

# Phase-Transfer Catalysis in Alkaline Hydrolysis of *N*-Benzyloxycarbonylglycine 4-Nitrophenyl Ester in the Two-Phase System Chloroform–Borate Buffer

O. V. Baranova<sup>1</sup>, V. V. Kosmynin<sup>1</sup>, V. A. Savelova<sup>2</sup>, A. F. Popov<sup>2</sup>,  
B. V. Panchenko<sup>2</sup>, and A. N. Shendrik<sup>1</sup>

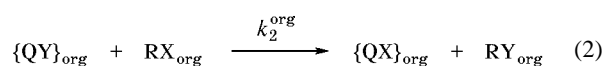
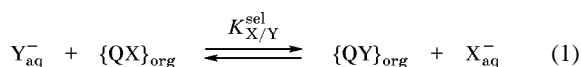
<sup>1</sup> Donetsk State University, ul. Universitetskaya 24, Donetsk, 383050 Ukraine

<sup>2</sup> Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian National Academy of Sciences, ul. R. Luxemburg 70, Donetsk, 340114 Ukraine

Received November 15, 1999

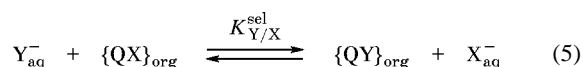
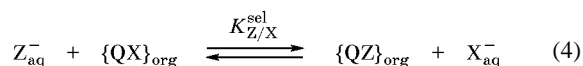
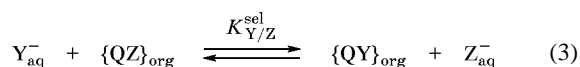
**Abstract**—Alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the two-phase system chloroform–borate buffer (pH 10 and 11) in the presence of C<sub>16</sub>H<sub>33</sub>NMe<sub>3</sub>Br and Ph<sub>4</sub>PZ (Z = Cl, Br, I) at 25°C follows the extraction mechanism where the rate-determining stage is the chemical reaction in the organic phase. The different kinetic profiles of the reaction depending on the nature of Z<sup>−</sup> were explained in terms of concurrent extraction of three kinds of anions: nucleophile OH<sup>−</sup>, nucleofuge 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>−</sup>, and foreign ion Z<sup>−</sup>.

Extraction mechanism of phase-transfer catalysis was the subject of a number of theoretical and experimental studies [1, 2] which were focused mainly on analysis of the scheme proposed by Starks [3] [reactions (1) and (2)].



Here,  $K_{Y/X}^{\text{sel}} = [X^-]_{\text{aq}} [QY]_{\text{org}} / [Y^-]_{\text{aq}} [QX]_{\text{org}}$  is the ion-exchange selectivity constant; the indices “aq” and “org” refer to the aqueous and organic phase, respectively. Ion pairs are enclosed in braces. The above scheme includes quickly establishing equilibrium (1) (competing extraction by catalyst Q<sup>+</sup> of two anions: nucleophilic reagent Y<sup>−</sup> and counterion X<sup>−</sup> of the catalyst) and rate-determining stage (2) (chemical reaction between the active form of the catalyst, ion pair QY, and substrate RX in the organic phase). Here, anion X<sup>−</sup> is a nucleofuge and at the same time counterion of the catalyst. Therefore, in the presence of a large excess of Y<sup>−</sup> ions, reaction (2) does not affect extraction equilibrium (1) which has established at the beginning of the process.

Kinetic verification of the proposed scheme gave rise to a series of fundamental principles determining the efficiency of phase-transfer processes in the system liquid–liquid (l/l). These are (1) dependence of the second-order kinetic profile on  $K_{Y/X}^{\text{sel}}$  [4]; (2) effect of the form of predominant nucleophile Y<sup>−</sup> (anion, ion pair, ion associate with conjugate acid, etc.) on the degree of transfer to the organic phase and reactivity [5]; and (3) interrelation between the rate-determining stage and the place where the chemical reaction occurs (bulk organic phase, a layer in the vicinity of phase boundary, or phase boundary itself) [6]. When the nucleofuge X<sup>−</sup> and catalyst counterion Z<sup>−</sup> are different species, the state of extraction equilibria is described by a more complex scheme including equilibria (3)–(5):



