Phase transfer catalysis and stereoselectivity in phenolysis of cyclic phosphazenes

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(received 07 Nov 04; accepted 22 Jun 05; published on the web30 Jun 05)

Abstract

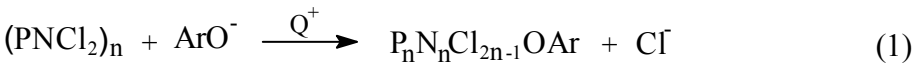
Kinetics of PTC phenolysis of cyclophosphazenes has been measured in liquid-liquid and liquid-solid two-phase systems. The PTC reactions can be described in terms of a single mechanism without resorting to subdivision into extraction and phase-transfer constituents. The rate-limiting stage and topology is determined by the ratio of rate constants responsible for transfer of the reactant between the phases and the rate of chemical interaction. In other words, the topology of phase-transfer reaction and its rate-limiting stage is influenced by the same factors. This provides a possibility of purposeful changing the reaction zone and, hence, stereoselectivity by variation in lipophilicity-nucleophilicity ratio of the reactants.

Keywords: Cyclophospazenes, phase-transfer catalysis, phenolysis, stereoselectivity

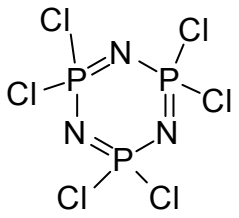
Introduction

Phase-transfer catalysis (PTC) as a versatile method for carrying out the reactions between non-polar substrates and ionic reactants is widely used in organic synthesis [1]. In this connection the studies on mechanisms and the factors influencing the rates and topology of PTC reactions are of great importance. It is noteworthy that PTC features both high selectivity and stereoselectivity, with the interface being a controlling factor.

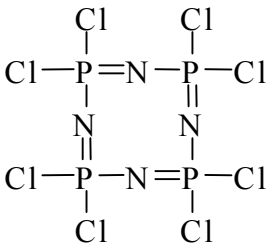
Here we report a study of mechanism and stereoselectivity in PTC phenolyis of cyclophosphazenes.



(1)



n=3



n=4

ArO^- = 4-NO_2PhO^-, **1**
2,5-$(NO_2)_2PhO^-$, **2**
2,4-$(NO_2)_2PhO^-$, **3**

$Q = Et_3BzN^+$, **a**
Bu_4N^+, **b**
K^+ (18-crown-6), **c**

PTC reaction (1) is attractive due to practical value of aryloxy- and alkoxy derivatives [2], which are easily formed under PTC conditions[3] and show considerable promise as phase-transfer catalysts.[4] Moreover, some typical aspects of the phenolysis can be extended to a variety of phase-transfer nucleophilic substitutions.

Results and Discussion

Major kinetic relationships of phase-transfer reaction (1) were established by reaction between 4-nitrophenol and phosphonitrile chloride trimer (n=3) in borate buffer (pH 9.18) – organic solvent (1:1 by volume) two-phase system in the presence of triethylbenzylammonium chloride (Q = **a**) as a phase-transfer catalyst.[5] With no catalyst added, the arylate ion fails to pass into the organic phase (trichloromethane, sym-tetrachloroethane, *o*-dichlorobenzene) and phenolysis of water-insoluble trimer escapes detection. Introduction of quaternary ammonium salt into the two-phase system gives rise to tetraalkylammonium arylate in the organic medium, whereas the solubility of the substrate in the borate buffer remains unchanged.

