The influence of detergentless microemulsion on the kinetics of hydrolysis of di(*p*-nitrophenyl) methylphosphonate catalyzed by amines

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The influence of the detergentless water/oil microemulsion formed in the *n*-hexane—water—2-propanol system on the kinetics of the hydrolysis of di(*p*-nitrophenyl) methylphosphonate under the conditions of general base catalysis by primary, secondary, and tertiary aliphatic amines was investigated. The leveling of the catalytic rate constants and basicities of the amines was found for this reaction in a microemulsion. The catalytic rate constants for the amines containing hydrophilic groups increase in microemulsions as compared to those in an aqueous medium, while the catalytic constants for the amines containing hydrophobic groups decrease.

Key words: microemulsion, esters of phosphorus acids, hydrolysis; rate constants, amines, general base catalysis.

Microemulsions (ME) are thermodynamically stable transparent dispersions of two immiscible liquids with micelles of 1—10 nm diameter stabilized by surfactant additives.[1] When alcohols, *e.g.*, 2-propanol, are used to stabilize micelles, "detergentless" ME containing no surfactants can be obtained. Detergentless ME of the "water/oil" (w/o) type have been proposed as a medium for fermentative processes[2,3] and some chemical reactions.[4,5] Data are available on the accelerating effect of w/o ME on the reactions of nucleophilic substitution[4] and oxidation.[5] The reactivity of amines in the reactions of nucleophilic substitution has been studied in such w/o ME containing either anionic or cationic surfactants.[6,7]

In this work, the ability of aliphatic amines to perform general base catalysis in detergentless w/o ME formed in a water—*n*-hexane—2-propanol system is studied for the hydrolysis of di(*p*-nitrophenyl) methylphosphonate.

$$\mathrm{MeP(O)(OC_6H_4NO_2\text{-}}p)_2 + \mathrm{H_2O\cdot NR_3} + 3\mathrm{H_2O} \rightarrow$$

$$\rightarrow \mathrm{MeP(O)(OC_6H_4NO_2\text{-}}p\mathrm{)O^-} + {}^-\mathrm{OC_6H_4NO_2\text{-}}p\ +$$

$$+\ 2\mathrm{H_3O} + \mathrm{H_2O\cdot NR_3}$$

Previously the kinetics of this reaction in an aqueous medium under general base catalysis by amines have been studied in detail.[8—10]

Experimental

We used di(*p*-nitrophenyl) methylphosphonate obtained according to the procedure described in Ref. 11. Amines were dried over NaOH and distilled directly before the runs. The ME samples were prepared by mixing specified volumes of *n*-hexane, 2-propanol, and water calculated taking into account their densities.

The kinetics of the reaction were studied spectrophotometrically on an SF-26 instrument by recording the optical density at 400 nm, which is due to the formation of *p*-nitrophenolate. The reaction was carried out in thermostatted (±0.5 °C) quartz cuvettes. The initial concentrations of the substrate were less than 0.0001 mol L^{-1}. The observed first-order rate constant (k_1) was determined by the relation

$$\ln(D_\mathrm{L} - D) = -k_1 \cdot t + \ln(D_\mathrm{L} - D_0),$$

where D_0, D, and D_L are the values of the optical density of the system at the beginning of the reaction, at the moment t, and after the reaction was completed, respectively. The k_1 values were calculated by the weighted least squares procedure. The effective bimolecular rate constants k_2 were calculated according to the formula

$$k_2 = k_1 \cdot (\mathrm{H}^+ + K_\mathrm{a})/(C_0 \cdot K_\mathrm{a}),$$

where C_0 is the total concentration of amine in the system. The values of the acidity constants (pK_a) of amines (at 25 °C) in ME and the relative content of the neutral forms of amines under the conditions of the runs $\alpha = K_\mathrm{a}/(\mathrm{H}^+ + K_\mathrm{a})$ were determined potentiometrically with the use of a pH-340 pH-meter.

Results and Discussion

The total rate of hydrolysis of *O,O*-di(*p*-nitrophenyl)methylphosphonate in water depends on the concentrations of amine and HO$^-$ ions.[8—10] Therefore, the rate constants in water k_2 were calculated taking into

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account the contribution of alkaline hydrolysis of the substrate into the overall rate of the process. When the reaction was carried out in the w/o ME formed in the system *n*-hexane (41.3 wt.%)—2-propanol (48.7 wt.%)—water (10%),[12] no alkaline hydrolysis of the substrate occurred at the concentrations of amines used. This is seen from the dependence of k_1 on the concentration of the neutral forms of amines $C_{am} = \alpha \cdot C_0$. Examples of such dependences are presented in Fig. 1 which shows the first order with respect to amine for the reaction in ME. The first order with respect to amine in ME is also observed in the case of *n*-cetylamine. When the latter is present in water, micelles are formed and deviations from the linear dependence of k_1 on the concentration of amine are observed.[13]