In this case, the mechanism of phase-transfer process radically differs from the Starks model since

the formation of product of reaction (2) is connected with appearance of two new extraction fluxes (4) and (5). As a result, the catalyst is continuously redistributed between the aqueous ( $Q^+$ ) and organic phase (QX, QY, QZ) during the process. In both cases, the rate of reaction (2) is formally given by Eq. (6):

$$-\partial c(\text{RX})/\partial \tau = k_2^{\text{org}} [\text{QY}]_{\text{org}} c(\text{RX})_{\text{org}} \quad (6)$$

When  $X \neq Z$  the quasiequilibrium concentrations of all forms of the catalyst, including the active one (QY), should be a function of time. For example, the concentration  $[\text{QY}]_{\text{org}}$  can be expressed through the equilibrium constant (5) [Eq. (7)]:

$$[\text{QY}]_{\text{org}} = K_{Y/X}^{\text{sel}} \frac{[\text{QX}]_{\text{org}}}{[\text{X}^-]_{\text{aq}}} [\text{Y}^-]_{\text{aq}} \quad (7)$$

As follows from Eq. (7), the kinetic relations of the process as a whole should be determined not only by the initial distribution of the catalyst but also by the substrate conversion. In the simplest case, when the rate-determining stage is reaction (2), the concentration of nucleophile  $Y^-$  in the aqueous phase is constant or much greater than the substrate concentration, and the concentration of the active form of catalyst QY is also constant, the process is expected to proceed as pseudounimolecular. Its rate is described by Eq. (8):

$$-\partial c(\text{RX})/\partial \tau = k^{2\text{-ph}} c(\text{RX}); \quad (8)$$

Here,  $k^{2\text{-ph}} = k_2^{2\text{-ph}} [\text{Y}^-]_{\text{aq}}$  and  $k_2^{2\text{-ph}} = k_2^{\text{org}} K_{Y/X}^{\text{sel}} \times [\text{QX}]_{\text{org}}/[\text{X}^-]_{\text{aq}}$  (the index "2-ph" refers to two-phase system).

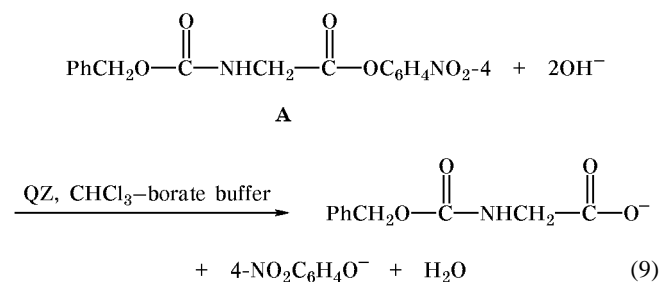
General relations holding in a system with three kinds of anions (nucleophile  $Y^-$ , nucleofuge  $X^-$ , and foreign ion  $Z^-$  which is introduced together with the catalyst  $Q^+$ ) for a particular case when cation  $Q^+$  is completely transferred to the organic phase were formulated in [7, 8]. Using these results, kinetic features of a reaction can be predicted on the basis of the values and ratios of the selectivity constants  $K_{Y/X}^{\text{sel}}$ ,  $K_{Y/Z}^{\text{sel}}$ , and  $K_{Z/X}^{\text{sel}}$ . However, experimental data on such systems are limited. Some studies deal mainly with the simplest cases, when  $K_{Y/X}^{\text{sel}} > 1$  and  $K_{Z/X}^{\text{sel}} \approx 1$  (see, e.g., [9]). As a rule, it doesn't matter which salt, QX or QZ, is added to the system as phase-transfer catalyst.

More interesting are systems for which  $K_{Y/X}^{\text{sel}} \ll 1$ . Here, the effect of catalyst poisoning is expected.