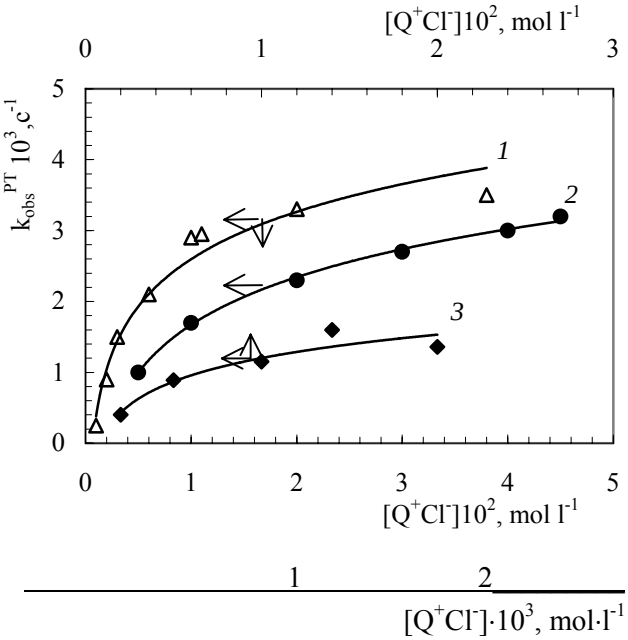


Figure 1. Change in observed rate constants of cyclophosphazene phenolysis with concentration of triethylbenzylammonium chloride in the system borate buffer – organic solvent at 25 °C. *1* – trichloromethane; *2* – *sym*-tetrachloroethane (bottom scale, $[Q^+Cl^-]\cdot10^3$ mol·l^{-1}); *3* – o-dichlorobenzene.

Substrate content of organic phase $[(PNCl_2)_3]_{org} = 2.25\cdot10^{-3}$ M (*1*) and $1\cdot10^{-3}$ M (*2*,*3*).

The observed rate of the phase-transfer reaction k_{obs}^{PT} remains unchanged during the reaction. In all cases the plots of k_{obs}^{PT} against concentration of the catalyst are non-linear and tend to reach a limiting value (Fig. 1). The equilibrium content of reactant **1a** of organic phase, as measured by an extent of arylate ion transfer (α_{ArO}) from aqueous phase (aq) into organic phase (org), is changed in a similar manner. As a result the rate constant $k_2^{PT} = k_{obs}^{PT}/[(PNC_2)_3]_{org}$ is linearly dependent on α_{ArO} (Fig. 2).

$$\alpha_{ArO} = \frac{[ArO^-]_{org}}{[ArO^-]_{aq}} \qquad (2)$$

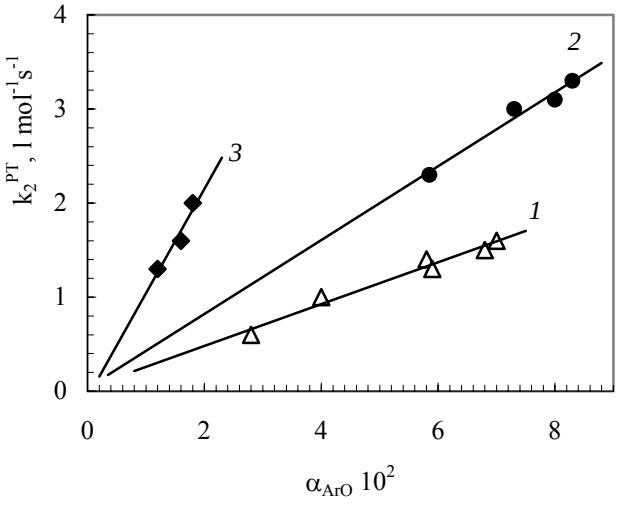


Figure 2. Rate constants of phenolysis of cyclotriphosphazene *vs*. partitioning of 4-nitrophenolate anion in borate buffer – organic solvent two-phase system at 25 °C: *1*-tetrachloromethane, *2* - *sym*-tetrachloroethane, *3* - o-dichlorobenzene.

