Russian Journal of Organic Chemistry, Vol. 38, No. 3, 2002, pp. 378–384. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 3, 2002, pp. 400–406.

Effect of the Structure of Phase-Transfer Catalyst on the Rate of Alkaline Hydrolysis of *N*-Benzyloxycarbonylglycine 4-Nitrophenyl Ester in the System Chloroform–Borate Buffer

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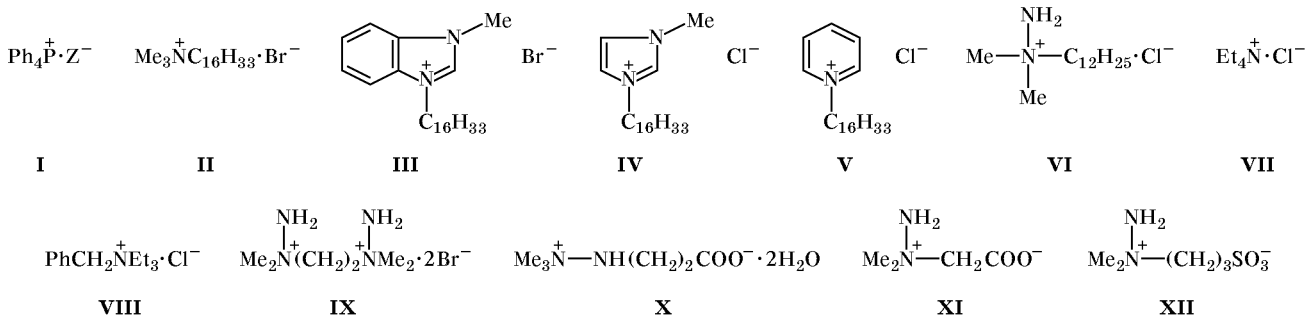
Received August 8, 2001

Abstract—Onium salts QZ (Z = Cl, Br) having a lipophilic (Q = R_3NR', where R′ = $C_{16}H_{33}$) or readily extractable (into organic phase) cation (Q = Ph_4P) exhibit a high catalytic activity in phase-transfer alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the two-phase system chloroform–borate buffer (pH 10). No catalytic effect is observed in the presence of hydrophilic ammonium salts [Et_4NCl, Et_3PhCH_2NCl, $Me_2(NH_2)\overset{+}{N}CH_2CH_2\overset{+}{N}(NH_2)Me_2\cdot 2Br^-$] and those insoluble in organic solvents [$(Me)_3\overset{+}{N}NH(CH_2)_2COO^-\cdot 2H_2O$, $Me_2(NH_2)\overset{+}{N}CH_2CO^-$, $Me_2(NH_2)\overset{+}{N}(CH_2)_3SO_3^-$]. These data suggest extraction mechanism of the process. The activity of lipophilic cation Q is determined mainly by two factors: its extractibility, on the one hand, and the ability to form micelles, on the other.

Hydroxide ion participates in many phase-transfer processes as a nucleophile or a base. However, studies on the kinetics of phase-transfer reactions involving hydroxide ion are very few in number [1–3]. As noted in [2], the problem of hydroxide ion transfer into organic phase is very important, but it has not been solved unequivocally. The main reason is that it is difficult to determine experimentally the concentration of hydroxide ion in weakly polar organic solvents. Therefore, interphase mechanism with participation of OH^- ion is generally considered [3].

We previously studied kinetic relations holding in alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the systems 1-butanol–borate buffer (pH 8.3, 10) [4] and chloroform–borate buffer (pH 10, 11) [5, 6] in the presence of some tetra-substituted ammonium and phosphonium salts. The results of these studies were interpreted in favor of

Scheme 1.



I, Z = Cl, Br.

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the extraction mechanism of catalysis, where the rate-determining stage is chemical reaction in the organic phase. Tetraphenylphosphonium salts **I** with various anions, tetrasubstituted ammonium bromide **II**, and benzimidazolium bromide **III** were used as phase-transfer catalysts. These salts are readily extractable into organic phase.