In particular, such anion extraction selectivity ratio should be observed in alkaline hydrolysis of amino acid nitrophenyl esters, catalyzed by onium halides, in a liquid-liquid two-phase system. High hydrophilicity of the nucleophile ( $\text{OH}^-$ ) and high lipophilicity of the nucleofuge ( $4\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$ ) [1, 2] predetermine complicated kinetic relations [10] as compared to systems with the reverse lipophilicity ratio of nucleophile and nucleofuge ( $X^-$ ).

We previously showed [10] that alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester (**A**) in the system 1-butanol-borate buffer both in the absence and in the presence of phase-transfer catalyst does not follow first-order kinetics. It was presumed that the higher initial reaction rate is the result of redistribution of quasiequilibrium concentrations according to reactions (3)–(5) as the nucleofuge ( $4\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$ ) accumulates in the system (poisoning of the catalyst). However, the system 1-butanol-borate buffer turned out to be inconvenient from the viewpoint of detailed study of the hydrolysis kinetics with regard to the structure of phase-transfer catalyst and some other factors. The reasons are (1) relatively high reaction rates which restrict the available pH range to a region below 8–9 and (2) considerable contribution of the noncatalytic process. Therefore, in the present work we examined the kinetics of alkaline hydrolysis of ester **A** in the presence of tetraphenylphosphonium halides  $\text{Ph}_4\text{PZ}$  ( $Z = \text{Cl}, \text{Br}, \text{I}$ ) in the system chloroform-borate buffer (1:1, pH 10). Chloroform is known as a solvent which effectively extracts onium salts [2].

The effect of pH on the rate of hydrolysis was studied using cetyltrimethylammonium bromide as phase-transfer catalyst. The borate buffers had pH 10 and 11. The concentrations of ester **A** (*a*) and catalyst (*m*) are given with respect to the entire volume of the two-phase system; the concentration of hydroxide ions refers to the aqueous phase and is assumed to be equal to  $10^{14-\text{pH}}$  (here, pH refers to the initial borate buffer, i.e., pH = 10 or 11). All experiments were carried out at 25°C. Alkaline hydrolysis of ester **A** follows scheme (9).



In the further treatment, the following notations are used for anions: Y = OH; X = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O (ArO); Z = Cl, Br, I.

We showed in [10] that in the system 1-butanol–borate buffer the process follows the extraction mechanism where the rate-determining stage is chemical reaction in the bulk organic phase: the reaction rate does not depend on the rate of stirring. Figure 1 shows semilog kinetic curves in the first-order coordinates for reaction (9) in the system chloroform–borate buffer in the presence of cetyltrimethylammonium bromide. The shape of the kinetic curves does not change on variation of the catalyst concentration and pH of borate buffer. A considerable part of the curve, which covers ~10–80% conversion of the initial ester, is linear. Hence the process follows first-order kinetics at least at that part of the kinetic curve. The initial part (up to 10–20% conversion) suggests a greater hydrolysis rate than might be expected from the next linear part. The linear parts of the kinetic curves in Fig. 1 can be described by Eq. (10) with a constant term  $b$ :

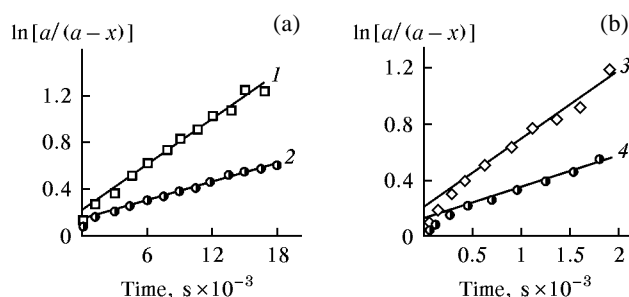
$$\ln[a/(a-x)] = k^{2-ph} \tau + b, \quad (10)$$

where  $a$  is the initial concentration of ester **A**, and  $x$  is the concentration of the hydrolysis product at time  $\tau$ . The quantity  $b$  makes no definite physical sense. Its positive sign indicates autoinhibition of the process in the initial period. An analogous pattern was observed for reaction (9) catalyzed by cetyltrimethylammonium bromide in the system 1-butanol–borate buffer [10].

