# Modeling and Experimental Study of a Sequential Phosphazene Reaction by Phase-Transfer Catalysis

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*The substitution reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with phenol was performed to synthesize the partially substituted (phenoxy) chlorocyclotriphosphazenes, $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1-6$ by phase-transfer catalysis (PTC) in an organic phase/alkaline solution. The steric hindrance effect plays a crucial role in this reaction. The reaction system was controlled by both chemical kinetics and mass-transfer effects. The mass transfer of the catalyst between two phases was investigated by a pseudo-steady-state liquid–liquid PTC (LLPTC) model. Also, the intrinsic reaction-rate constants of the series substitution and the overall mass-transfer coefficient of the catalyst from the organic phase to the aqueous phase were determined by a combined model. In addition, the corresponding energies, enthalpies, and entropies of activation of the series substitution were also estimated.*

## Introduction

Phase-transfer catalyst (PTC) is considered an effective tool in synthesizing organic chemicals from two immiscible reactants. The reaction's reactivity by PTC is generally controlled by the reaction rates in the organic and aqueous phases, two mass-transfer steps between the organic and aqueous phases, as well as the partition equilibrium of the catalysts between the two phases (Weber and Gokel, 1977; Dehmlow and Dehmlow, 1993; Starks et al., 1994). The mass-transfer problems and the kinetics are extremely important in the field of phase-transfer catalysis. To date, only a limited number of investigators (Lele et al., 1983; Wang and Wu, 1990b, 1991a) have addressed the mass-transfer effect in the liquid–liquid phase-transfer catalytic reaction.

Organophosphazenes can be used as pressurized working fluids, flame retardants, and lubricants (Allcock, 1972). Phase-transfer catalysis has also been applied to the field of synthesizing phosphazene. Austin et al. (1983) initially applied phase-transfer catalysis in the conventional way. Carr and Nichols (1986) filed a patent of a process for preparing phosphazene esters. These results demonstrate that PTC is an effective method for preparing fully substituted (aryloxy) phosphazenes and (fluoroalkanoxy)phosphazenes. Wang and Wu (1990a,b; 1991a,b) also performed a kinetic study of the reaction between hexachlorocyclotriphosphazene $(NPCl_2)_3$ and 2,2,2-trifluoroethanol. In recent years, only a few studies have investigated the reaction kinetics of $(NPCl_2)_3$ (Sorokin and Latov, 1966; Wang and Wu, 1991a,b). Since the method of synthesizing phosphazene is complicated, kinetic analysis of the reaction has received scant attention. Such an analysis is particularly desirable for large-scale applications.

In this study, we aim to thoroughly understand the substitution reaction of chloride from hexachlorocyclotriphosphazene by phenol in an organic solvent/alkaline solution that was carried out in a batch reactor. Tetra-*n*-butyl ammonium cation serves as the phase-transfer catalyst. Also, the mechanism and kinetics of the series substitution reaction for one to six chlorides are investigated in detail. Three methods of a batch reaction are considered for the reaction kinetics and mass transfer of a catalyst between two phases. Moreover, the six intrinsic reaction-rate constants for the series reaction in the organic phase are evaluated by a combined model, using the method of nonlinear least squares for estimating parameters. The proposed reaction mechanism for the present system is as follows:

$$
\begin{array}{lll}
HOC_6H_5 + NaOH \longrightarrow H_2O + NaOC_6H_5 & & \\
\qquad\qquad\text{(initiator: QBr)} \ \downarrow & & \\
NaCl + QOC_6H_5 \longleftarrow \ QCl + NaOC_6H_5 & & \text{(aqueous)} \\
\qquad \downarrow K_{QOR} \quad \uparrow K_{QX} & & \text{(organic)} \\
N_3P_3Cl_{6-i}(OC_6H_5)_i + QOC_6H_5 \xrightarrow{k_i} QCl & & \\
\qquad\qquad + N_3P_3Cl_{5-i}(OC_6H_5)_{i+1}, & i = 0 \sim 5, & (1)
\end{array}
$$

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where QBr is the tetra-*n*-butyl ammonium bromide. At the beginning of the reaction, QBr initially reacts with sodium phenolate to form $QOC_6H_5$. Nevertheless, QCl instead of QBr is the main function of the catalyzed reaction.

## Experimental Section

### *Material*

Hexachlorocyclotriphosphazene (Aldrich), phenol, tetra-*n*-butylammonium bromide, and other reagents are all from R. G. Chemical. The silica gel is the product of Merck Co., Art. 9385.

### *Procedure*

An aqueous solution of sodium hydroxide, phenol, and tetra-*n*-butylammonium bromide (phase-transfer catalyst) was prepared and introduced into the reactor (250 mL, three-necked flask), which was thermostated at the desired temperature (30 ± 0.02°C). Measured quantities of phosphazene reactant $(NPCl_2)_3$ (5 g, 14 mmol) and dichloromethane (50 mL), which were also at the desired temperature, were then added to the reactor. The reaction mixture was agitated for a predetermined length of time. After the reaction, the oil phase, which was separated from the aqueous phase, was washed with water and sodium hydroxide solution several times, and dried with $MgSO_4$. Most of the solvent from the organic phase was removed by using aspiration. A yellowish oil-like product was subsequently obtained. Finally, the products were separated by pressurized column chromatography (Wang and Wu, 1990a).

The products, $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1$–$4$, were separated by pressurized column chromatography. A portion (4 g) of the crude oil was chromatographed on silica gel (70 g), *n*-hexane-chloroform eluted product. A pressurized control flow rate (10–15 mL/min) enhanced the separation effect. Thin-layer chromatography indicated the presence of the products. The products, $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 5$–$6$, were separated by using cooling crystallization.