Varied slopes of the curves in Fig. 2 suggest that k_{obs}^{PT} is influenced both by the extractability of the salt **1a** into the organic phase and polarity of organic solvent. Therefore, the phenolysis of cyclotriphosphazene proceeds in the bulk organic phase or, alternatively, in the organic sublayer adjacent to the interface. As a first approximation (without regard for the reaction zone, i.e., the place where the reaction occurs), the phenolysis of cyclotriphosphazene can be described by the scheme involving the activated species of the reactant – tetraalkylammonium arylate - initially formed at the first equilibrium stage:

$$ArO^-_{aq} + Q^+Cl^-_{org} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArO^-Q^+_{org} + Cl^-_{aq} \quad (3)$$

$$ArO^-Q^+_{org} + (PNCl_2)_{3\,org} \xrightarrow{k_{org}} P_3N_3Cl_5OAr_{org} + Q^+Cl^-_{org} \quad (4)$$

where k_{org} is the rate constant of cyclotriphosphazene phenolysis in the organic phase (or at the interface); k_1 and k_{-1} are the rate constants of the forward and reverse transfer of the reactant between the phases, respectively. It is the k_1/k_{-1} rate ratio, which determines the selectivity of the ion exchange:

$$K^{sel}_{ArO/Cl} = \frac{k_1}{k_{-1}} = \frac{\alpha_{ArO}}{\alpha_{Cl}} = \frac{[ArO^-Q^+]_{org}[Cl^-]_{aq}}{[ArO^-]_{aq}[Q^+Cl^-]_{org}} \quad (5)$$

At $[(PNCl_2)_3]>>[ArO^-]$, assuming the steady-state concentration of tetraalkylammonium arylate, slow exchange of $Q^+Cl^-_{org}$ by ArO^-_{aq}, and rapid reaction of $ArO^-Q^+_{org}$ both with Cl^-_{aq} and the substrate, we get [6]:

$$k_{obs}^{PT} = \frac{k_{org} K_{ArO/Cl}^{sel} [Q^+Cl^-]_{org} [(PNCl_2)_3]_{org}}{[Cl^-]_{aq} + k_{org}[(PNCl_2)_3]/k_{-1}} \quad (6)$$

According to Equation (6) the effect of the substrate concentration on k_{obs}^{PT} is determined by the catalyst content of the two-phase system. Thus, both a decrease in total concentration of Q^+Cl^- and an increase in $[(PNCl_2)_3]_{org}$ give rise to $k_{org}\ [(PNCl_2)_3]_{org}/k_{-1} >> [Cl^-]_{aq}$ and, as a consequence, k_{obs}^{PT} is determined by partitioning of the reactant between the phases:

$$k_{obs}^{PT} = k_{-1}\ \alpha_{ArO}[Cl^-]_{aq}\ , \quad (7)$$

Under these conditions the plots of the observed rate constants of the phase-transfer phenolysis against the concentration of cyclotriphosphazene are flattened: the higher the concentration of phase-transfer catalyst of the system, the later the "saturation" occurs (Fig. 3, a-c).

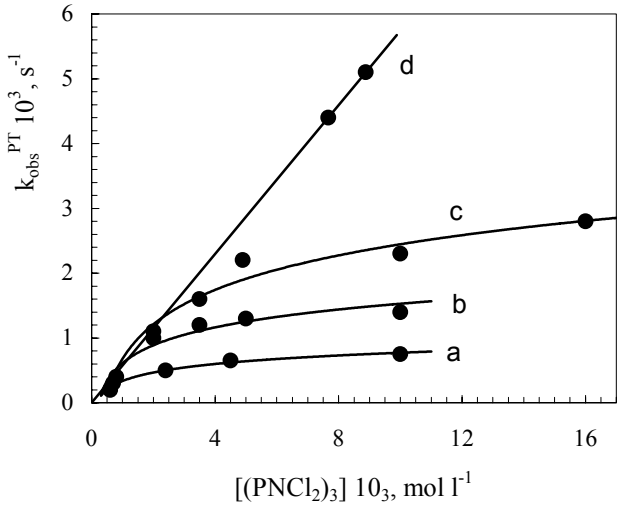


Figure 3. Observed rate constant of phenolysis of cyclotriphosphazene *vs* substrate concentration in borate buffer – trichloromethane system at 25 °C. a - $[Cl^-]_{aq} = 3.65\cdot10^{-3}$ mol·l^{-1}, b - $[Cl^-]_{aq} = 2\cdot10^{-2}$ mol·l^{-1}, c - $[Cl^-]_{aq} = 2.9\cdot10^{-2}$ mol·l^{-1}, d – $[Cl^-]_{aq} = 5.00\cdot10^{-2}$ mol·l^{-1}.