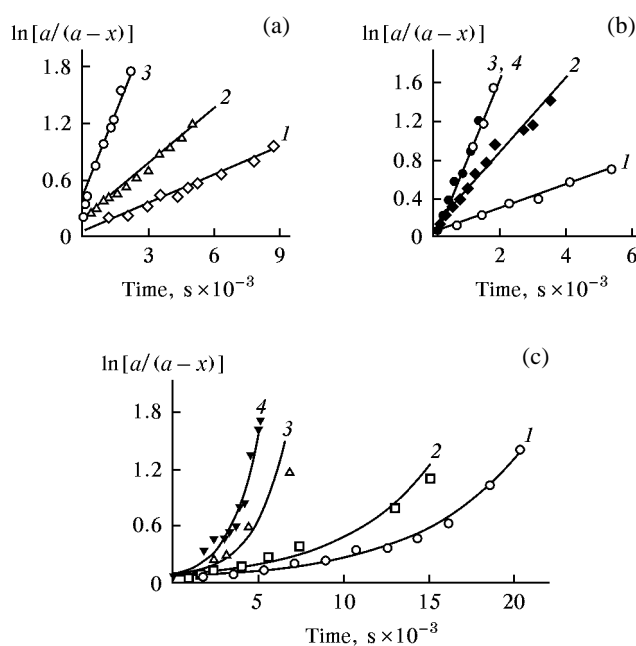
The pseudofirst-order rate constants  $k^{2-ph}$  were calculated by Eq. (10) from the linear parts of the kinetic plots (see table). The  $k^{2-ph}$  values obtained for different pH values of initial buffer solutions and different concentrations of cetyltrimethylammonium bromide are given in table which also contains the apparent second-order rate constants  $k_{OH}^{2-ph} = k^{2-ph}/[OH]_{aq}$ . It is seen that the  $k_{OH}^{2-ph}$  values for pH 10 and 11 are almost similar, the catalyst concentration being constant. This suggests first order of the reaction with respect to hydroxide ion, i.e., the reaction rate in the two-phase system is described by Eq. (11):

$$-\partial c(RX)/\partial \tau = k_{OH}^{2-ph} c(RX)_{org} [OH^-]_{aq}. \quad (11)$$

These data led us to presume (cf. [11, 12]) that the alkaline hydrolysis of ester **A** in the system CHCl<sub>3</sub>–borate buffer, as well as in 1-butanol–borate buffer [10], follows the extraction mechanism and that the



**Fig. 1.** Plots of  $\ln[a/(a-x)]$  versus time for alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester in the two-phase system chloroform–borate buffer in the presence of cetyltrimethylammonium bromide at 25°C; (a) pH 10 and (b) pH 11;  $a = 5 \times 10^{-3}$  M; (1, 3)  $m = 5 \times 10^{-2}$ , (2, 4)  $m = 10^{-2}$  M.



**Fig. 2.** Plots of  $\ln[a/(a-x)]$  versus time for alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester ( $a = 5 \times 10^{-3}$  M) at 25°C in the two-phase system chloroform–borate buffer (pH 10) in the presence of various tetraphenylphosphonium halides Ph<sub>4</sub>PZ: (a) Z = Cl,  $m \times 10^3$ , M: (1) 0.5, (2) 1, (3) 10; (b) Z = Br,  $m \times 10^3$ , M: (1) 0.2, (2) 0.5, (3) 1, (4) 1.5; (c) Z = I,  $m \times 10^3$ , M: (1) 5, (2) 10, (3) 20, (4) 30.

rate-determining stage is the chemical reaction in the organic phase. In keeping with our previous data [10], the observed shape of the kinetic plot (which is characterized by higher initial rate, see Fig. 1) results from appearance of concurrent equilibrium processes (4) and (5) as 4-nitrophenoxide ion is released into the system. Equilibria (4) and (5) determine the quasiequilibrium concentration of hydroxide ion in