For a kinetic run, an aliquot sample was withdrawn from the reaction solution at a selected time interval. The sample (0.2 mL) was immediately added to the solution (0.5 mL dichloromethane/0.5 mL of diluted hydrochloric acid) to quench the reaction. The organic phase content was then quantitatively analyzed by high-performance liquid chromatography (HPLC) using the method of internal standard. The accuracy of our analytical techniques was within 2 to 3%, and most of the data could be reproduced well within 5% of the values reported in this work.

Liquid chromatography was carried out in a Shimadzu LC-10AD instrument, using a column packed with Chemcosorb, 5-ODS H C/N. The eluent was $CH_3OH/H_2O = 4.7/1$, with a flow rate of 1.0 mL/min and was monitored at 210 and 254 nm (UV detector). Elemental analysis was performed by a Perkin-Elmer 2400-CHN. Mass spectra were obtained from a JEOL SX-102A mass spectrometer. Finally, nuclear magnetic resonance (NMR) spectra were observed in deuteriated chloroform on a JEOL, 300-MHz FT-NMR spectrometer.

## Mathematical Modeling

### *Relative reaction-rate constant for a series reaction*

(*A*.1) $k_i^* \left( = \frac{k_{i+1}}{k_i} \right) > 0.01$ *and* $y_0 \neq 0$. Allcock (1972) has demonstrated that the substitution reaction between hexachlorocyclotriphosphazene $(NPCl_2)_3$ and phenol follows the $S_N2$ mechanism. Therefore, each step in the series substitution reaction shown in Eq. 1 can be described by the following rate expression:

$$\frac{dy_i}{dt} = -k_i y_i [Q^*]; \qquad i = 0 \tag{2}$$

$$\frac{dy_i}{dt} = k_{i-1} y_{i-1} [Q^*] - k_i y_i [Q^*]; \qquad i = 1 \sim 5 \tag{3}$$

$$\frac{dy_i}{dt} = k_{i-1} y_{i-1} [Q^*]; \qquad i = 6, \tag{4}$$

where $y_i$ is defined below, and $[Q^*]$ is the concentration of the chemical form of the catalyst in the organic phase. By eliminating the time variable in the sequential reaction-rate equations, the concentrations of the desired product and the intermediate products can be expressed in terms of the amount of the reactant $(NPCl_2)_3$, that is,

$$\frac{dy_{i+1}}{dy_0} = k_{i+1}^* \frac{y_{i+1}}{y_0} - k_i^* \frac{y_i}{y_0}; \qquad i = 0 \sim 4 \tag{5}$$

$$\frac{dy_{i+1}}{dy_0} = -k_i^* \frac{y_i}{y_0}; \qquad i = 5, \tag{6}$$

where the dimensionless variables and parameters are defined as

$$y_i = \frac{\overline{[N_3P_3Cl_{6-i}(OC_6H_5)_i]}}{\overline{[(NPCl_2)_3]}_I} \tag{7}$$

and

$$k_i^* = \frac{k_i}{k_0}, \tag{8}$$

in which $\overline{[(NPCl_2)_3]}_I$ represents the initial concentration of reactant, $(NPCl_2)_3$, in the organic phase. The overbar, $\overline{\phantom{xx}}$, denotes the characteristics of the species in the organic phase.

Notably, Eq. 5 predicts the reaction trajectory of the intermediates relative to the initial concentration of the primary reactant. Also, this relationship between the $y_i$ values is independent of both the concentrations of the catalyst and water-soluble reactant, $NaOC_6H_5$. Equation 5 was solved by Wang and Wu (1991a) with the following initial condition of $y_i$:

$$y_0 = 1; \qquad y_i = 0 \quad (i = 1 \sim 6). \tag{9}$$

The solutions are

$$y_{i+1} = \sum_{l=0}^{i+1} \frac{\left(\prod_{n=0}^{i} k_n^*\right) y_0^{k_l^*}}{\prod_{\substack{n=0 \\ n \neq l}}^{i+1} (k_n^* - k_l^*)}; \qquad i = 0 \sim 4; \qquad y_0 \neq 0 \quad (10)$$

and

$$y_{i+1} = \sum_{l=0}^{i} \frac{k_i^* \left(\prod_{n=0}^{i-1} k_n^*\right) (y_0^{k_l^*} - 1)}{k_l^* \prod_{\substack{n=0 \\ n \neq l}}^{i} (k_n^* - k_l^*)}; \qquad i = 5; \qquad y_0 \neq 0. \quad (11)$$

Concentrations of distributed products, $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1 \sim 6$, including the intermediate and final products, are determined from Eqs. 10 and 11. Equations 10 and 11 can also be used to estimate the parameters $k_1^* \sim k_5^*$ by providing the experimental data. In general, $y_0$ should have a nonzero value in using Eqs. 10 and 11 either to estimate the parameters $k_1^* \sim k_5^*$ or to calculate the values of $y_1 \sim y_5$. If $y_0$ has a nonzero value during the reaction, Eqs. 10 and 11 cannot be used to simultaneously obtain the parameters $k_1^* \sim k_5^*$.