At sufficiently high concentrations of Q^+Cl^- ($[Cl^-]_{aq} >> k_{org}\,[(PNCl_2)_3]_{org}/k_{-1}$) the reaction is controlled by the rate of phenolysis, with k_{obs}^{PT} being linearly dependent on the content of cyclotriphosphazene (Fig. 3, d):

$$k_{obs}^{PT} = k_{org}\alpha_{ArO}[(PNCl_2)_3]_{org} \qquad (8)$$

Phase-transfer phenolysis of cyclotriphosphazenes is adequately described by equation (6), as evidenced by similarity in k_{org} calculated from the data in Figs. 1 and 3 by Eq. (6) and by its modified form (8) at maximum values of α_{ArO} (Table 1).

Table 1. Rate constants of the reaction between the salt **1a** and hexacyclotriphosphazene in organic phase

Organic phase	k_{org} , $l\cdot mol^{-1}\cdot s^{-1}$		
	Calculated by Eq. (6)	Calculated by Eq. (8)	Direct measurement in separated organic phase
Trichloromethane	21.4 ± 1.0	21.9 ± 3,3	15.7 ± 0,6
sym-Tetrachloroethane	42.6 ± 4.1		40.0 ± 4.2
o-Dichlorobenzene		141 ± 71	166 ± 15

Similar kinetic behavior has been reported in our recent study of reactions (9) and (10) with tetraalkylammonium arylate as a nucleophile, i.e. at $[Cl^-]_0 = 0$ [7].

$$ArO^-_{aq} + Q^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArO^-Q^+_{org} \qquad (9)$$

$$ArO^-Q^+_{org} + (PNCl_2)_{n\,org} \xrightarrow{k_2} P_nN_nCl_{2n-1}OAr + Q^+Cl^- \qquad (10)$$

Again, at low conversions the observed pseudo-first order rate constant of phenolysis is described by equation (11).

$$k_{obs}^{PT} = \frac{k_1k_2[Q^+]_{aq}[(PNCl_2)_n]_{org}}{k_{-1} + k_2[(PNCl_2)_n]_{org}} \; . \qquad (11)$$

The latter, as with (6), was deduced assuming quasi steady-state concentration of arylate ion. In this case the observed rate constant of phenolysis is linearly dependent on arylate ion content of the organic phase (Fig. 4). The corresponding data on reactivity of $ArO^-\,Q^+$ are given in Table 2.

Table 2. Reactivity of tetraalkylammonium arylates in phenolysis of hexacyclotriphosphazene in water-saturated organic solvents (25 °C)

Solvent	ArO^-Q^+ [a]	$k_{2(rel)}$ [b]
PhCl	3a	1.0
PhCl	1b	500.0
PhCl	1a	430.0
$CHCl_3$	1a	9.3

[a] At $[ArO^-Q^+]_o = 1\cdot10^{-4}$ mol·l^{-1} and $[(PNCl_2)_3]_o:[ArO^-Q^+]_o$= (10-30); [b] In units of k_2 = (2.32±0.10) l·mol^{-1}·s^{-1} for **3a**.

