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 web 30 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: Cyclophosphazenes, 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. 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 phenolysis of cyclophosphazenes.

\[
(P\text{NCI}_2)_n + \text{ArO}^- \xrightarrow{Q^+} P_nN_{n-1}\text{Cl}_{2n-1}\text{OAr} + \text{Cl}^-
\]  

(1)
PTC reaction (1) is attractive due to practical value of aryloxy- and alkoxy derivatives, which are easily formed under PTC conditions and show considerable promise as phase-transfer catalysts. 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 = Et3BzN+) as a phase-transfer catalyst. 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, \([\text{Q}^+\text{Cl}^-] \cdot 10^3 \text{ mol} \cdot \text{l}^{-1}\); 3 – o-dichlorobenzene.

Substrate content of organic phase \([(\text{PNCI}_2)_3]_{\text{org}} = 2.25 \cdot 10^{-3} \text{ M (1)} \) and \(1 \cdot 10^{-3} \text{ M (2,3)}\).

The observed rate of the phase-transfer reaction \(k_{\text{obs}}^{\text{PT}}\) remains unchanged during the reaction. In all cases the plots of \(k_{\text{obs}}^{\text{PT}}\) 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 (\(\alpha_{\text{ArO}}\)) from aqueous phase (aq) into organic phase (org), is changed in a similar manner. As a result the rate constant \(k_2^{\text{PT}} = k_{\text{obs}}^{\text{PT}}/[(\text{PNC}_2)_3]_{\text{org}}\) is linearly dependent on \(\alpha_{\text{ArO}}\) (Fig. 2).

\[
\alpha_{\text{ArO}} = \frac{[\text{ArO}^-]_{\text{org}}}{[\text{ArO}^-]_{\text{aq}}} \quad (2)
\]
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 $k_{\text{obs}}^{\text{PT}}$ 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:

$$\begin{align*}
\text{ArO}^-_{\text{aq}} + \text{Q}^+_{\text{org}} & \xrightarrow{k_1} \text{ArO}^+_{\text{org}} + \text{Cl}^-_{\text{aq}} \\
\text{ArO}^-_{\text{org}} + (\text{PNCI})_3_{\text{org}} & \xrightarrow{k_{\text{org}}} \text{P}_3\text{NCl}_5 \text{OAr}_{\text{org}} + \text{Q}^+_{\text{org}} \text{Cl}^-_{\text{org}}
\end{align*}$$

(3)

(4)

where $k_{\text{org}}$ 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:

$$K_{\text{ArO/Cl}}^{\text{sel}} = \frac{k_1}{k_{-1}} = \frac{\alpha_{\text{ArO}}}{\alpha_{\text{Cl}}} = \frac{[\text{ArO}^+_{\text{org}}][\text{Cl}^-_{\text{aq}}]}{[\text{ArO}^-_{\text{aq}}][\text{Q}^+_{\text{Cl}^-}]_{\text{org}}}$$

(5)
At \([(PNCl_2)_3] >> [ArO^-]\), assuming the steady-state concentration of tetraalkylammonium arylate, slow exchange of \(Q^+\text{Cl}^-\) by \(\text{ArO}^-\text{aq}\), and rapid reaction of \(\text{ArO}^-Q^+\text{org}\) both with \(\text{Cl}^-\text{aq}\) and the substrate, we get [6]:

\[
k_{\text{obs}}^{\text{PT}} = \frac{k_{\text{org}}K_{\text{ArOCl}}[Q^+\text{Cl}^-]_{\text{org}}[(PNCl_2)_3]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}} + k_{\text{org}}[(PNCl_2)_3]/k_{-1}}
\]  

(6)

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

\[
k_{\text{obs}}^{\text{PT}} = k_{-1} \alpha_{\text{ArO}}[\text{Cl}^-]_{\text{aq}}
\]  

(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 - \([\text{Cl}^-]_{\text{aq}} = 3.65 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}\), b - \([\text{Cl}^-]_{\text{aq}} = 2 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}\), c - \([\text{Cl}^-]_{\text{aq}} = 2.9 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}\), d – \([\text{Cl}^-]_{\text{aq}} = 5.00 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}\).
At sufficiently high concentrations of Q$^+$\text{Cl}^- ([\text{Cl}^-]_{\text{aq}} \gg k_{\text{org}} [(\text{PNCl}_2)_3]_{\text{org}}/k_{-1}) the reaction is controlled by the rate of phenolysis, with $k_{\text{obs}}^{PT}$ being linearly dependent on the content of cyclotriphosphazene (Fig. 3, d):

$$ k_{\text{obs}}^{PT} = k_{\text{org}} \alpha_{\text{ArO}} [(\text{PNCl}_2)_3]_{\text{org}} \quad (8) $$