Parameters of Eq. (10) for alkaline hydrolysis of *N*-benzyloxycarbonylglycine 4-nitrophenyl ester ( $a = 5 \times 10^{-3}$  M) in the two-phase system chloroform–borate buffer (pH 10 and 11) at various concentrations of phase-transfer catalyst QZ; temperature 25°C

Phase-transfer catalyst QZ	pH	$m \times 10^3$ , M	$b$	$k^{2-ph} \times 10^4$ , s <sup>-1</sup>	$k_{OH}^{2-ph}$ , l mol <sup>-1</sup> s <sup>-1</sup>	$N$	$S_{tot}$	$R$
C <sub>16</sub> H <sub>33</sub> Me <sub>3</sub> NBr	10	10	0.111±0.006	0.24±0.05	0.24±0.05	26	0.01	0.995
	11	10	0.06±0.03	2.5±0.2	0.25±0.02	18	0.06	0.933
	11	10 <sup>a</sup>	-0.08±0.02	5.4±0.2	0.54±0.02	38	0.048	0.974
	10	50	0.21±0.02	0.53±0.02	0.53±0.02	40	0.08	0.979
	11	50	0.12±0.01	4.9±0.2	0.49±0.02	19	0.04	0.990
Ph <sub>4</sub> PCl	10	0.5	0.12±0.03	0.94±0.05	0.94±0.05	23	0.07	0.966
		0.8	0.18±0.03	1.10±0.07	1.10±0.07	19	0.06	0.966
		1	0.22±0.02	1.82±0.07	1.82±0.07	28	0.05	0.982
		3	0.10±0.04	2.9±0.2	2.9±0.2	21	0.12	0.971
		3 <sup>a</sup>	-0.01±0.03	3.1±0.2	3.1±0.2	21	0.09	0.967
		5	0.29±0.03	4.0±0.3	4.0±0.3	10	0.06	0.983
		10	0.36±0.09	6.9±0.53	6.9±0.53	11	0.13	0.974
Ph <sub>4</sub> PBr	10	30	0.3±0.1	24.0±2.3	24.0±2.3	11	0.91	0.959
		2	0.03±0.03	1.28±0.09	1.28±0.09	14	0.07	0.969
		5	0.08±0.04	3.4±0.2	3.4±0.2	27	0.12	0.965
		10	-0.05±0.03	8.3±0.3	8.3±0.3	16	0.08	0.988
		15	-0.07±0.05	9.0±0.56	9.0±0.56	7	0.06	0.990

<sup>a</sup> 4-Nitrophenol,  $c = 5 \times 10^{-4}$  M, was preliminarily added to the system.

the organic phase,  $[QOH]_{org}$ . In the general case this concentration changes in parallel with the substrate conversion [Eq. (7)]. Therefore, it is difficult to expect the entire kinetic plot to be linear in the coordinates corresponding to first-order reaction. The semilog kinetic curves plotted in Figs. 1 and 2 support our expectations.

With tetraphenylphosphonium chloride as catalyst (Fig. 2a), the kinetic curves are similar to those given in Fig. 1 for cetyltrimethylammonium bromide. At the initial part of the kinetic curve {substrate conversion 10–20%;  $[ArO^-]_{org} \approx (0.5-1) \times 10^{-4}$  M}, the reaction rate is higher than at the subsequent linear part (catalyst poisoning). The dependence of  $\ln[a/(a-x)]$  on  $\tau$  is described by Eq. (10) with a statistically significant free term  $b$  at all the examined Ph<sub>4</sub>PCl concentrations (see table). For tetraphenylphosphonium bromide, the kinetic plots in the first-order coordinates (Fig. 2b) pass through the origin regardless of the catalyst concentration, i.e., the free term in Eq. (10) is close to zero (see table). Finally, the kinetic plots obtained for catalysis by tetraphenylphosphonium iodide (Fig. 2c) are different from those found for tetraphenylphosphonium chloride (Fig. 2a). Initially, the reaction rate is low, and then it sharply increases (autocatalysis).