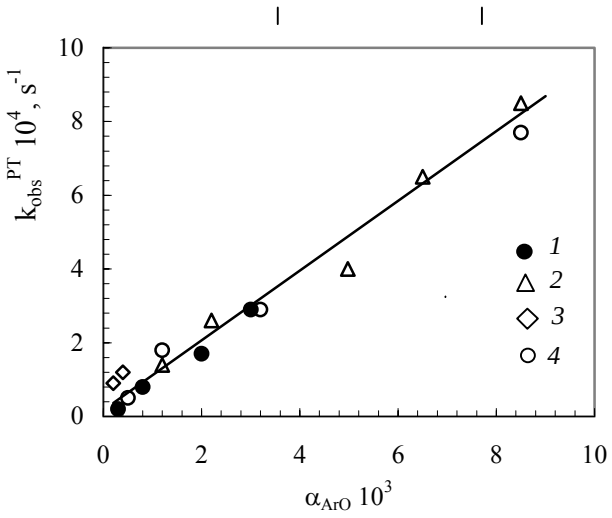


Figure 4. Observed rate constant of PTC reaction between tetraalkylammonium arylates and hexachlorocyclotriphosphazene vs. α_{Aro} in borate buffer (pH 9.18) – chlorobenzene two-phase system (25 °C): *1* – **3a**, *2* – **1б**, *3* - **1a**, 4 – **1a** , trichloromethane.

Equation (11) can be reduced to two limiting cases:

1) at $k_{-1} >> k_2 [(PNCl_2)_n]_{op}$ the equation (11) takes the form

$$k_{obs}^{PT} = k_2 \alpha_{ArO} [(PNCl_2)_n]_{org} \quad (12)$$

In this case the observed rate constant of phenolysis is linearly dependent on the concentration of cyclophosphazene (Fig. 5, curves *1*, *1'*, *4*), with the chemical interaction between arylate ion and substrate being the rate-limiting factor.

2) at $k_{-1} << k_2 [(PNCl_2)_n]_{org}$ the equation (11) is simplified to

$$k_{obs}^{PT} = k_1[Q^+]_{aq} \quad (13)$$

In this case the observed rate constant is independent of the substrate content of the two-phase system (Fig. 5, curves *2′*, *3*) and transfer of the nucleophile is the rate-limiting stage.

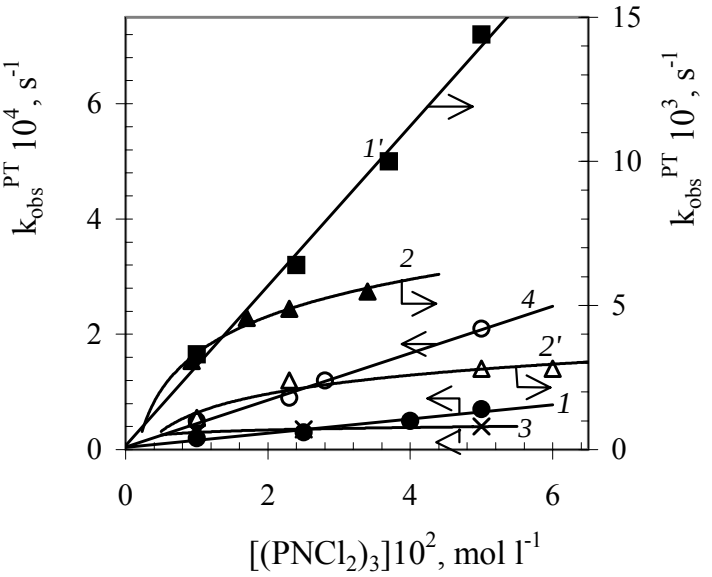
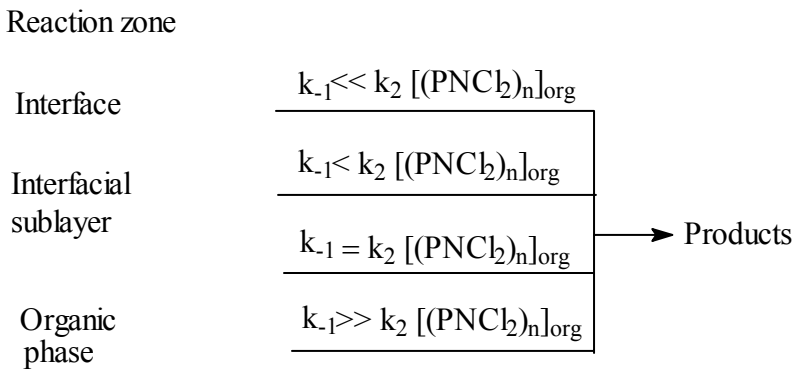