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

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

<table>
<thead>
<tr>
<th>Organic phase</th>
<th>$k_{\text{org}}$, l-mol$^{-1}$-s$^{-1}$ Calculated by Eq. (6)</th>
<th>$k_{\text{org}}$, l-mol$^{-1}$-s$^{-1}$ Calculated by Eq. (8)</th>
<th>Direct measurement in separated organic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloromethane</td>
<td>21.4 ± 1.0</td>
<td>21.9 ± 3.3</td>
<td>15.7 ± 0.6</td>
</tr>
<tr>
<td>sym-Tetrachloroethane</td>
<td>42.6 ± 4.1</td>
<td></td>
<td>40.0 ± 4.2</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>141 ± 71</td>
<td></td>
<td>166 ± 15</td>
</tr>
</tbody>
</table>

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

$$ \text{ArO}^-_{\text{aq}} + Q^+_{\text{aq}} \xrightleftharpoons[k_{-1}]{k_1} \text{ArO}^+Q^+_\text{org} \quad (9) $$

$$ \text{ArO}^+Q^+_\text{org} + (\text{PNCl}_2)_n \xrightarrow{k_2} P_nN_n\text{Cl}_{2n-1}O\text{Ar} + Q^+\text{Cl}^- \quad (10) $$

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

$$ k_{\text{obs}}^{PT} = \frac{k_1 k_2 [Q^+]_{\text{aq}} [(\text{PNCl}_2)_n]_{\text{org}}}{k_{-1} + k_2 [(\text{PNCl}_2)_n]_{\text{org}}} \quad (11) $$

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 \text{ArO}^- Q^+$ are given in Table 2.
Table 2. Reactivity of tetraalkylammonium arylates in phenolysis of hexacyclotriphosphazene in water-saturated organic solvents (25 °C)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ArO’Q⁺ᵃ</th>
<th>k₂(rel)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCl</td>
<td>3a</td>
<td>1.0</td>
</tr>
<tr>
<td>PhCl</td>
<td>1b</td>
<td>500.0</td>
</tr>
<tr>
<td>PhCl</td>
<td>1a</td>
<td>430.0</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>1a</td>
<td>9.3</td>
</tr>
</tbody>
</table>

ᵃ At [ArO’Q⁺]₀ = 1·10⁻⁴ mol·l⁻¹ and [(PNCl₂)₃]₀:[ArO’Q⁺]₀ = (10⁻³₀); ᵇ In units of k₂ = (2.32±0.10) l·mol⁻¹·s⁻¹ for 3a.

Figure 4. Observed rate constant of PTC reaction between tetraalkylammonium arylates and hexachlorocyclophosphazene vs. α_Aro in borate buffer (pH 9.18) – chlorobenzene two-phase system (25 °C): 1 – 3a, 2 – 1b, 3 - 1a, 4 – 1a, trichloromethane.

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

1) at k⁻¹ >> k₂ [(PNCl₂)ₙ]₀ the equation (11) takes the form

\[ k_{obs}^{PT} = k_2 \alpha_{ArO} [(PNCl₂)ₙ]_{org} \] (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 << k₂ [(PNCl₂)ₙ]₀ the equation (11) is simplified to

\[ k_{obs}^{PT} = k_1 [Q⁺]_{aq} \] (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 – 3α, chlorobenzene; 1' – 3β, chlorobenzene; 2 – 16, octachlorocyclooctetraphosphazene, chlorobenzene; 2' – 16, chlorobenzene; 3 – 1α, chlorobenzene; 4 – 1a, 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. 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-transfer phenolysis of monoaryloxy derivatives of phosphazene trimer.

\[
\begin{align*}
\text{Cl} & \quad \text{Ar} & \quad \text{Cl} & \quad \text{N} & \quad \text{P} & \quad \text{O} & \quad \text{Q} & \quad + & \quad \text{Ar'O}^{-} & \quad \text{Q}^{+} & \quad \rightarrow & \quad \text{Cl} & \quad \text{N} & \quad \text{P} & \quad \text{O} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{N} & \quad \text{P} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{O} & \quad \text{Ar}' & & \quad \text{cis} & & \quad \text{trans} \\
(14)
\end{align*}
\]