*(A.2)* $k_i^{\neq} < 0.01$ *and* $y_0 = 0$. If the ratio of the rate constant of the latter substitution reaction to the former substitution reaction for a series reaction is small ($k_i^{\neq} < 0.01$), the reaction can be considered to be a pseudo one-step reaction. The rate-determining step is the latter substitution reaction. Reactant consumption is almost equal to the production of the former product. The concentration of the latter product is extremely small when the concentration of reactant approaches zero. That is, if all $k_i^{\neq}$ values are less than 0.01, only two compounds exist during the course of the reaction, that is, $N_3P_3Cl_3(OC_6H_5)_3$ can be seen as a reactant, and $N_3P_3Cl_2(OC_6H_5)_4$ is the product between 3 and 4 of the $C_6H_5OH/(NPCl_2)_3$ consumption ratio in Figure 2. From Eqs. 2–4, the rate equations are rewritten as

$$\frac{dy_{i+1}}{dy_i} = k_{i+1}^{\neq} \frac{y_{i+1}}{y_i} - 1; \qquad i = 0 \sim 4 \quad (12)$$

$$\frac{dy_{i-1}}{dy_i} = -1; \qquad i = 5 \quad (13)$$

and

$$k_i^{\neq} = \frac{k_{i+1}}{k_i} \quad (14)$$

$$y_i = y_{i,I}; \qquad y_{i+1} = y_{i+1,I} \quad (i = 1 \sim 6). \quad (15)$$

The solutions are

$$y_{i+1} = \frac{y_i}{k_{i+1}^{\neq} - 1} + \left( \frac{y_{i+1,I}}{y_{i,I}^{k_{i+1}^{\neq}}} - \frac{y_{i,I}^{l-k_{i+1}^{\neq}}}{k_{i+1}^{\neq} - 1} \right) y_i^{k_{i+1}^{\neq}}; \; i = 0 \sim 4; \qquad y_{i,I} \neq 0 \quad (16)$$

$$y_{i+1} = -y_i + (y_{i,I} + y_{i+1,I}); \qquad i = 5. \quad (17)$$

According to Eqs. 16 and 17, the parameters $k_1^* \sim k_5^*$ are estimated by the experimental data provided.

*(A.3) Combined Model.* In general, electronic and steric effects influence the series reaction-rate constants. The parameter $k_i^*$ decreases when the degree of substitution increases. Hence, the range from $k_1^*$ to $k_5^*$ is wide. Some $k_i^{\neq}$ values are likely greater than 0.01; the others are less than 0.01. Hence, methods A.1 and A.2 were combined to solve the relationships between $k_1^* \sim k_5^*$ and $y_0 \sim y_6$. In this study, we estimated the parameters $k_1^* \sim k_5^*$ using six sets of experimental data from a nonlinear least-squares method. Computational strategies to estimate $k_1^* \sim k_5^*$ are:

(i) First, $k_1^* \sim k_3^*$ are estimated for the experimental data of $y_0 \sim y_3$. Only those sets of experimental data with nonzero values of $y_0$ can be used to estimate the parameters $k_1^* \sim k_3^*$ by using method A.1.

(ii) The $y_1$ and $y_2$ values are used to calculate the value of $y_0$ in order to estimate and check $k_1^* \sim k_3^*$ by Eq. 10. The standard errors of the parameters are less than 0.005.

(iii) The value of $k_4^*$ and $k_5^*$ are estimated by method A.2. The standard errors of the parameters are less than 0.05.

### *First intrinsic reaction-rate constant and overall mass-transfer coefficient in a phase-transfer catalytic reaction*

*(B.1) Pseudo-Steady-State LLPTC Model.* The rate of phase-transfer catalyzed reaction is typically controlled by (1) reaction rates in the organic phase and in the aqueous phase; (2) mass-transfer steps between the phases; and (3) the partition equilibrium of the catalyst between the two phases. Starks et al. (1994) offered a classic diagram of the phase-transfer catalytic cycle:

$$\begin{array}{lll} RX + Q^{+-}Y & \overset{k}{\rightarrow} \; Q^{+-}X + RY & \text{organic phase} \\ \hline K_{QY} & \quad\quad K_{QX} & \text{aqueous phase} \\ MX + Q^{+-}Y & \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \; Q^{+-}X + MY & \end{array} \quad (18)$$

On the basis of the experimental data and earlier literature (Dehmlow and Dehmlow, 1993; Starks et al., 1994; Weber and Gokel, 1977; Wu, 1996), a generalized approach describing the phase-transfer catalyzed reaction system is to use a pseudo-first-order reaction. The rate expression is written as

$$-\frac{d\overline{[RX]}}{dt} = k_{\text{app}} \overline{[RX]} \quad (19)$$

$$k_{\text{app}} = k \overline{[QY]}. \quad (20)$$

The fixed value of $k_{\text{app}}$ is called the apparent first-order reaction-rate constant.

Wu (1993) confirmed that if the concentration variation of the catalyst is even as large as 10% in the reaction period, a liquid–liquid phase-transfer-catalyzed (LLPTC) reaction might still be described as pseudo-first-order. Previous works

(Wang and Wu, 1991a; Wu, 1996) indicated that the pseudo-steady-state LLPTC model could describe the complicated nature of the LLPTC reaction. Hence, the catalysts are seen to be in both the organic phase and the aqueous phase in the pseudo-steady-state. That is,

$$\frac{d[QY]}{dt} \cong 0, \quad \frac{d\overline{[QY]}}{dt} \cong 0, \quad \frac{d\overline{[QX]}}{dt} \cong 0, \quad \frac{d[QX]}{dt} \cong 0. \tag{21}$$

The rate equation from Wu's (1996) report is expressed as

$$\frac{d\overline{[RX]}}{dt} = \frac{k\overline{[RX]}Q_i/\bar{V}}{\dfrac{\alpha m_{QY}+1}{\alpha m_{QY}} + \left(\dfrac{Da_{QY}}{\alpha m_{QY}} + Da_{QX}\right) + (1+\alpha m_{QX})\left(\dfrac{Da_{QY}+1}{\alpha m_{QY}}\beta + \alpha\gamma\right)}, \tag{22}$$

where

$$Da_{QY}\left(= \frac{k\overline{[RX]}}{K_{QY}A/\bar{V}}\right) \quad \text{and} \quad Da_{QX}\left(= \frac{k\overline{[RX]}}{K_{QX}A/\bar{V}}\right)$$