Figure 5. Effect of substrate concentration on observed rate constant of phenolysis (k_{obs}^{PT}) in the system borate buffer – organic solvent (25 °C): *1* – **3а**, chlorobenzene; *1′* – **3б**, chlorobenzene; *2* – **1б**, octachlorocyclotetraphosphazene, chlorobenzene; *2′* – **1б**, chlorobenzene; *3* – **1а**, chlorobenzene; *4* – **1а**, trichloromethane.

The data presented here suggest that the PTC reaction can be described in terms of a single mechanism, as opposed to the generally accepted subdivision of the mechanism into extraction and phase-transfer constituents.[8,9,10] This mechanism is summarized (Scheme 1).

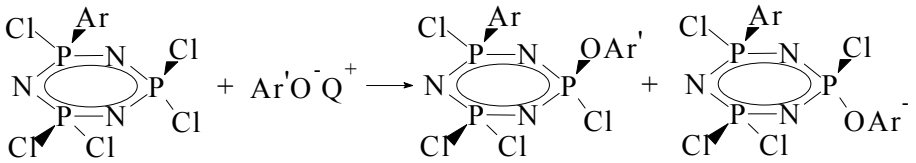


Scheme 1

Therefore, the topology of PTC reactions is influenced by the same factors as the rate-limiting stage. This provides a possibility of purposeful changing the interaction zone of

the substrate with phase-transfer reactant by choosing an appropriate lipophilicity-nucleophilicity ratio of the latter. The topology of the PTC reactions must be sensitive to such changes, provided that the rate of the corresponding homogeneous reaction and hydrophilic properties of the ionic reactant are sufficiently high.

The above requirements are valid for formation of cis and trans isomers of bis(aryloxy)cyclophosphazenes in phase-transer phenolysis of monoaryloxy derivatives of phospazene trimer.



I *cis* *trans* (14)

Ar = 4-$NO_2C_6H_4$ (1), 2,4-$(NO_2)_2C_6H_3$ (3), Ph (4);
Ar'= Ph, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
Q = Et_3NCH_2Ph (a), Bu_4N (b), Me_4N (c), $Me_3NCH_2CH_2Cl$ (d), Na (f).

In a two-fold excess of the substrate, the reaction (14) gives rise to a mixture of 1,3-substituted *cis*- and *trans*-isomers (admixed with a ~3 % of 1,1-substitutuion products) in 95% yield. Under homogeneous conditions the cis/trans ratio of the products was found to be 57:43 irrespective of the structure of the reactant and the nature of organic solvent. Slight excess of cis-isomer is usually attributed to the "through-space" interaction between oxygen 2p orbitals in aryloxy group and phosphorus 3d orbital in the substrate.[11] The reactivity of monoaryl substituted cyclophosphazenes in reaction (14) is 2-3 times lower than that for hexacyclotriphosphazene (k_2 ~1000 $l \cdot mol^{-1} \cdot s^{-1}$ for reaction with $1 \cdot 10^{-4}$ $mol \cdot l^{-1}$ of **1a** in water-saturated chlorobenzene). An extent of transportation (α_{Aro}) from water phase into chlorobenzene amounts to < 1.0 for tetraalkylammonium arylate **3b**, the most lipophilic compound from those studied; otherwise it is about 10^2-10^4 times lower.[7] This suggests that the rate-limiting stage and, hence, the zone of PTC reaction (14) can be changed easily. As evidenced by the above data on PTC reaction between unsubstituted hexachlorocyclophosphazene and salt **1a**, with the use of trichloromethane the reaction proceeds in the bulk of organic phase, whereas with chlorobenzene, as a solvent of lower solvating ability toward tetraalkylammonium arylate, the reaction proceeds at the interface. Our study of reaction 14 between substrate (Ar' = 4-$NO_2C_6H_4$) and reactant **1a** provides further support for these conclusions. It was found that in borate buffer (pH 9.18) – tetrachloromethane two-phase system an extent of transfer of triethylammonium 4-nitrophenolate into the organic phase is sufficiently high ($\alpha_{Aro} = 3 \cdot 10^{-3}$ at $[1a]_0 = 1.25 \cdot 10^{-3}$ $mol \cdot l^{-1}$) and is 10 times that found in chlorobenzene, whereas the reaction rate in water-saturated trichloromethane (i.e. under conditions similar to those in the bulk organic phase) is ~10 times lower than that in wet chlorobenzene. The observed rate of phase-transfer reaction is linearly increased with concentration of