Ar = 4-NO\(_2\)C\(_6\)H\(_4\) (1), 2,4-(NO\(_2\))\(_2\)C\(_6\)H\(_3\) (3), Ph (4);
Ar' = Ph, 4-NO\(_2\)C\(_6\)H\(_4\), 2,4-(NO\(_2\))\(_2\)C\(_6\)H\(_3\);
Q = Et\(_3\)NCH\(_2\)Ph (a), Bu\(_4\)N (b), Me\(_4\)N (c), Me\(_3\)NCH\(_2\)CH\(_2\)Cl (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-substitution 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.\(^\text{11}\) The reactivity of monoaryl substituted cyclophosphazenes in reaction (14) is 2-3 times lower than that for hexacyclotriphosphazene (\(k_2 \sim 1000 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\) for reaction with \(1 \cdot 10^{-4} \text{ mol}\cdot\text{l}^{-1}\) of \(1a\) in water-saturated chlorobenzene). An extent of transportation (\(\alpha_{\text{Aro}}\)) 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.\(^\text{7}\) 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\(_2\)C\(_6\)H\(_4\)) 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 (\(\alpha_{\text{Aro}} = 3 \cdot 10^{-3}\) at \([1a]_0 = 1.25 \cdot 10^{-3} \text{ mol}\cdot\text{l}^{-1}\)) 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, 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) .

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 (Ar¹ = 4-NO₂C₆H₄) and tetraalkylammonium 4-nitrophenolates at 25 °C*

<table>
<thead>
<tr>
<th>ArO⁻Q⁺</th>
<th>Solvent</th>
<th>Region of PTC reaction</th>
<th>cis/trans Product ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>CHCl₃</td>
<td>Organic phase</td>
<td>55 : 45</td>
</tr>
<tr>
<td>la</td>
<td>PhCl</td>
<td>Interface</td>
<td>65 : 35</td>
</tr>
<tr>
<td>la</td>
<td>PhCl</td>
<td>Organic phase **</td>
<td>57 : 43</td>
</tr>
<tr>
<td>lb</td>
<td>PhCl</td>
<td>Organic phase</td>
<td>58 : 42</td>
</tr>
<tr>
<td>Under…Homogeneous reaction</td>
<td></td>
<td></td>
<td>57 : 43</td>
</tr>
</tbody>
</table>

* [(PNCl₂)₃]₀ = 0.04 mol·l⁻¹; [ArO⁻Q⁺]₀ = 0.02 mol·l⁻¹.

** [(PNCl₂)₃]₀ = 0.008 mol·l⁻¹; [ArO⁻Q⁺]₀ = 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 selectivity.

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\textsuperscript{10} of a thick layer ranging from 5-6 Å\textsuperscript{10} to 8-12 Å\textsuperscript{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 \( \text{Ar}' \), the phosphazene ring is sufficiently lipophilic\textsuperscript{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)

<table>
<thead>
<tr>
<th>Substrate ArO-</th>
<th>Effect of cation Q+</th>
<th>cis/trans-Isomeric ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
<td>1e</td>
<td>62 : 38</td>
</tr>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
<td>1( \gamma )</td>
<td>65 : 35</td>
</tr>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
<td>1( \delta )</td>
<td>63 : 37</td>
</tr>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
<td>1a</td>
<td>65 : 35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar}' = 2,4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
</tr>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
</tr>
<tr>
<td>( \text{Ar}' = \text{Ph} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of anion ArO-</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
</tr>
<tr>
<td>( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 )</td>
</tr>
<tr>
<td>( \text{Ar}' = \text{Ph} )</td>
</tr>
<tr>
<td>( \text{Ar}' = \text{Ph} )</td>
</tr>
<tr>
<td>( \text{Ar}' = \text{Ph} )</td>
</tr>
</tbody>
</table>

*We failed to carry out the similar reaction of salt 4e with phosphazene 1 (\( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 \)) 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 \( \text{C}_{16}\text{H}_{33}\text{(CH}_3\text{)}_2\text{N}^+\text{CH}_2\text{COO}^- \) and \( (\text{CH}_3)\text{_3N}^+\text{CH}_2\text{COO}^- \), whose analogues were used in some reactions under PTC conditions.\textsuperscript{8} It was shown that the former is sufficiently hydrophobic and capable of transferring 4-nitrophenoxy ion into the organic phase, so the phenolysis of 1 (\( \text{Ar}' = 4\text{-NO}_2\text{C}_6\text{H}_4 \)) 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-nitrophenoxy-cyclophosphazene 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**


References