In order to obtain more reliable proofs for the extraction mechanism of the reaction under study, we thought it reasonable to extend the series of lipophilic catalysts and also to examine the process in the presence of hydrophilic salts. For this purpose, we used salts **IV**–**XII** as phase-transfer catalysts (Scheme 1). The first three of these, salts **IV**–**VI**, are lipophilic; compounds **VII**–**IX** are hydrophilic; and zwitterionic compounds **X**–**XII** are interesting as potential phase-transfer catalysts.

The hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in a two-phase system follows the stoichiometric equation given in Scheme 2 [4, 5].

Scheme 2.

$$PhCH_2OC(O)NHCH_2COOC_6H_4NO_2\text{-}4 + 2OH^- \xrightarrow{QZ,\ CHCl_3-\text{borate buffer}} PhCH_2OC(O)NHCH_2COO^- + 4\text{-}O_2NC_6H_4O^- + H_2O$$

The kinetics of the reaction were monitored by accumulation of 4-nitrophenoxide ion ($4\text{-}NO_2C_6H_4O^-$) in the two-phase system chloroform–borate buffer (volume ratio 1:1, pH 10, temperature 25°C). The given concentrations of the ester and catalyst (c_{cat}) were calculated on the overall volume of the two-phase system. The indices "org," "aq," and "2-ph" denote the organic phase, aqueous phase, and two-phase system as a whole, respectively.

Our preliminary experiments showed that hydrophilic salts **VII**–**IX** and dipolar salts **X**–**XII** having no long-chain lipophilic groups on the nitrogen do not exhibit catalytic activity. In the presence of these salts we failed to detect by UV spectroscopy accumulation of the hydrolysis product (4-nitrophenoxide ion) in the two-phase system over a period exceeding the half-conversion period in the presence of salts **I**–**VI** by a factor of 10 to 50. Lipophilic salts **IV**–**VI** ensured a sufficiently high rate of the hydrolysis in the two-phase system.

The observed differences in the catalytic activity of salts **I**–**XII** may be interpreted as follows. The main function of a phase-transfer catalyst in S_N2 reactions following the extraction mechanism is to transfer inorganic anions from aqueous to organic phase. Therefore, the rate of such reactions strongly depends on the lipophilicity of onium cation [7]. On the other hand, hydrophilic phase-transfer catalysts having short hydrocarbon radicals exhibit the highest catalytic activity in reactions following the interphase mechanism. In this case, the decisive factor is accessibility of the positively charged center in onium cation for association with organic anion, which increases as the alkyl chain shortens [8]. Taking into account that dipolar salts are as a rule almost insoluble in organic solvents, phase-transfer reactions catalyzed by such salts are believed [9] to follow the interphase mechanism. Then, a fairly high catalytic activity of salts **I**–**VI** and the absence of catalytic activity of hydrophilic (**VII**–**IX**) and dipolar salts (**X**–**XII**) can be regarded as an indirect evidence in favor of the extraction mechanism.

In order to estimate the catalytic activity of salts **IV**–**VI** in the hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester we examined its kinetics at a constant substrate concentration (5×10^{-3} M) on variation of the concentration of catalyst. Figure 1 shows semilog kinetic curves in the first-order reaction coordinates. The plots are linear up to a ~80% conversion of the substrate, i.e., the process can formally be regarded as pseudounimolecular. These