are Damköhler numbers of $QY$ and $QX$, respectively; $\beta$ ($= (k_{-2}[MX]/k_2[MY])$) is the reaction ratio of the aqueous reverse reaction to the forward reaction; and $\gamma$ ($= (k\overline{[RX]}/k_2[MY])$) is the reaction ratio of the organic phase to the aqueous forward reaction. The catalyst effectiveness, $\eta$, defined as the relation of the actual reaction rate to the reaction rate with the catalyst completely employed, is given as

$$\begin{aligned}\eta &= \frac{k\overline{[RX]}\,\overline{[QY]}}{k\overline{[RX]}Q_i/\bar{V}} \\ &= \left[\frac{\alpha m_{QY}+1}{\alpha m_{QY}} + \left(\frac{Da_{QY}}{\alpha m_{QY}} + Da_{QX}\right)\right. \\ &\qquad \left. + (1+\alpha m_{QX})\left(\frac{Da_{QY}+1}{\alpha m_{QY}}\beta + \alpha\gamma\right)\right]^{-1}.\end{aligned} \tag{23}$$

The $k_{\text{app}}$ expression is thus obtained by Eqs. 19 and 23:

$$\begin{aligned}k_{\text{app}} &= \frac{kQ_i}{\bar{V}}\left[\frac{\alpha m_{QY}+1}{\alpha m_{QY}} + \left(\frac{Da_{QY}}{\alpha m_{QY}} + Da_{QX}\right)\right. \\ &\qquad \left. + (1+\alpha m_{QX})\left(\frac{Da_{QY}+1}{\alpha m_{QY}}\beta + \alpha\gamma\right)\right]^{-1}.\end{aligned} \tag{24}$$

Generally, the following characteristics occur in the LLPTC reaction: (1) the intermediate product of the catalyst $QY$ is highly lipophilic ($m_{QY} \gg 1$). (2) The concentration of aqueous reactant $MY$ is greater than the concentration of organic reactant $RX$. The rate of the aqueous-phase forward reaction is greater than that of the organic phase ($\beta \ll 1$, $\gamma \ll 1$). (3) The catalyst concentration is small, and the equilibrium constant of the ion exchange reaction in the aqueous phase is large. The concentration of the onium cation $Q^+$ in the aqueous phase is zero ($[Q^+] \cong 0$). Therefore, Eqs. 23 and 24 are simplified as

$$\eta = (1 + Da_{QX})^{-1} \tag{25}$$

$$k_{\text{app}} = \frac{kQ_i}{\bar{V}}(1 + Da_{QX})^{-1} = \frac{kQ_i}{\bar{V}}\left(1 + \frac{k\overline{[RX]}}{K_{QX}A/\bar{V}}\right)^{-1}. \tag{26}$$

According to Wang and Wu (1991a), the effect of mass-transfer resistance can be neglected, as $Da_{QX} < 0.02$. Otherwise, we need to consider the mass-transfer effect of a catalyst between two phases.

In the present system, the experimental results of reactant consumption with time correspond to a simple, first-order kinetic model (Eq. 19). The regression factor $r$ of the least-squares regression was exceeded by 0.99. The following discussion of the apparent reaction-rate constant is based on $k_{\text{app}}$. Since in this study the reaction is a series reaction, $k\overline{[RX]}$ in Eq. 26 is assumed to include the six-step sequential reaction, and is modified as

$$k\overline{[RX]} = \sum_{i=0}^{5} k_i\overline{[\mathrm{N_3P_3Cl_{6-\mathit{i}}(OC_6H_5)_\mathit{i}}]}. \tag{27}$$

Define $\phi$ as

$$\phi = \frac{k\overline{[RX]}\bar{V}}{k_0}. \tag{28}$$

The following expression for $k_{\text{app}}$ is obtained from Eqs. 26 and 28:

$$\frac{1}{k_{\text{app}}} = \frac{\bar{V}}{K_{QX}AQ_i}\phi + \frac{\bar{V}}{kQ_i}. \tag{29}$$

The plot of $1/k_{\text{app}}$ vs. $\phi$, in which the data were measured at the starting times of the different experimental runs, allows us to obtain the mass-transfer coefficient, $K_{QX}A$, and the intrinsic reaction-rate constant, $k_0$, from the slope and intercept distances of the straight line. Notably, the constant $\phi$ value, which depends on the initial concentration of $(\mathrm{NPCl_2})_3$, is evaluated at the start of the reaction.

*(B.2) Extrapolation Method.* In general, one assumes that the mass-transfer and chemical-reaction resistances in the aqueous phase can be neglected for a slow reaction in the

organic phase by LLPTC. The active catalyst is on the extraction equilibrium.

The intrinsic reaction-rate constant $k$ is calculated from Eq. 24:

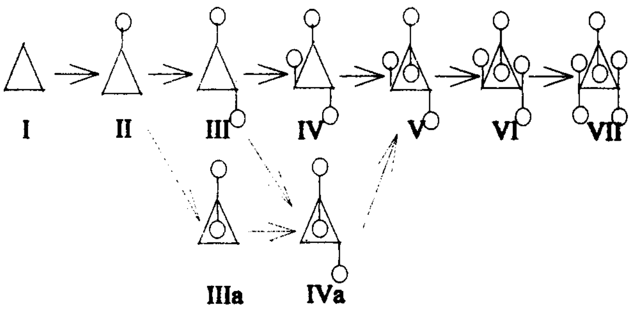
$$k = k_{\mathrm{app}} \left( \frac{Q_i}{\overline{V}} \frac{\alpha m_{QY}}{\alpha m_{QY} + 1} \right)^{-1} \tag{30}$$

If mass-transfer resistance influences the reaction, the concentration of the active catalyst $QY$ cannot remain constant during the course of the reaction. The apparent first-order reaction-rate constant is increased by decreasing the concentration of organic reactant $RX$ (Wang and Wu, 1990a). When the concentration of organic reactant decreases, both the reaction rate and the effect of mass transfer decrease. If the organic reactant concentration extrapolates to zero ($[\overline{RX}] \rightarrow 0$), the effect of mass transfer can be neglected. The intrinsic reaction-rate constant, $k_0$, is easily evaluated from Eq. 30.

