 = 0.93$							
298	0.420	7.30±0.06	2.04±0.07	308	0.350	8.20±0.06	2.45±0.09
	0.560	9.38±0.04			0.420	9.40±0.08	
	0.840	15.2±0.6			0.840	19.2±0.1	
	0.980	17.6±0.2			1.40	34.3±0.4	
	1.40	27.2±0.2					

[a] Rate constants for the reaction of morpholine with 4-nitrophenyl benzoate **I**. [b] Rate constants for the reaction of piperidine with 2,4-dinitrophenyl benzoate **II**.

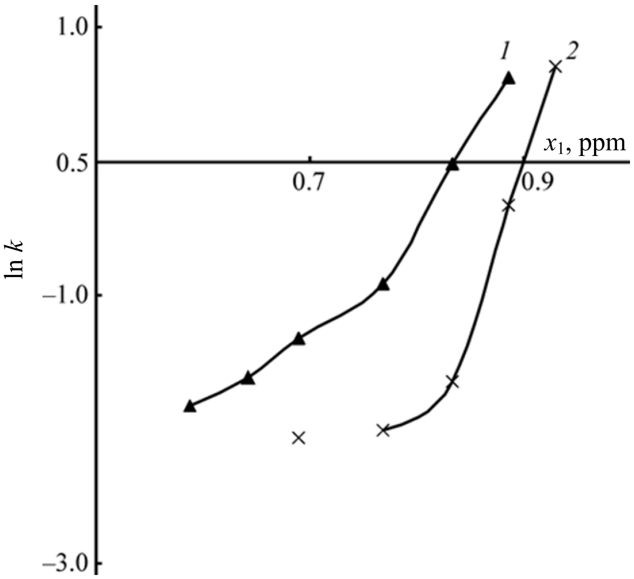


Fig. 1. Dependence of ln k for the reactions of (*1*) piperidine with ester **I** and (*2*) morpholine with ester **II** (*2*) on the molar fraction of water x_1 in the system water–2-propanol at 298 K.

Table 3. Rate constants k_{obs} and k for the reactions of piperidine and morpholine with 4-nitrophenyl benzoate **I** and 2,4-dinitrophenyl benzoate **II** in the system water–dioxane[a]

T, K	c_0, mol/L	$k_{obs} \times 10^3$, s^{-1}	k, L mol^{-1} s^{-1}
	Morpholine + **I**		
298	0.0113	1.06±0.07	0.0958±0.0006
	0.0111	1.05±0.07	0.0955±0.0006
	Piperidine + **I**		
298	0.00367	9.42±0.06	2.56±0.02
	0.00507	13.6±0.3	2.68±0.06
	0.00155	3.84±0.01	2.61±0.05
	Morpholine + **II**		
298	0.0145	3.26±0.02	0.225±0.001
	0.00868	1.65±0.01	0.229±0.001
	0.00483	1.99±0.01	0.227±0.002
303	0.0145	4.12±0.08	0.285±0.005
	0.0145	4.08±0.05	0.283±0.003
308	0.00724	2.67±0.05	0.369±0.0007
	0.00724	2.60±0.02	0.359±0.003
	Piperidine + **II**		
298	0.00309	42.3±0.2	13.7±0.6
	0.00155	19.5±0.2	12.6±0.1
	0.00184	23.7±0.1	12.9±0.5

[a] $x_1 = 0.77$, c_0 is the initial concentration of amine.

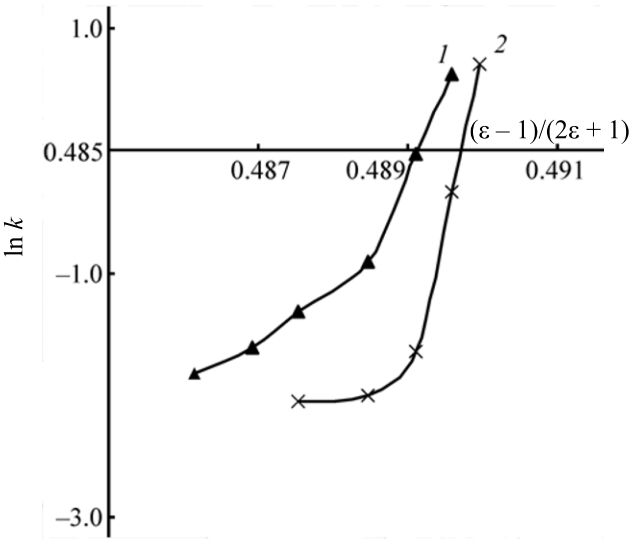


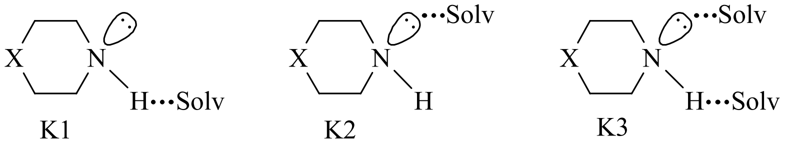
Fig. 2. Dependence of ln k for the reactions of (*1*) piperidine with ester **I** and (*2*) morpholine with ester **II** on the Kirkwood function for the solvent water–2-propanol at 298 K.