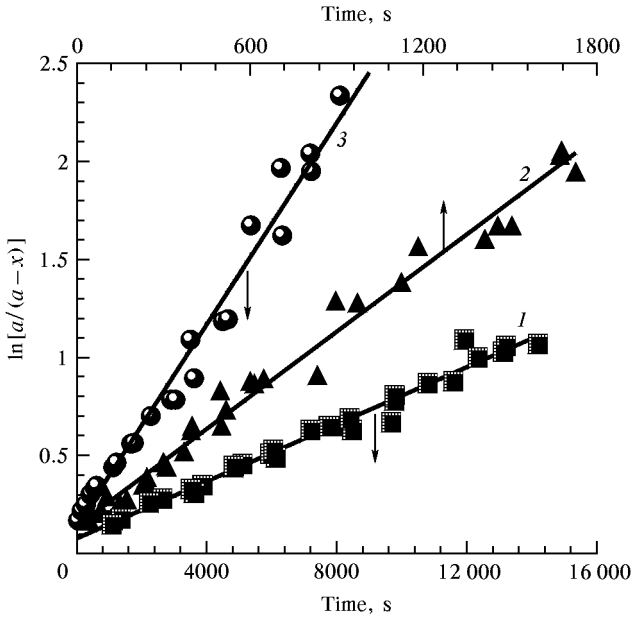

Fig. 1. Plots of $\ln[a/(a - x)]$ versus time (τ) for alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the two-phase system chloroform–borate buffer, pH 10 (1:1), in the presence of phase-transfer catalysts (*1*) **V**, $c_{cat} = 3\times10^{-3}$ M; (*2*) **IV**, $c_{cat} = 8\times10^{-3}$ M; and (*3*) **VI**, $c_{cat} = 5\times10^{-2}$ M. Temperature 25°C.

Pseudofirst-order rate constants ($k^{2\text{-ph}}$) and ($k^{2\text{-ph}'}$) determined by approximation of the experimental kinetic data using Eqs. (1) and (1′), respectively, for phase-transfer catalysts **IV**–**VI** on variation of their concentration (c_{cat}); 25°C

Catalyst	$c_{cat} \times 10^3$, M	$k^{2\text{-ph}} \times 10^4$, s^{-1}	$k^{2\text{-ph}'} \times 10^4$, s^{-1}	b	N[a]
IV	1	1.5±0.1	1.60±0.05	0.25±0.06	31
	2	2.5±0.1	3.0±0.1	0.30±0.02	34
	5	4.6±0.3		0.5±0.1	27
	8	11.2±0.3	10.9±0.4	0.1±0.1	36
	10	14.0±0.3	12.7±0.5	0.12±0.04	41
	20	15.0±0.6	17.5±0.7	0.12±0.02	25
V	1	0.31±0.02	0.22±0.01	0.11±0.03	26
	3	0.61±0.06	0.65±0.02	0.16±0.05	28
	5	0.79±0.07	0.71±0.03	0.22±0.08	22
	8	1.1±0.1	1.21±0.03	0.27±0.03	32
	9	1.62±0.01	1.45±0.07	0.11±0.01	25
	9.5	1.8±0.1		0.14±0.03	33
	10	3.2±0.7		0.28±0.06	64
	12.5	3.9±0.9		0.32±0.07	30
	15	2.5±0.4		0.19±0.06	32
	20	2.4±0.2	2.7±0.1	0.18±0.01	26
	30	2.48±0.05		0.30±0.01	29
VI	3	0.29±0.02		0.38±0.07	26
	5	0.5±0.1	0.64±0.02	0.29±0.02	45
	10	1.09±0.04	1.03±0.03	0.15±0.01	41
	30	1.65±0.02		0.5±0.1	26
	50	2.4±0.2	2.50±0.05	0.20±0.03	36

[a] N is the number of points.

plots do not pass through the origin but cut statistically reliable intercepts on the y axis. The corresponding values (b) are given in table. They were obtained by linear approximation of the kinetic results using the following equation:

$$\ln[a/(a - x)] = k^{2\text{-ph}}\,\tau + b. \qquad (1)$$

Here, $k^{2\text{-ph}}$ (s^{-1}) is the apparent pseudofirst-order rate constant; a is the initial substrate concentration (M); and x is the product concentration (M) by a moment τ. Analogous relations were observed by us previosuly for the same reaction in the presence of salts **I** (Z = Cl) and **II** [5]. They were explained [5] in terms of competing anion (Z^-) exchange between the initial form of phase-transfer catalyst and 4-nitrophenoxide ion (X^-) fromed during the process. Another possible reason is variation of the ion exchange selectivity constant $K^{sel}_{X/Z}$, depending on the concentration of 4-nitrophenoxide ion in the initial period of the reaction. It is known [10] that selectivity constants often depend upon ion concentration.