*(B.3) Half-reaction in the Organic Phase.* The substitution reaction of hexachlorocyclotriphosphazene with phenol is a sequential reaction. The reaction rate of hexachlorocyclotriphosphazene with phenol was extremely rapid when the degree of substitution was less than three. However, the rate of the following three substitution reactions is very slow. Hence, we allow chloropentaphenoxycyclotriphosphazene ($N_3P_3Cl(OC_6H_5)_5$) to react with tetra-*n*-butyl ammonium phenolate in a homogeneous organic phase. The $k_5$ value is easily found from a second-order reaction equation. The intrinsic reaction-rate constant, $k_0$, is calculated from $k_0 = k_5/k_5^*$.

## Results and Discussion

The system chosen for study was the reaction of phenol with hexachlorocyclotriphosphazene, with tetra-*n*-butylammonium bromide as the phase-transfer catalyst in an organic solvent/alkaline solution. Applying phase-transfer catalysis had a dramatic accelerating effect on the reaction. The products of $N_3P_3Cl_{6-i}(OC_6H_5)_i$, $i = 1-6$, were successfully separated by pressurized column chromatography and cooling crystallization. On the basis of $^{31}P$ and H NMR spectra, the reaction type belonging to a transnongeminal path was expressed in the following scheme:



The two isomers are the *trans*-nongeminal and geminal isomers III and IIIa. The *trans* bis (phenoxy) isomer III predominates in the mixture (> 96%). The major tris isomer was assigned a *trans* configuration (IV). The minor tris isomer (IVa) (less than 20% of the total tris components) that produced an ABC spectrum was the tris geminal isomer. The peaks of the tri isomers (IV and IVa) cannot be separated to be monitored on an HPLC instrument. In this study, in order to study the kinetics phenomenon, the tri isomers are observed on the same compound. Also, the reaction of hexachlorocyclotriphosphazene with phenol followed a *trans*-geminal pathway. Our results resemble those of Chen-Yang et al. (1991).

The reaction rate was dramatically increased by increasing the agitation rate up to 800 rpm. When the agitation rate exceeded 800 rpm, the reaction rate increased only slightly. Therefore, the agitation rate was set at 1,000 rpm to allow us to study the kinetic phenomena in the present reaction.

### *Ratio of reactant-rate constants for different products*

Figure 1 displays the relation between the consumption of the reactant and the production of the products vs. time on various amounts of tetra-*n*-butyl ammonium bromide (TBAB, PTC). The increasing degree of the series substitution reaction decreased the reaction rate. Phase-transfer catalysis markedly enhanced the reaction rate. If the amount of TBAB was only slight, reactant consumption and production of the products could be easily observed during the course of the reaction On the other hand, it took a long time to complete the reaction. If various amounts of TBAB were used, consumption of the reactant and product production could be observed at selected time intervals on various reaction sys-

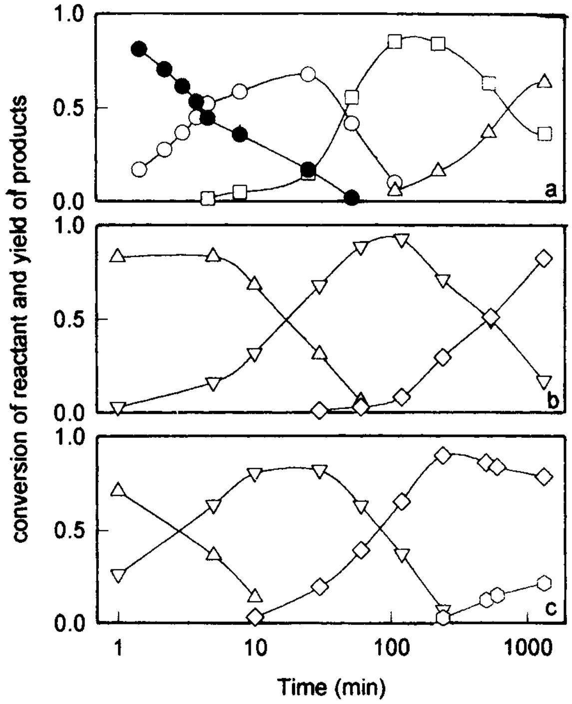


**Figure 1. Consumption of reactant and the production of products vs. time on various amounts of TBAB.**

TBAB = (a) $7.8 \times 10^{-3}$ mmol; (b) 3.1 mmol; (c) 15.5 mmol: $H_2O$ = 50 mL; NaOH = 45 mmol; $C_6H_5OH$ = 37 mmol; $CH_2Cl_2$ = 50 mL; $(NPCl_2)_3$ = 2.9 mmol; 1,000 rpm; 20°C. (●)$(NPCl_2)_3$; (○)$N_3P_3Cl_5(OC_6H_5)_1$; (□) $N_3P_3Cl_4(OC_6H_5)_2$; (△) $N_3P_3Cl_3(OC_6H_5)_3$; (▽) $N_3P_3Cl_2(OC_6H_5)_4$; (◇) $N_3P_3Cl(OC_6H_5)_5$; (⬡) $N_3P_3(OC_6H_5)_6$.