cyclophosphazene and remains unchanged at the stirring rates from 750 to 1400 rpm. Under these conditions, therefore, the reaction proceeds predominantly in the bulk organic phase. In contrast, as reported,[9] in borate buffer (pH 9.18) –chlorobenzene two-phase system the plot of observed rate constants of phenolysis against substrate concentration is nonlinear. Energy of activation of the overall reaction is different for various portions of the curve and decreases from 10.8±1.2 kcal·mol^{-1} (as for chemical interaction) to 4.2±2.0 kcal·mol^{-1} (diffusion-controlled reaction) .[9]

Table 3 illustrates the effects of changing the reaction zone on cis/trans product ratio in reaction (14).

Table 3. Effects of PTC conditions on isomeric composition of the products in reaction between phosphazene 4 (Ar' = 4-$NO_2C_6H_4$) and tetraalkylammonium 4-nitrophenolates at 25 °C*

ArO^-Q^+	Solvent	Region of PTC reaction	*cis/trans* Product ratio
1a	$CHCl_3$	Organic phase	55 : 45
1a	PhCl	Interface	65 : 35
1a	PhCl	Organic phase **	57 : 43
1б	PhCl	Organic phase	58 : 42
	Under…Homogeneous reaction		57 : 43
* $[(PNCl_2)_3]_o = 0.04$ mol·l^{-1}; $[ArO^-Q^+]_o = 0.02$ mol·l^{-1}.			
** $[(PNCl_2)_3]_o = 0.008$ mol·l^{-1}; $[ArO^-Q^+]_o = 0.04$ mol·l^{-1}.			

As is the case with unsubstituted substrate, increased extractability of phase-transfer reactant when going from triethylbenzylammonium cation in chlorobenzene to more lipophilic tetrabutylammonium cation in tetrachloromethane causes the reaction to proceed into the organic phase and, as a result, gives rise to a decrease in its stereoselectivity to the value similar to that found under homogeneous conditions (Table 3). The same is true for 5-fold decrease in analytical concentration both of the substrate and the reactant at the same concentration ratio, since Eq. 13 is no longer valid and, again, the reaction moves into the bulk of organic phase (Table 3).

In addition, we studied also the effects of hydrophilicity of phase-transfer catalyst Q^+ on cis/trans ratio, since it is hydrophilic phase-transfer agents for arylate ions that causes the reaction (14) to proceed predominantly at the interface and, hence, give rise to increase in selectitvity.

Contrary to the expectations, increased hydrophilic properties of cation Q^+ in the order **1a**, **2d**, **2e** up to such a weak* "phase-transfer" catalyst as Na^+ provides no changes in cis/trans products ratio and, moreover, is accompanied by a decrease in catalytic activity of the cations. With the same hydrophilic $Q^+ = Na^+$, however, increased hydrophobic properties both of arylate ion and substrate result with an increase in selectivity (Table 4). It seems likely that the interface causes cross-orientation

* Two-phase reactions were carried out only to 10% conversion (approximately 100 hr), since sodium nitrophenolates are incapable of transferring into chlorobenzene.

of the substrate and the reactant according to their hydrophobic-hydrophilic characteristics. It is known that the interface is structurally similar to the Stern layer[10] of a thick layer ranging from 5-6 Å[10] to 8-12 Å [12] rather than a monomolecular layer. Arylate ion is confined by hydrophilic cation at the interface thus favoring the formation of cis-substituted derivative.