All salts **IV**–**VI** in the initial form contain the same counterion Cl^-, i.e., in all cases competing transfer of Cl^- (Z) and 4-NO_2ArO^- (X) ions occurs through the phase boundary by the cation. Taking into account that salts **IV**–**VI** have different cations, we cannot assert with certainty that the $K^{sel}_{X/Z}$ values for all catalysts change in parallel, depending on the concentration of 4-NO_2ArO^-. However, such a possibility cannot be ruled out for the following reasons. The lengths b (see table) almost do not depend on the catalyst concentration and its structure, as follows from the results of statistical treatment of data arrays obtained for particular catalyst. For this purpose, the experimental data for each catalyst at various concentrations were approximated using Eq. (1′), which is analogous to Eq. (1):

$$\ln[a/(a - x)] = k^{2\text{-ph}'}\,\tau + b'. \qquad (1')$$

Here, b' is a parameter which is constant within the given data array; and $k^{2\text{-ph}'}$ is the apparent rate constant analogous to $k^{2\text{-ph}}$ in Eq. (1) but determined by

approximation under the constraint that b does not change whithin the series of kinetic measurements for a single catalyst. The values of b' for catalysts **IV**–**VI** were thus estimated at 0.17 ± 0.02, 0.15 ± 0.01, and 0.16 ± 0.01, respectively. It is seen that these values coincide with each other within the mean-square deviation. The rate constants $k^{2\text{-ph}\prime}$ given in table also coincide with $k^{2\text{-ph}}$. Figure 2 shows the results of approximation for the whole array of experimental data. In the region of substrate conversion up to ~80% a normal dispersion of points with respect to the straight line with a unit slope is observed. At higher conversions, a tendency to autoacceleration appears. The reasons for the observed pattern are still not clear.

The low rate of the reaction in the initial period may also be explained in terms of microtopology of the chemical process. As noted above, we believe that the process follows extraction mechanism. The latter implies that the reaction can occur both at the phase boundary (at the side of organic phase) or in the bulk organic phase [2, 11]. Preliminary stirring of a solution of phase-transfer catalyst QZ with aqueous buffer solution in a two-phase system could lead (depending on the counterion Z) to increased concentration of OH^- ions at the phase boundary and in the boundary layer, as compared to its quasistationary concentration which establishes during the process. Therefore, the reaction in the boundary layer in the initial period (after addition of the ester) may be faster.

According to our previous data [4, 5], the reaction is of first order with respect to hydroxide ion concentration in the aqueous phase ($[OH^-]_{aq}$). Then, for a given catalyst concentration the rate constant $k^{2\text{-ph}}$ is expressed by Eq. (2):

$$k^{2\text{-ph}} = k_{OH}^{2\text{-ph}}[OH]_{aq}, \qquad (2)$$

where $k_{OH}^{2\text{-ph}}$ ($l\ mol^{-1}\ s^{-1}$) is the apparent second-order rate constant which is a function of concentration of phase-transfer catalyst. Figure 3 shows the dependence of $k_{OH}^{2\text{-ph}}$ on the overall catalyst concentration in the two-phase system. This dependence is generally nonlinear, which is typical of phase-transfer processes. Estimation of the slopes at the initial part of the above dependences gave $\tan\beta$ values which may be regarded as an integral parameter characterizing the efficiency of phase-transfer catalyst:

Catalyst	**I** [5], Z = Br	**I** [5], Z = Cl	**II** [6]
$\tan\beta$	650	890	10

Catalyst	**III** [6]	**IV**	**V**	**VI**
$\tan\beta$	1600	1400	110	110

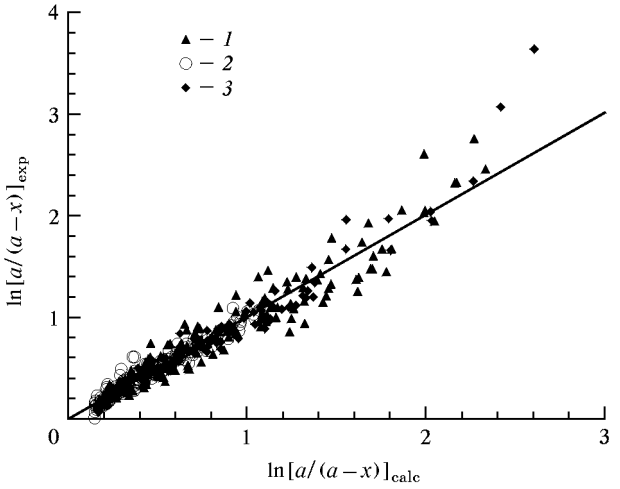

Fig. 2. Correlation between $\ln[a/(a-x)]_{exp}$ values calculated from the experimental data and $\ln[a/(a-x)]_{calc}$ values approximated by Eq. (1′) for phase-transfer catalysts (*1*) **IV**, N = 151; (*2*) **V**, N = 158; and (*3*) **VI**, N = 129; N is the number of points.

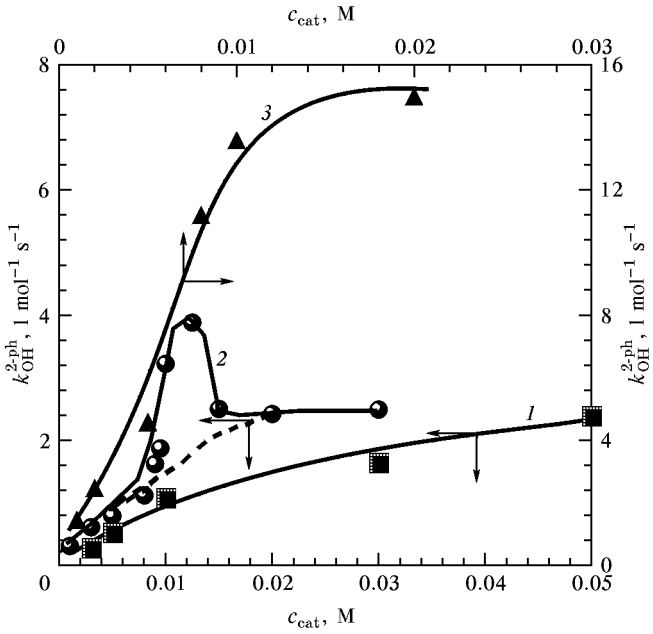

Fig. 3. Dependence of $k_{OH}^{2\text{-ph}}$ on the overall concentration of phase-transfer catalyst: (*1*) **VI**, (*2*) **V**, (*3*) **IV**.

Worthy of note is insignificant difference in the activity of chloride and bromide salts having the same or similar cationic part (cf. **Ia** and **Ib**, **III** and **IV**). As previously [5], this fact is explained in terms of competing extraction of the catalyst counterion and 4-nitrophenoxide ion formed: transfer of the latter into the organic phase predominates. On the other

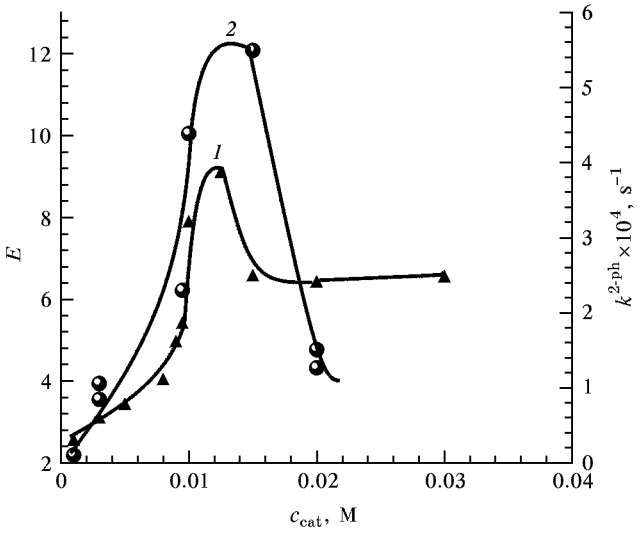

Fig. 4. Dependences of (*1*) the distribution coefficient of *N*-hexadecylpyridinium cation ($E = c_{org}/c_{aq}$) and (*2*) pseudo-first-order rate constant $k^{2\text{-ph}}$ on the overall concentration of hexadecylpyridinium chloride in the two-phase system chloroform–borate buffer (pH 10); 25°C.