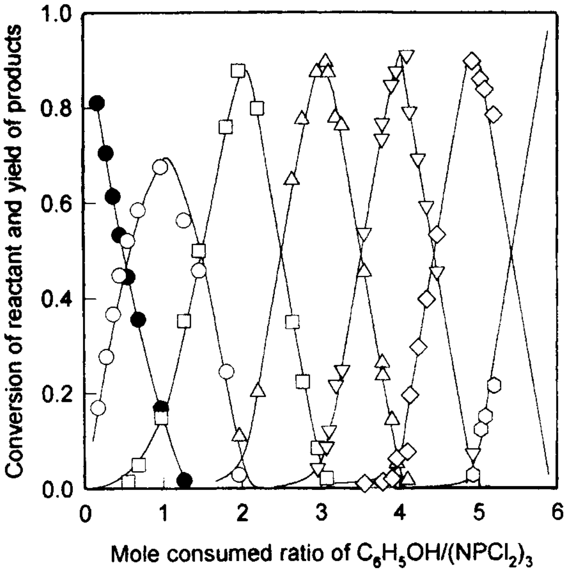


**Figure 2. Yields of the six distributed products and reactants as a function of the reactant $C_6H_5OH/(NPCl_2)_3$ consumption ratio.**

The operating conditions are the same as those given Figure 1. (●) $(NPCl_2)_3$; (○) $N_3P_3Cl_5(OC_6H_5)_1$; (□) $N_3P_3Cl_4(OC_6H_5)_2$; (△) $N_3P_3Cl_3(OC_6H_5)_3$; (▽) $N_3P_3Cl_2(OC_6H_5)_4$; (◇) $N_3P_3Cl(OC_6H_5)_5$; (⬡) $N_3P_3(OC_6H_5)_6$. The solid lines are the simulated results by Eqs. 10 and 16.

tems (Figure 1). The concept of phase-plane was used to change the variable from time to the ratio of moles of $C_6H_5OH/(NPCl_2)_3$ consumed. Likewise, the concept of superposition was used to superpose the three figures in Figure 1 on Figure 2.

In the organic phase, the reaction mechanism of the reaction of $(NPCl_2)_3$ with $(n\text{-}C_4H_9)_4NOC_6H_5$ can be expressed by Eq. 1. The expression cannot be directly solved to yield compositions as a function of time (Eqs. 2–4) because the magnitude of the individual rate constants is unknown (only their ratios are known). Those rate-expression equations (Eq. 5), along with the mass balance, can be solved for the desired yields of the products in terms of the amount of $(NPCl_2)_3$ (by eliminating time as a variable).

Figure 2 reveals that the relationships between six distributed products and the reactant cannot be obtained simultaneously. The reactant's concentration approaches zero when the third product is manufactured. Equations 10 and 11 cannot describe the reaction system, but can only solve the value of $k_1^* \sim k_3^*$. When the ratio of moles of $C_6H_5OH/(NPCl_2)_3$ consumed was more than two, only two compounds existed during the course of the reaction. Hence, the values of $k_4^*$ and $k_5^*$ were obtained by the combined model (Eqs. 16 and 17). The computational strategies are described in method A.3. The $k_i^*$, $i = 1–5$, were thus determined, that is, the values of $k_i^*$ were $k_1^* = 0.179$, $k_2^* = 6.73 \times 10^{-3}$, $k_3^* = 1.9 \times 10^{-4}$, $k_4^* = 3.52 \times 10^{-6}$, and $k_5^* = 4.52 \times 10^{-8}$. By using values just obtained for $k_i^*$, Figure 2 displays the estimated trajectories of the six products and the reactant in terms of the ratio of moles of $C_6H_5OH/(NPCl_2)_3$ consumed. The standard errors of the parameters are less than 0.05.

**Table 1. Relative Reaction-Rate Constants vs. Temperature in an Organic Solvent/Alkaline Solution by Phase-Transfer Catalysis**

| Solvent | $T$(°C) | $k_1^* \times 10$ | $k_2^* \times 10^3$ | $k_3^* \times 10^4$ | $k_4^* \times 10^6$ | $k_5^* \times 10^8$ |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 10 | 1.03 | 3.19 | 1.11 | 1.88 | 2.47 |
| | 20 | 1.79 | 6.73 | 1.90 | 3.52 | 4.52 |
| | 30 | 2.45 | 8.52 | 3.00 | 6.14 | 11.1 |
| | 35 | 2.57 | 9.93 | 4.35 | 9.11 | 15.1 |
| $ClC_6H_5$ | 10 | 0.859 | 3.10 | 0.9 | 1.9 | 1.27 |
| | 20 | 0.965 | 3.87 | 1.20 | 3.4 | 3.41 |
| | 30 | 1.07 | 4.56 | 1.70 | 5.82 | 5.19 |
| | 40 | 1.13 | 5.41 | 2.10 | 9.85 | 16.9 |
| | 50 | 1.17 | 6.80 | 3.10 | 14.9 | 26.3 |

Reaction conditions: $H_2O = 50$ mL; NaOH = 45 mmol; $C_6H_5OH = 37$ mmol; solvent = 50 mL; $(NPCl_2)_3 = 2.9$ mmol.

Dichloromethane and chlorobenzene are usually used as a solvent in the phase-transfer catalyzed reaction. Table 1 lists the relative reaction-rate constants $k_i^*$ in the dichloromethane and chlorobenzene/alkaline solution by phase-transfer catalysis. The relative reaction-rate constant decreased when the degree of the substitution of the reaction increased. The values of $k_i^*$ were all less than one. The steric hindrance effect plays a crucial role in this reaction. The $k_i^*$-values in dichloromethane were more than those in chlorobenzene.