Table 4. Energies, enthalpies, and entropies of activation for the reactions of piperidine and morpholine with esters **I** and **II** at 298 K[a]

x_1	E_a, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
	Piperidine + **I**, water–2-propanol		
0.59	38	36	142
0.64	35	33	150
0.69	29	27	168
0.77	24	22	180
0.83	18	15	193
0.87	11	9	211
	Morpholine + **II**, water–2-propanol		
0.69	48	45	109
0.77	43	41	125
0.83	32	30	159
0.87	24	27	175
0.93	14	12	200
	Morpholine + **II**, water–dioxane		
0.69	36	33	144

[a] Error in determination of E_a and $\Delta H^{\neq}$ does not exceed 4 kJ/mol, of $\Delta S^{\neq}$ – 10 J mol^{-1} K^{-1}.

Scheme 1.



X = CH_2, O; Solv = H_2O, *i*-PrOH, dioxane.

group and suggest the similarity of the mechanisms of the studied reactions [14].

The increase in the rate constants and decrease in the energy and entropy of activation with increase in water content in the mixture can be due to the rearrangement of the structure of the binary solvent and the corresponding variations in the structure of the solvate shells of the amine molecules and transition states of the reactions. For better understanding of the role of specific solvation of amines in the studied reactions we performed quantum-chemical simulation of molecular complexes of three types of the studied amines with one and two molecules of the components of binary muxtures (Scheme 1).

In complexes of the type K1: piperidine–H_2O (**Ia**), piperidine–dioxane (**IIa**), piperidine–*i*-PrOH (**IIIa**), morpholine–H_2O (**IVa**), morpholine–dioxane (**Va**) and morpholine–*i*-PrOH (**VIa**) the H-bond is formed by the proton of the NH group, and the molecule of the solvent acts as an H-acceptor. In complexes of the type

Table 5. Quantum-chemical parameters of solvate complexes K1–K3

Comp. no.	$-\Delta E_c$, kJ/mol	E_{HOMO}, eV	$Cp_z^2(N)$	$\varphi p_z(N)$	$r_{N–H}$, Å	$r_{N\cdots H}$, Å	$r_{O\cdots H}$, Å
K1							
Ia	13.1	–9.28	0.863	1.683	1.001	–	2.258
IIa	13.1	–9.39	0.891	1.702	0.999	–	2.180
IIIa	15.7	–9.28	0.848	1.674	1.000	–	2.195
IVa	10.5	–9.50	0.817	1.694	1.001	–	2.233
Va	7.9	–9.58	0.837	1.716	0.999	–	2.150
VIa	10.5	–9.52	0.797	1.683	1.001	–	2.200
K2							
VIIa	28.9	–10.37	0.506	1.509	1.002	2.132	–
VIIIa	31.5	–10.31	0.511	1.503	1.002	2.024	–
IXa	21.0	–10.56	0.331	1.441	1.001	2.124	–
Xa	23.6	–10.50	0.452	1.530	1.001	2.117	–
K3							
XIa	42.0	–9.90	0.839	1.689	1.002	2.133	2.213
XIIa	42.0	–9.90	0.846	1.693	1.002	2.132	2.128
XIIIa	39.3	–9.93	0.545	1.490	1.001	2.067	2.093
XIVa	36.7	–10.10	0.755	1.698	1.003	2.122	2.193
XVa	34.1	–10.10	0.740	1.695	1.018	1.929	2.010
XVIa	36.7	–10.12	0.498	1.505	1.002	2.088	2.074

K2: piperidine–H_2O (**VIIa**), piperidine–*i*-PrOH (**VIIIa**), morpholine–H_2O (**IXa**), morpholine–*i*-PrOH (**Xa**) the H-bond is formed by the lone pair of the nitrogen atom, and the solvent acts as an H-donor. Also the formation is possible of mixed complexes of the type K3: piperidine–$2H_2O$ (**XIa**), piperidine–H_2O–*i*-PrOH (**XIIa**), piperidine–H_2O–dioxane (**XIIIa**), morpholine–$2H_2O$ (**XIVa**), morpholine–H_2O–*i*-PrOH (**XVa**), morpholine–H_2O–dioxane (**XVIa**), in which, according to calculations, the molecule of water (or one of water molecules in complexes **XIa, XIVa**) is always coordinated to the lone electronic pair, being the H-donor.