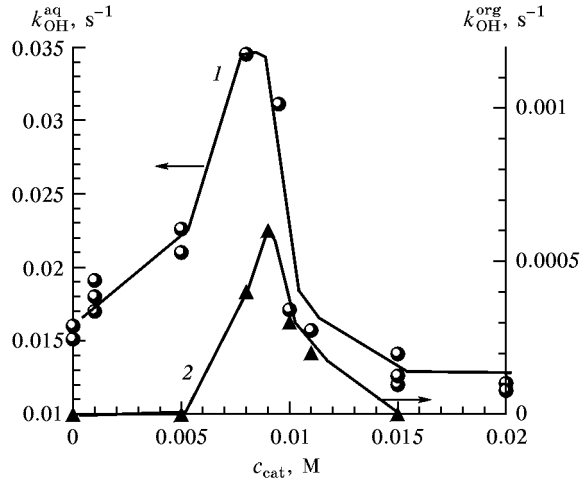

Fig. 5. Dependence of the pseudofirst-order rate constant in the separated (*1*) aqueous phase, k_{OH}^{aq}, and (*2*) organic phase, k_{OH}^{org}, on the overall concentration of *N*-hexadecylpyridinium chloride.

hand, the efficiency of phase-transfer catalysts in the reaction under study strongly depends on the cation nature. Among lipophilic compounds **II**–**VI** the most active are imidazolium salts **III** and **IV**. Unfortunately, we have no data on distribution of these salts in systems water–organic solvent; therefore, it is impossible to correlate the catalytic activity with extractibility of the respective cations. The available data allow us only to state the fact of high catalytic activity of salts having a heteroaromatic cation in processes following the extraction mechanism. The same applies to *N*-alkylpyridinium salts having strong electron-acceptor substituents in the pyridine ring [12].

The alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the presence of *N*-hexadecylpyridinium chloride should be considered separately. In this case, an extremal dependence of $k_{OH}^{2\text{-ph}}$ on the catalyst concentration is observed (Fig. 3, curve *2*), which is typical of micelle catalysis in aqueous solution [13]. Starting from a concentration of 8×10^{-3} M, the reaction rate sharply increases, reaching a maximum at c_{cat} = ~1.2×10^{-2} M. After that, the reaction rate falls down as sharply as it rose before. Had that part been cut from the plot (Fig. 3, curve *2*, dashed line), the dependence would be similar to those obtained for salts **IV**, **VI**, and **I**–**III** [5, 6]. These data suggest that the acceleration effect produced by catalyst **V** originates from at least two factors: (1) phase-transfer catalysis of hydrolysis with chemical reaction in the organic phase as the rate-determining stage (extraction mechanism) throughout the range of variation of the salt concentration and (2) micelle formation in the aqueous phase in the region of critical micelle concentration (CMC).

Figure 4 (curve *1*) shows the dependence of the distribution coefficient of *N*-hexadecylpyridinium chloride $E = c_{org}/c_{aq}$ versus its overall concentration (calculated on the entire volume of the two-phase system). It is seen that the dependence also passes through a maximum located approximately in the same range of concentrations as for the reaction rate peak (Fig. 4, curve *2*). The experimental concentration of *N*-hexadecylpyridinium cation in the aqueous phase at the midpoint (c_{cat} = 0.01 M) was estimated at $(1.6–1.8) \times 10^{-3}$ M. This value approaches the critical micelle concentration of the salt in water (0.9×10^{-3} M [14]). We can thus presume that micelle catalysis in the aqueous phase is responsible for increase of the reaction rate in the two-phase system in range of salt **V** concentrations from 0.8×10^{-2} to 1.2×10^{-2} M. On the other hand, the dependence of *E* on the concentration of salt **V** in the two-phase system (Fig. 4, curve *1*) implies that another explanation is possible, namely in terms of increased extraction of the salt cation into the organic phase. Obviously, *N*-hexadecylpyridinium cation can be transferred to organic phase as ion pair not only with hydroxide ion but also with chloride ion as counterion. In order to check the possibility for increased extraction of hydroxide ion into organic phase, we examined the kinetics of alkaline hydrolysis of *N*-benzyloxycarbonylglycine