### *Effects of temperature*

Table 1 lists the relative reaction-rate constants for six distributed products at various temperatures derived by using a combined model. The values of $k_i^*$ were increased by increasing the temperature. The values of $k_5^*$ were much more sensible than those of $k_1^*$ for temperature. To find the relationships between the reaction-rate constant and temperature, the Arrhenius and Eyring equations are rewritten for $k_i^*$:

$$\log k_0 = \log k_{0,0} - \frac{E_0}{2.303RT} \tag{31}$$

$$\log\frac{k_i}{k_0} = \log\frac{k_{i,0}}{k_{0,0}} - \frac{\Delta E_{i,0}}{2.303RT} \tag{32}$$

$$\Delta E_{i,0} = E_i - E_0 \tag{33}$$

and

$$\log\frac{k_0}{T} = \log\frac{k_B}{h} + \frac{\Delta S_0}{2.303R} - \frac{\Delta H_0}{2.303RT} \tag{34}$$

$$\log\frac{k_i}{k_0} = \frac{\Delta S_{i,0}}{2.303R} - \frac{\Delta H_{i,0}}{2.303RT} \tag{35}$$

$$\Delta S_{i,0} = \Delta S_i - \Delta S_0 \tag{36}$$

$$\Delta H_{i,0} = \Delta H_i - \Delta H_0. \tag{37}$$

Table 1 and Eqs. 31–37 easily yield the $k_i^*$ values, which are shown in Figures 3 and 4, in addition to the differences in the energies and enthalpies of activation. Tables 2 and 3 contain the corresponding activation entropies and frequency factors. The frequency factor ratios for the series substitution

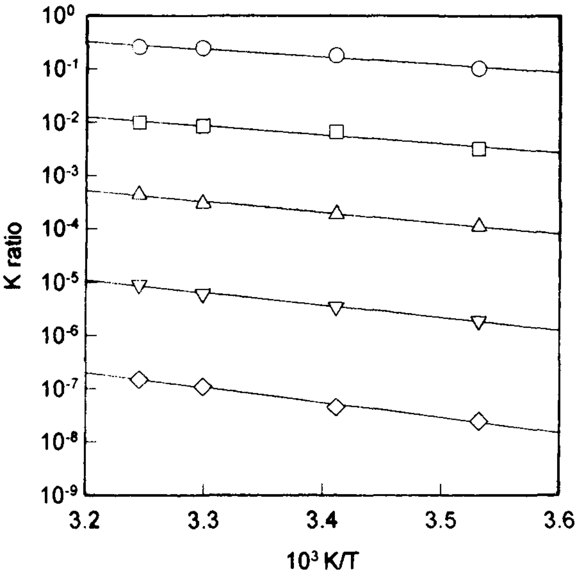


**Figure 3. Effect of temperature on the quotient of the intrinsic reaction rate constants in dichloromethane.**

The operating conditions are the same as those given Figure 1. (○) $k_1^*$; (□) $k_2^*$; (△) $k_3^*$; (▽) $k_4^*$; (◇) $k_5^*$.

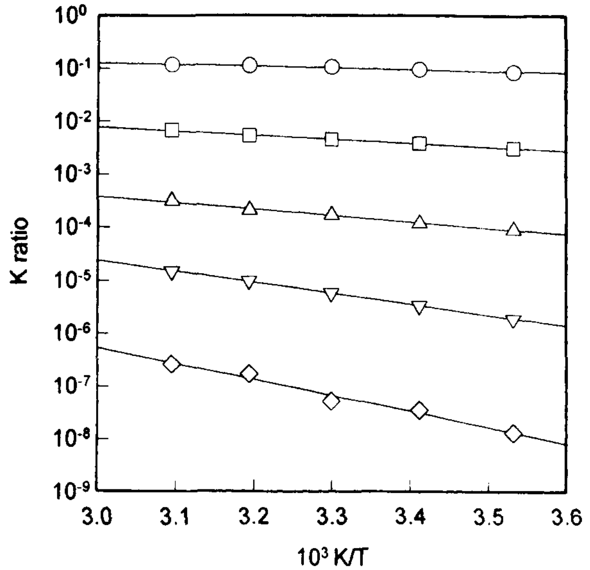


**Figure 4. Effect of temperature on the quotient of the intrinsic reaction-rate constants in chlorobenzene.**

The operating conditions are the same as those given Figure 1. (○) $k_1^*$; (□) $k_2^*$; (△) $k_3^*$; (▽) $k_4^*$; (◇) $k_5^*$.

reaction decreased in dichloromethane when the reaction temperature increased, while those in chlorobenzene increased. The order of increase for the Arrhenius activation energy and Eyring enthalpy of activation is that increased for both by the incremental substitution of from one to six chlorine atoms in the reaction. This finding implies that, in a high-temperature reaction, the high activation energy reaction is more sensitive than the low activation energy reaction.

### *Effects of mass transfer and intrinsic reaction-rate constant*

The experimental data in this study (Wang and Yang, 1990; Wang and Wu 1991a) indicate that the pseudo-first-order reaction-rate constant $k_{app} = k\overline{[QY]}$ increases by decreasing the concentration of organic reactant $RX$. Such an effect is not reasonably explained according to a conventional kinetics model in which the reaction-rate constant is independent of the concentration of the reactant. From the simulation results of Wu (1996) and experimental data, the contradictory point suggests that the $k_{app}$ values vary when the concentration of reactant $RX$ is changed. In addition, the mass-transfer rate influences the reaction rate. Based on the experimental results and the wide range of $k_1^* \sim k_5^*$, the reaction could be controlled first by both mass transfer and chemical kinetics, and then by chemical kinetics. Figure 5 plots $k_{app}$ vs. $(NPCl_2)_3$. The $k_{app}$-value depends heavily on the $(NPCl_2)_3$ concentration. The reaction is obviously controlled both by chemical kinetics and mass transfer. According to method B.2, when the concentration of the organic reactant decreases, the reaction rate and the effect of mass transfer decreases. If the concentration of organic reactant extrapolates to zero ($\overline{[RX]} \rightarrow 0$), the effect of mass transfer can be ignored. The intrinsic reaction-rate constant $k_0$ is evaluated in Eq. 29. Figure 5b shows the apparent reaction-rate constants for various amounts of $(NPCl_2)_3$ in chlorobenzene. When the amount of $(NPCl_2)_3$ was less than 1.45 mmol, the $k_{app}$ value remained constant (0.0373 $min^{-1}$), and the reaction was controlled by