There are no data on  $K_{ZArO}^{sel}$  values for the catalysts under study in the system CHCl<sub>3</sub>–borate buffer. These values can be estimated from analysis of the extraction constants  $E_{QZ}$  (12) for a series of related systems, which were collected in [2].

$$E_{QZ} = [QZ]_{org}/([Q^+]_{aq}[Z^-]_{aq}). \quad (12)$$

There are data on extraction of ion pairs Bu<sub>4</sub>NZ (Z = Cl, Br, I, TsO) in the system chloroform–water (I). For the system 1,2-dichloroethane–water, the series of anions Z also includes 4-nitrophenoxide ion. Comparison of  $\log E_{QZ}^I$  with  $\log E_{QZ}^{II}$  gives rise to a linear relation shown in Fig. 3 (plot 1); and we can estimate the value of  $\log E_{QZ}$  for extraction of ion pairs Bu<sub>4</sub>N<sup>+</sup>·<sup>-</sup>OC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4 in the system CHCl<sub>3</sub>–H<sub>2</sub>O. Comparison of  $\log E_{QZ}$  for Bu<sub>4</sub>NZ (including Z = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O) in the system CHCl<sub>3</sub>–H<sub>2</sub>O with  $\log E_{QZ}$  for Ph<sub>4</sub>AsZ in 1,2-dichloroethane–H<sub>2</sub>O (Fig. 3, plot 2) shows that straight lines 1 and 2 in Fig. 3 are parallel. This means that the ratio  $E_{QZ}^I/E_{QZ}^{II}$  can be estimated with an accuracy to a constant factor. Therefore, we can calculate the  $E_{QZ}$  values for extraction of Ph<sub>4</sub>AsZ ion pairs (Z = Cl, Br, I, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O) in the system CHCl<sub>3</sub>–H<sub>2</sub>O and assume their product with a constant coefficient  $\alpha$  to be equal to the extraction constants

for  $\text{Ph}_4\text{PZ}$  ion pairs in the same system on the basis of proportionality of  $E_{\text{QZ}}$  for  $\text{Ph}_4\text{AsCl}$  and  $\text{Ph}_4\text{PCl}$  in the system 1,2-dichloroethane–water. Below are given the extraction constants  $E_{\text{Ph}_4\text{PZ}}$  and selectivity constants  $K_{\text{Z/ArO}}^{\text{sel}}$  for the system  $\text{CHCl}_3\text{--H}_2\text{O}$ , estimated as described above:

Z	Cl	Br	$\text{OC}_6\text{H}_4\text{NO}_2\text{-4}$	I
$E_{\text{Ph}_4\text{PZ}}$ , l/mol	$\alpha \times 45$	$\alpha \times 1.1 \times 10^3$	$\alpha \times 2.4 \times 10^4$	$\alpha \times 5.2 \times 10^4$
$K_{\text{Z/ArO}}^{\text{sel}}$	$1.9 \times 10^{-3}$	$4.6 \times 10^{-2}$	1	2.2

The quantity  $K_{\text{Z/ArO}}^{\text{sel}}$  does not contain indefinite coefficient  $\alpha$ ; therefore, it can be used for qualitative analysis in the system  $\text{CHCl}_3\text{--borate}$  buffer. According to the results of simulation performed in [7], the kinetic profile with poisoning of catalyst should be expected at  $K_{\text{Z/ArO}}^{\text{sel}} \ll 1$ , whereas a normal pseudo-first-order kinetic curve should be obtained at a  $K_{\text{Z/ArO}}^{\text{sel}}$  value close to unity. This suggests that the observed change of the kinetic pattern (Fig. 2), depending on the anion nature, is qualitatively consistent with the above variation of  $K_{\text{Z/ArO}}^{\text{sel}}$  values.