4-nitrophenyl ester in the separated aqueous and organic phases on variation of the catalyst concentration. Figure 5 shows the dependences of the apparent pseudofirst rate constants in the separated aqueous (k_{OH}^{aq}) and organic phases (k_{OH}^{org}) on the concentration of salt **V**. The dependences obtained for the separated phases are qualitativly similar with that observed in the two-phase system (cf. Fig. 5 and Fig. 4, *2*), i.e. all these pass through a maximum. This means that in the region of critical micelle concentration, extraction of hydroxide ion into the organic phase sharply increases, which can give rise to the observed "jump" of the reaction rate.

It is difficult to speak unequivocally which factors or interactions in the system in the region of CMC are responsible for acceleration of the process. Among these, the following should be noted: (1) variation of the solvation energy ratio of Cl^- and OH^- ions due to predominant binding of one kind of ions to micelle surface in the aqueous phase; (2) formation in the organic phase of structurized ionic species (up to reverse micelle-like structures) which retain OH^- ions better than in ion pairs; (3) a different mechanism of anion exchange between the phases; etc.

To conclude, we can state that organic salts having a heterocyclic moiety in the cationic part exhibit the highest catalytic effect in the alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the two-phase system chloroform–borate buffer. This fact, together with our previous findings [5], provides an additional support to the extraction mechanism of the reaction under study.

EXPERIMENTAL

The kinetic measurements were performed using an SF-26 spectrophotometer; pH values were measured with the aid of an EV-74 ionometer. Standard borate buffer was prepared by the procedure described in [15]. The reaction kinetics in the two-phase system were studied following the procedure reported in [5]. The reaction rates in the separated organic and aqueous phases were measured as follows. Equal volumes of chlorofom and borate buffer were mixed in a vessel maintained at a specified temperature, and a required amount of the catalyst was added. The mixture was stirred for at least 15 min at 25°C, and the organic and aqueous phases were separated by centrifugation at 3000 rpm. The separated phase was placed in a spectrophotometric cell maintained at a specified temperature, a solution of *N*-benzyloxycarbonylglycine in dioxane was added dropwise, and the optical density at λ 410 nm was measured (accumulation of 4-nitrophenoxide ion).

Distribution of *N*-hexadecylpyridinium cation. Equal volumes of chloroform and borate buffer were mixed, *N*-hexadecylpyridinium chloride was added, and the mixture was stirred for at least 15 min at 25°C. The phases were separated by centrifugation, and the concentration of *N*-hexadecylpyridinium ion in each phase was determined by spectrophotometry at λ 260 nm.

N-Benzyloxycarbonylglycine 4-nitrophenyl ester was synthesized and purified as described in [16], mp 127°C; published data [16]: mp 126–128°C. Solvents were purified by standard procedures [17].

3-Hexadecyl-1-methylimidazolium chloride (IV). A mixture of 0.06 mol of hexadecyl chloride and 0.062 mol of 1-methylimidazole was heated for 20–30 h at 100°C (water bath) in a sealed ampule. When the reaction was complete (the mixture usually crystallized), trace amounts of unreacted initial compounds were removed by heating the product in a mixture of acetone with methanol under reflux. The salt was filtered off, recrystallized from acetone–methanol, and dried in a vacuum desiccator over P_2O_5, mp 59.5–61°C. Found, %: C 70.00; H 11.30; Cl 10.30; N 8.20. $C_{20}H_{38}ClN_2$. Calculated, %: C 70.07; H 11.39; Cl 10.36; N 8.18.

N-Hexadecylpyridinium chloride (**V**) was purified by the procedure described in [18], mp 81–82°C; published data [18]: mp 80–83°C.