The results of calculations are presented in Table 5. The comparison of the geometrical and charge characteristics of the NH group of the solvated amines with the rate constants of the studied reactions revealed no correspondence. Previously we have shown that some reactions of acylation of aliphatic amines and α-amino acids are orbital controlled, and that the values of population [φp_z(N)] and squares of contribution of the $2p_z$–AO of nitrogen in the HOMO [Cp_z^2(N)] can serve as descriptors of reactivity of amines and their molecular complexes with the components of the solvents in N-acylation [15].

Some conclusions can be made by comparing the rate constants with the characteristics of $2p_z$–AO of nitrogen in the solvate complexes. The analysis of Table 5 shows that the least stable are the complexes of amines with one molecule of the solvent acting as an H-acceptor (K1), as follows from small energies of their formation ΔE_c. These complexes must be most reactive, since they are characterized by maximum values of squares of contributions of the $2p_z$–AO of nitrogen to the HOMO and high values of population of $2p_z$–AO, as well as highest lying HOMO. The highest reactivity should be observed for the complexes with one molecule of dioxane (see **IIa** and **Va**, Table 5), having maximum values of Cp_z^2(N) and φp_z(N).

The results of calculations agree with the kinetic data showing that the reactions in aqueous dioxane proceed with higher rates that in aqueous 2-propanol: for both amines the complexes with dioxane have larger values of Cp_z^2(N) and φp_z(N) than the complexes with 2-propanol (see **IIa, IIIa, Va** and **VIa** in Table 5).

One should keep in mind that the experimental rate constants of acylation of amines are effective values, which include the constants of acylation of the solvate complexes of different structure. It can be assumed that in the system water–dioxane the main reacting species are the solvate complexes **Ia, IIa, IVa**, and **Va**, while in the system water–2-propanol they are **Ia, IIIa, IVa**, and **VIa**. The results of calculations prove the suggestion of low reactivity of solvate complexes in which the bond with the solvent molecule is formed by the lone electron pair of nitrogen. These complexes are most stable and do not contribute significantly in the kinetics of the process since they require large energy expenditure for breaking the hydrogen bond formed by the nitrogen atom with the solvent.

It is presumable basing on the results of quantum-chemical simulation that the variations in the solvate shells of amines is not the main reason of the increase in the rate constants of acylation of amines with the increase in water content in the mixed solvent. Apparently, the main factor affecting the rates of the studied reactions is the interaction of the components of the binary solvent with the transition states of the reactions. This assumption is based on the results of previous calculations [11] of the potential energy surface for the reaction of ammonia with phenyl benzoate. The simulation has shown that the increase in the number of water molecules in the transition state decreases the activation energy and increases the acylation rate constants when the fraction of water in the binary solvent is increased.

EXPERIMENTAL

Piperidine and morpholine (pure for analysis) were distilled in a vacuum. 2-Propanol (“chemically pure” grade) was dried with anhydrous copper sulfate and distilled on a column at atmospheric pressure. Dioxane (“pure for analysis” grade) was dried with KOH and distilled over sodium metal. For preparation of solutions saturated solution of NaOH (“chemically pure” grade) and bidistillated water was used. Esters **I**, **II** were synthesized by acylation of nitrophenols with benzoyl chloride and identified by melting points [16]. All physicochemical constants of the reagents and solvents used in this study corresponded to the literature data [16, 17].

The kinetics of the reactions was studied spectrophotometrically measuring the variation of concentration of nitrophenolate ions formed in the course of the reaction at working wavelength 400 nm. The optical density was measured on a KFK-2UKhL 4.2 photocolorimeter, equipped with a digital voltmeter. The observed rate constants k_{obs} were calculated from the Guggenheim equation.

Quantum-chemical calculations were performed using Firefly 7.1.G program [18] in the supermolecule approximation with full geometry optimization of all solvate complexes by the RHF/6-311+G** method. Correspondence of the found structures of the solvate complexes to the minima on the potential energy surface was proved by vibrational calculations at the same level of theory. The energy of complex formation was calculated as the difference of the total energies of the solvate complex and the isolated molecules constituting it.

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