If (as with the monophenoxy phosphazene) the substrate contains a less hydrophobic Ar', the phosphazene ring is sufficiently lipophilic[2] to favor the trans-substitution (Table 4).

Table 4. Structure effects of reactant and substrate on stereoselectivity of PTC phenolysis of monoaryloxypentachlorocyclotriphosphazenes in borate buffer (pH 9.18) – chlorobenzene two-phase system (25 °C)

Substrate	ArO^-Q^+	*cis/trans*-Isomeric ratio
Effect of cation Q^+		
Ar' = 4-$NO_2C_6H_4$	1e	62 : 38
Ar' = 4-$NO_2C_6H_4$	1г	65 : 35
Ar' = 4-$NO_2C_6H_4$	1д	63 : 37
Ar' = 4-$NO_2C_6H_4$	1a	65 : 35
Effect of substrate		
Ar' = 2,4-$NO_2C_6H_4$	3e	75 : 25
Ar' = 4-$NO_2C_6H_4$	3e	68 : 32
Ar' = Ph	3e	49 : 51
Effect of anion ArO^-		
Ar' = 4-$NO_2C_6H_4$	3e	68 : 32
Ar' = 4-$NO_2C_6H_4$	1e	62 : 38
Ar' = Ph	3e	49 : 51
Ar' = Ph	1e	54 : 46
Ar' = Ph	4e*	58 : 42

*We failed to carry out the similar reaction of salt **4e** with phosphazene **1** (Ar' - 4-$NO_2C_6H_4$) due to considerable contribution from the exchange between phenoxy and 4-nitrophenoxy groups in the substrate.

The description proposed can also be extended to other phase-transfer catalysts, such as betaines $C_{16}H_{33}(CH_3)_2N^+CH_2COO^-$ and $(CH_3)_3N^+CH_2COO^-$, whose analogues were used in some reactions under PTC conditions.[8] It was shown that the former is sufficiently hydrophobic and capable of transferring 4-nitrophenolate ion into the organic phase, so the phenolysis of **1** (Ar' = 4-$NO_2C_6H_4$) proceeds in the bulk of organic phase with the cis/trans product ratio of 56 : 44, i.e., its stereoselectivity similar to that under homogeneous conditions. In contrast, the latter, as a more hydrophilic compound, is strongly confined at

the interface due to its carboxylic moiety and, in spite of some decrease in catalytic activity, which results in increased cis/trans product ratio for bis(4-nitrophenoxy)cyclophosphazene to 69:31.

Preliminary studies of interfacial effects in liquid-solid two-phase systems showed than in anhydrous chlorobenzene-solid ArO~Q^+ systems, the following three types of interaction are possible:

1) reaction of insoluble potassium arylate with 4-nitrophenoxycyclophosphazene fails to occur;
2) in the presence of 18-crown-6, the complexed potassium 4-nitrophenolate is transferred into chlorobenzene (as judged from change in its color) and the reaction proceeds in the bulk of organic phase with a selectivity of 58:42 normally observed for of the reactions under homogeneous conditions;
3) with **1a** as a reactant, cis/trans product ratio in phenolysis was found to be 65:35 and corresponds to that normally observed for the reactions which proceed at the interface of liquid/liquid systems.

Biographical Sketch

Anatolii Afon'kin. Born in 14 February 1960. Graduated from Chemical Faculty of Donetsk State University (1982). Candidate of Chemistry (Ph.D.). Senior researcher. Areas of scientific interest: phase-transfer catalysis, chemistry and biotechnology of natural antitumor substances. He has about 80 publications.

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Mihail Kostrikin. Born in 6 July 1973. Graduated from Chemical Faculty of Donetsk State University (1995). Junior researcher. Areas of scientific interest: phase-transfer catalysis, chemistry of alkaloids. He has 13 publications.

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