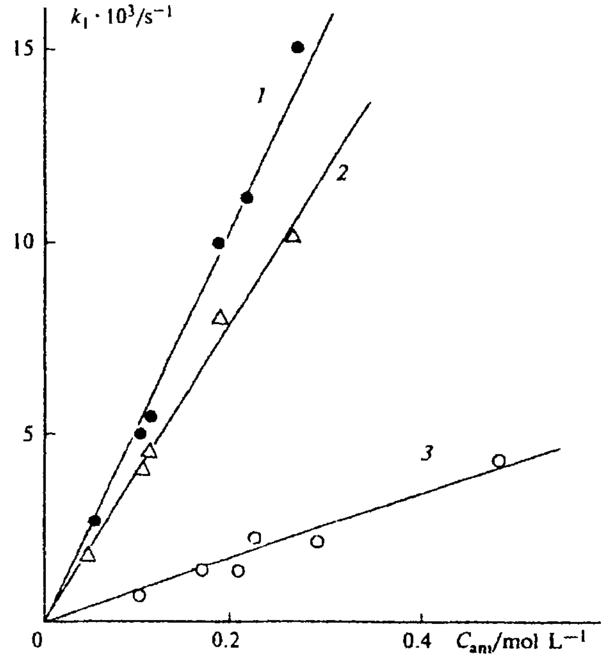


Fig. 1. Dependence of k_1/s^{-1} at 25 °C in the water/oil microemulsion on the concentration of amines: *1*, $BuNH_2$ ($\alpha = 0.96$), *2*, Et_2NH ($\alpha = 0.94$), *3*, Et_3N ($\alpha = 0.97$).

The catalytic effect of amines on the hydrolysis of a substrate is characterized by the effective rate constants k_2 presented in Table 1 along with the pK_a values for amines. On going from water to ME, a decrease in k_2 for amines containing either alkyl or benzene group at the N atom is observed. The decrease in k_2 becomes more pronounced when the length of the alkyl groups and their number at the N atom increase. On the other hand, in the case of ethanolamine and morpholine containing hydrophilic groups in the alkyl radicals, a similar change in the medium results in an increase in k_2. The influence of the reaction medium on the catalytic abilities of various amines is characterized by the $k_2(ME)/k_2(H_2O)$ value (see Table 1).

Together with the change in k_2, a significant decrease in pK_a, *i.e.*, a decrease in basicity, is observed for hydrophobic amines on going from water to ME. Unlike this, the pK_a values for hydrophilic amines (*e.g.*, ethanolamine, morpholine) increase only slightly in ME as compared to water. A dependence between the pK_a values for the primary and secondary amines in the two media (ME and water) exists, which points to the leveling of the pK_a values in ME.

$$pK_{a,ME} = (0.62 \pm 0.10) \cdot pK_{a,H_2O} + (3.2 \pm 1.1)$$

$$n = 10,\ r = 0.902,\ s = 0.28$$

The basicities of the tertiary amines also approach each other considerably on going from water to ME.

Table 1. The catalytic rate constants for the hydrolysis of di(*p*-nitrophenyl) methylphosphonate in water and w/o ME at 25 °C and pK_a of amines studied

Amine	pK_a		$k_2 \cdot 10^2/mol^{-1}\ L\ s^{-1}$		k_{ME}/k_{H_2O}
	H_2O^a	ME	H_2O	ME	
n-Butylamine	10.83	10.08	6.31[8]	4.66	0.74
n-Hexylamine	10.60	9.63	—	5.1	—
Cyclohexylamine	10.64	9.87	3.95[11]	3.37	0.85
n-Heptylamine	10.66	9.60	—	5.28	—
n-Decylamine	10.3^b	9.25	—	5.64	—
n-Cetylamine	—	9.07	103^c	3.92	0.04
Benzylamine	9.35	8.79	2.69^d	1.33	0.50
2-Ethanolamine	9.50	9.62	1.40[11]	3.1	2.21
Diethylamine	10.94	10.30	15.9[11]	4.27	0.27
Piperidine	11.25	10.26	15.4[8]	6.09	0.40
Morpholine	8.36	8.42	0.684[11]	1.19	1.75
Dimethylbenzylamine	8.91	7.66	—	0.350	—
N-Butylpiperidine	10.53	8.26	—	0.29	—
N-Methylmorpholine	7.41	7.21	0.252[11]	0.109	0.43
Triethylamine	10.71	9.30	9.43[11]	0.57	0.060

^{a} The literature data.[14] ^{b} The literature data.[15] ^{c} Extrapolated from the temperature dependence of the rate constant of the reaction at pre-micellar region.[11] ^{d} The constant is determined by us.

$$\mathrm{p}K_{a,\mathrm{ME}} = (0.519\pm0.18)\cdot \mathrm{p}K_{a,\mathrm{H_2O}} + (3.23\pm1.7)$$

$$n = 4,\ r = 0.90,\ s = 0.49$$

Leveling of catalytic activities of amines is observed in w/o ME (see Table 1). As a consequence, the Brønsted relation $\log k_2 = f(\mathrm{p}K_a)$ for the primary and secondary amines is characterized by a smaller slope as compared to that obtained for the same reaction in water.[13]

$$\log(k_{2,\mathrm{ME}}) = (0.360\pm0.037)\mathrm{p}K_a - (4.99\pm0.35)$$

$$n = 7,\ r = 0.975,\ s = 0.07$$

Long-chain amines (*e.g.*, *n*-hexylamine—*n*-cetylamine), for which significant deviations from the dependence found are observed, are not included in the latter correlation. A similar dependence for tertiary amines also shows a smaller slope as compared to that in an aqueous medium.[13]