Analysis of the kinetic curves for catalysis by cetyltrimethylammonium bromide (Fig. 1) and  $\text{Ph}_4\text{PCl}$  (Fig. 2a) leads us to conclude that the poisoning effect of 4-nitrophenoxide ion operates at a relatively small part of the kinetic curve, up to  $[\text{ArO}^-]_{\text{org}} \approx (5\text{--}10) \times 10^{-4}$  M. It is still possible to study the reaction rate at such concentration of 4-nitrophenoxide ion by adding 4-nitrophenol to the system  $\text{CHCl}_3\text{--borate}$  buffer before the reaction start. The free term  $b$  in Eq. (10) for catalysis by cetyltrimethylammonium bromide (pH 11,  $m = 0.01$  M) and  $\text{Ph}_4\text{PCl}$  (pH 10,  $m = 0.003$  M) with addition of  $5 \times 10^{-4}$  mol/l of 4-nitrophenol is statistically insignificant, indicating that poisoning effect of 4-nitrophenoxide ion disappears. In this case, the kinetic pattern conforms to the first-order equation, starting from the first experimental points.

From the above stated we can draw the following conclusion. The linear parts of the kinetic curves plotted in the first-order coordinates (Figs. 1a, 1b, 2a, 2b) correspond to the situation in which concurrent distribution of  $\text{Z}^-$  and  $\text{ArO}^-$  ions between the aqueous and organic phases does not affect (or almost does not affect) the quasiequilibrium concentration of  $\text{QOH}$  in the organic phase, so that  $[\text{QOH}]_{\text{org}}$  remains constant along a considerable part of the kinetic curve, despite accumulation of 4-nitrophenoxide ion. This should level out the catalytic activity of  $\text{Ph}_4\text{PCl}$  and  $\text{Ph}_4\text{PBr}$ .

Figure 4 shows the dependence of  $k_{\text{OH}}^{2\text{-ph}}$  values given in table on the phosphonium salt concentration

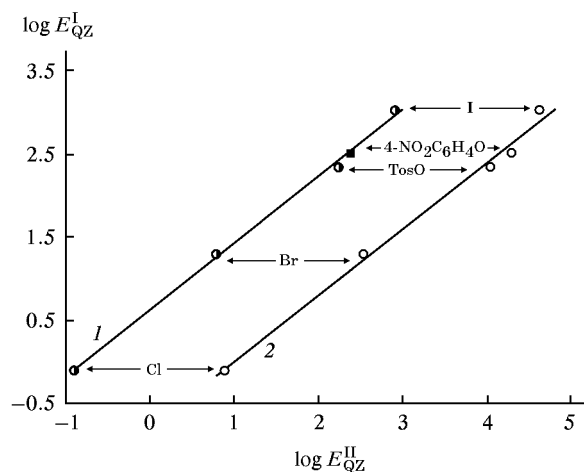


Fig. 3. Correlation between  $\log E_{\text{QZ}}^{\text{I}}$  ( $\text{Q} = \text{Bu}_4\text{N}$ ) for the system chloroform–water and  $\log E_{\text{QZ}}^{\text{II}}$ , (1)  $\text{Q} = \text{Bu}_4\text{N}$  and (2)  $\text{Q} = \text{Ph}_4\text{As}$ , for the system 1,2-dichloroethane–water [2].

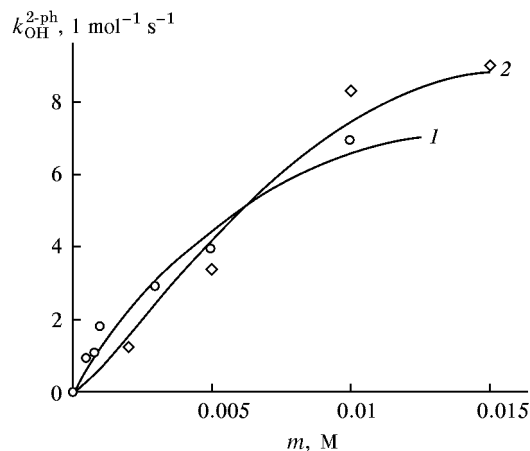


Fig. 4. Plot of  $k_{\text{OH}}^{2\text{-ph}}$  versus overall concentration of phase-transfer catalyst  $\text{Ph}_4\text{PX}$  in alkaline hydrolysis of *N*-benzyl-oxycarbonylglycine 4-nitrophenyl ester in the two-phase system  $\text{CHCl}_3\text{--borate}$  buffer (pH 10) at 25°C: (1)  $\text{X} = \text{Cl}$ , (2)  $\text{X} = \text{Br}$ .