1-Dodecyl-1,1-dimethylhydrazinium chloride (VI). A mixture of 15.2 ml (0.2 mol) of 1,1-dimethylhydrazine and 52.82 ml (0.22 mol) of dodecyl chloride was heated for 11 h at 60°C. Diethyl ether, 30 ml, was added, the mixture was ground, and the precipitate was filtered off. Yield of salt **VI** 24.4 g (94%). mp 80–82°C (from toluene; the melt became perfectly transparent at 150°C). ^{1}H NMR spectrum (DMSO-d_6): 0.90 t (CH_3C), 1.22 m (2H, CH_2C), 1.75 m (2H, CH_2CN), 3.24 s (6H, CH_3N), 3.48 m (2H, CH_2N), 6.25 s (2H, NH_2). Found, %: C 63.7; H 12.4; N 10.7; Cl 13.3. $C_{14}H_{33}ClN_2$. Calculated, %: C 63.5; H 12.6; N 10.6; Cl 13.4.

Tetraethylammonium chloride (**VII**) was purified by the procedure described in [19]. Benzyltriethylammonium chloride **VIII** was purified by the procedure described in [20], mp 194.5–195°C; published data [21]: mp 195°C.

1,2-Bis(1,1-dimethyl-1-hydrazinio)ethane dibromide (IX) [21] was synthesized as desribed above for salt **VI** from 30.4 ml (0.2 mol) of 1,1-dimethylhydrazine and 9.9 g (0.1 mol) of 1,2-dibromoethane. The mixture was heated for 4 h at 50°C or for 3 h at

60°C. Yield of salt **IX** 17.1 g (78%). mp 214–216°C (from methanol–2-propanol, 1 : 1). Found, %: C 28.8; H 7.4; Br 47.2; N 16.5. $C_8H_{24}Br_2N_4$. Calculated, %: C 28.6; H 7.2; Br 47.5; N 16.7.

3-(2,2,2-Trimethyl-1-hydrazinio)propanoate dihydrate (X) was synthesized by the known procedure for preparation of Mildronat [22], starting from acrylic acid esters and 1,1-dimethylhydrazine, mp 254–255°C; published data [22]: mp 254.6°C.

1,1-Dimethyl-1-hyidrazinioethanoate (XI). A solution of 1.11 ml (0.01 mol) of ethyl bromoacetate and 2.37 ml (0.03 mol) of 1,1-dimethylhydrazine in 5 ml of acetonitrile was refluxed for 1 h (the conversion of the ester was complete). The solution was evaporated to dryness, the precipitate of 1,1-dimethyl-1-ethoxycarbonylmethylhydrazinium bromide was dissolved in a mixture of 10 ml of methanol and 5 ml of water, and the solution was passed through a column charged with AV-17-8 anion exchanger (in the OH-form). The resulting solution was evaporated under reduced pressure, and the residue was recrystallized from water. Yield 1.1 g (93%), mp 236–238°C (from 2-propanol). ^{1}H NMR spectrum (DMSO-d_6): 3.20 s (6H, CH_3N), 3.65 s (2H, CH_2N), 6.51 s (2H, NH_2). Found, %: C 40.5; H 8.6; N 23.4. $C_4H_{10}N_2O_2$. Calculated, %: C 40.7; H 8.5; N 23.7.

3-(1,1-Dimethyl-1-hydrazinio)propanesulfonate (XII) was synthesized as described above for salt **VI** from 3.8 ml (0.05 mol) of 1,1-dimethylhydrazine and 6.1 g (0.05 mol) of propanesulfonate. Reaction time 3 h. Yield 7.9 g (87%). mp 283–284°C (from DMF). ^{1}H NMR spectrum (DMSO-d_6): 1.82 s (2H, CH_2C), 3.17 s (6H, CH_3N), 3.30 m (2H, CH_2N), 3.50 m (2H, CH_2S), 4.40 br.s (2H, NH_2). Found, %: C 33.3; H 7.7; N 15.3; S 17.9. $C_5H_{14}N_2O_3S$. Calculated, %: C 33.0; H 7.7; N 15.4; S 17.6.

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