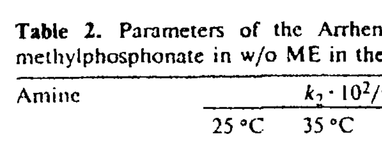
$$\log(k_{2,\mathrm{ME}}) = (0.222\pm0.070)\mathrm{p}K_a - (4.32\pm0.59)$$

$$n = 4,\ r = 0.908,\ s = 0.11$$

Leveling of the reactivity of amines of different structure was previously observed in the aminolysis of esters of carboxylic acids in the w/o ME formed in the system cetylpyridinium bromide (16.7)—*n*-butanol (16.1)—*n*-hexane (3.7)—water (63.5) (wt.%).[7]

The study of the temperature effect on the hydrolysis of the substrate showed that the activation energy (E_a) in the w/o ME (Table 2) is 20—30 kJ mol^{-1} lower than that in water and the pre-exponential factor of the Arrhenius equation (A) is 3—4 orders lower that those for the reactions in water.[10] The E_a and A values found are effective and depend on the thermodynamic parameters of the intermediate equilibrium stages.

The results obtained are in line with the below-presented scheme of the hydrolysis of the substrate (s) catalyzed by amines in the w/o ME



Here K_1, K_2 and K_{11}, K_{22} are the equilibrium constants for the distribution of the substrate between the ME aqueous core, the surface of micelles, and the hydrocarbon phase, respectively.

It can be suggested that hydrophilic amines, ethanolamine and morpholine, are able to catalyze the hydrolysis of the substrate in the bulk of micelles and at the interface. A minor transfer of these amines into the hydrocarbon phase is suggested. Amines with enhanced hydrophobicity can partially occur in the hydrocarbon phase, where the hydrolysis of the substrate is impossible because of the practical absence of water. In particular, the lowering of the rate constants k_2 in ME for tertiary amines containing three hydrophobic substituents at the N atom can be due to the smaller content of amines at the interface.

When the substrate and amine capable of nucleophilic attacking pass into the hydrocarbon phase, aminolysis of the substrate can occur.[16] We studied the kinetics of the reactions of the substrate with *n*-butylamine and *n*-cetylamine in hexane. At 19, 25, and 35 °C, the bimolecular rate constants for the reaction with *n*-butylamine (k_2/mol^{-1} L s^{-1}) are equal to 0.059, 0.057, and 0.060, respectively. This fact indicates that the activation energy for the aminolysis reaction is close to zero and is consistent with the data for similar reactions.[16,17] In the case of *n*-cetylamine, the k_2 values at 19, 25, and 35 °C are equal to 0.052, 0.053, and 0.049, respectively, also indicating that the activation energy is close to zero. The estimation of the possible contribution of a side reaction to the catalytic rate constant observed was performed by us based on the yield of *p*-nitrophenol.

The hydrolysis of the substrate occurs with the elimination of only one *p*-nitrophenoxyl group, whereas the aminolysis of the substrate involves successive replacement of two *p*-nitrophenoxyl groups. For the reaction with *n*-butylamine in the w/o ME, the formation of one mole of *p*-nitrophenol was observed (based on the extinction of the product), in accord with the general scheme of the process presented above, *i.e.*, no noticeable contribution of the aminolysis of the substrate to the rate constant being estimated is seen.

The catalytic alcoholysis of the substrate can be another side process during the reaction in ME.[18] The values of the catalytic rate constants of the alcoholysis of the substrate in 2-propanol estimated at 25 °C are equal to 0.005 mol^{-1} L s^{-1} in the presence of *n*-butylamine

Table 2. Parameters of the Arrhenius equation for the hydrolysis of di(*p*-nitrophenyl) methylphosphonate in w/o ME in the presence of alkylamines at various temperatures

Amine	$k_2\cdot10^2$/mol^{-1} L s^{-1}				E_a /kJ M^{-1}	log*A*
	25 °C	35 °C	45 °C	55 °C		
Bu^{n}NH$_2$	4.66	5.83	7.12	10.9	22.2±3.4	2.55±0.56
n-C$_{16}$H$_{33}$NH$_2$	3.92	5.59	6.57	—	20.4±4.0	2.19±0.68
Et$_2$NH	4.27	5.64	8.49	10.1	24.4±0.4	2.90±0.38
Et$_3$N	0.57	0.82	1.09	1.62	27.8±1.5	2.62±0.24

and to 0.0005 mol^{-1} L s^{-1} in the presence of triethylamine. These values are one order less than the rate constants for the reaction in ME in the presence of the same amines; therefore one can suggest that the alcoholysis of the substrate does not contribute substantially to the rate constants k_2 obtained in ME (see Table 1).

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