$m$ . In the region corresponding to small values of  $k_{\text{OH}}^{2\text{-ph}}$  and  $m$  the dependence is linear. These linear parts were used to calculate the slopes ( $\tan \beta$ ) for the catalysts  $\text{Ph}_4\text{PCl}$  and  $\text{Ph}_4\text{PBr}$ , which are given below:

Salt	$\tan \beta \times 10^{-1}$	$N$	$S_{\text{tot}} \times 10^5$	$R$
$\text{Ph}_4\text{PCl}$	$65 \pm 7.6$	5	2.92	0.980
$\text{Ph}_4\text{PBr}$	$89 \pm 7$	3	4.2	0.996

In the reaction catalyzed by  $\text{Ph}_4\text{PI}$  (Fig. 2c), the concentration  $[\text{QOH}]_{\text{org}}$  changes during the process up to a high conversion of the substrate. Therefore,

unlike tetraphenylphosphonium chloride and bromide, it is impossible to select a linear part for quantitative estimation of  $\tan\beta$ . A rough graphical approximation of  $k^{2-ph}$  using the final parts of kinetic curves in Fig. 2c gives values which approach those obtained for  $\text{Ph}_4\text{PZ}$  ( $Z = \text{Cl}, \text{Br}$ ) at the corresponding concentration. Insofar as the values of  $E_{\text{Ph}_4\text{POAr}}$  and  $E_{\text{Ph}_4\text{PI}}$  are close to each other, the kinetic profile involving autocatalysis is unlikely to result from concurrent extraction of 4-nitrophenoxide and iodide ions. Obviously, the reason is some contribution of a different process whose nature is not clear so far.

Thus, despite strongly different selectivities of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, the apparent catalytic activities of the corresponding phosphonium salts approach each other as 4-nitrophenoxide ion accumulates in the system. The activity of  $\text{Ph}_4\text{PCl}$  is the highest in the initial period, but it falls down as the reaction progresses. By contrast, the activity of  $\text{Ph}_4\text{PI}$  is the lowest in the initial period, but it increases with time. As a result, both these approach the activity of  $\text{Ph}_4\text{PBr}$  when concurrent extraction of  $\text{ArO}^-$  ions becomes predominating over extraction of  $Z^-$ .

#### EXPERIMENTAL

The kinetic measurements were performed using an SF-26 spectrophotometer; pH values were determined on an EV-74 pH-meter. Standard borate buffer solutions with pH 10 and 11 were prepared as described in [13].

*N*-Benzyloxycarbonylglycine 4-nitrophenyl ester was synthesized and purified according to the procedure reported in [14], mp 126°C. The solvents were purified by usual methods [15]. Tetraphenylphosphonium chloride (Merck) was used without additional purification. Tetraphenylphosphonium bromide and tetraphenylphosphonium iodide were synthesized by reactions of tetraphenylphosphonium chloride with potassium bromide and iodide, respectively. Their purity was checked by titration of the anion. Cetyltrimethylammonium bromide was recrystallized from 1:1 ethyl acetate–benzene.

**Procedure for measuring reaction rate in the two-phase system.** The reactions were performed in a closed vessel maintained at a constant temperature. The mixture was stirred using a magnetic stirrer (at a maximal speed). Chloroform and borate buffer, 4.8 ml each, were mixed, and appropriate phase-transfer catalyst was added (its amount was calculated on a volume of 10 ml). The mixture was stirred for 15 min at 25°C, and 0.4 ml of a 0.125 N solution of ester **A** in dioxane was added. This moment was taken as reaction start. Samples (0.1 ml) were withdrawn

from the mixture at specified time intervals under continuous stirring and were poured into 5 ml of 0.1 M hydrochloric acid to stop the reaction. By special experiments we showed that no acid hydrolysis of ester **A** occurs under these conditions. The resulting solution was analyzed for 4-nitrophenol by spectrophotometry ( $\lambda$  320 nm). Its concentration was determined using calibration curves which were obtained from appropriate artificial mixtures.

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