**Table 2. Kinetic Parameters of the Reaction of $(NPCl_2)_3$ Derivatives with Phenol in Dichloromethane by Phase-Transfer Catalysis**

| | | * | *i* | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 |
| Activation energy | $\Delta E_{i,0}$ (kcal/mol) | 7.05 | 6.45 | 7.61 | 9.18 | 10.7 | 12.9 |
| Frequency factor | $k_{i,0}/k_{0,0}$ | $6.6\times10^8$ | 10,500 | 5,650 | 1,340 | 339 | 211 |
| Activation enthalpy | $\Delta H_{i,0}$ (kcal/mol) | 6.5 | 6.45 | 7.61 | 9.18 | 10.7 | 12.9 |
| Activation entropy | $\Delta S_{i,0}$ (kcal/mol·K) | 24.7 | 18.4 | 15.6 | 14.3 | 11.6 | 10.6 |

*The intrinsic kinetic parameters of the reactant $(NPCl_2)_3$ were calculated by method B.3.
Reaction conditions: $H_2O$ = 50 mL; NaOH = 45 mmol; $C_6H_5OH$ = 37 mmol; $CH_2Cl_2$ = 50 mL; $(NPCl_2)_3$ = 2.9 mmol.

**Table 3. Kinetic Parameters of the Reaction of $(NPCl_2)_3$ Derivatives with Phenol in Chlorobenzene by Phase-Transfer Catalysis**

| | | * | *i* 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|
| Activation energy | $\Delta E_{i,0}$ (kcal/mol) | 14.2 | 1.44 | 3.46 | 5.48 | 9.43 | 13.9 |
| Frequency factor | $k_{i,0}/k_{0,0}$ | $1.0\times10^{13}$ | 1.14 | 1.45 | 1.49 | 36.0 | 741.3 |
| Activation enthalpy | $\Delta H_{i,0}$ (kcal/mol) | 13.6 | 1.44 | 3.46 | 5.48 | 9.43 | 13.9 |
| Activation entropy | $\Delta S_{i,0}$ (kcal/mol · K) | 43.9 | 0.26 | 0.73 | 0.79 | 7.12 | 13.3 |

*The intrinsic kinetic parameters of the reactant $(NPCl_2)_3$ were calculated by method B.3.
Reaction conditions: $H_2O$ = 50 mL; NaOH = 45 mmol; $C_6H_5OH$ = 37 mmol; $ClC_6H_5$ = 50 mL; $(NPCl_2)_3$ = 2.9 mmol.

chemical kinetics. The intrinsic reaction-rate constant was 260 $(M \cdot min)^{-1}$ from Eq. 30 because experimental results indicated that the tetra-*n*-butylammonium cation distributed itself in the organic phase ( > 99%) rather than in the aqueous phase by the extractive titration method (Sakai et al., 1977; Wu and Lin, 1994). When the amount of $(NPCl_2)_3$ was extrapolated to zero by using a second-order polynomial approximation, the $k_{app}$ value was 0.04 $min^{-1}$ and, according to method B.2, the intrinsic reaction-rate constant was 279 $(M \cdot min)^{-1}$. The error of both intrinsic reaction-rate constants was 7% [ = (279-260)/260]. Figure 5a shows the apparent reaction-rate constants for various amounts of $(NPCl_2)_3$ in dichloromethane. The $k_{app}$ value increased when the amount of $(NPCl_2)_3$ decreased. A region could not be obtained that was only under chemical kinetic control. When the amount of $(NPCl_2)_3$ was extrapolated to zero, the $k_{app}$ value was 0.57 $min^{-1}$, and the intrinsic reaction rate constant was 3,685 $(M \cdot min)^{-1}$. Table 4 lists the intrinsic reaction-rate constants at various temperatures by method B.2.

By using Eq. 28, Figure 6 plots $1/k_{app}$ vs. $\phi$. The slope and intercept increase as time increases. This increase is due to

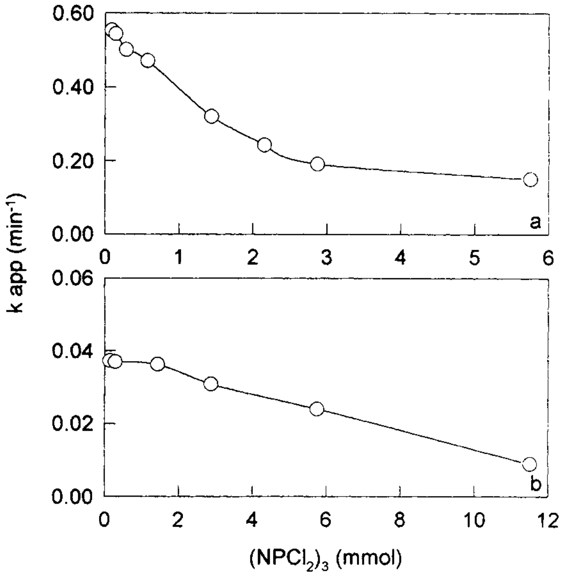


**Figure 5. Relation between apparent reaction-rate constant and amount of reactant $(NPCl_2)_3$.**

The experimental data are obtained from different runs. (a) Chlorobenzene; (b) dichloromethane.

**Table 4. Intrinsic Reaction-Rate Constants and Overall Mass-Transfer Coefficient vs. Temperature in an Organic Solvent/Alkaline Solution by Phase-Transfer Catalysis**

| Solvent | *T*(°C) | Method B.1 $k_0$ $(M \cdot min)^{-1}$ | Method B.1 $K_{QX}A$ (L/min) | Method B.2 $k_0$ $(M \cdot min)^{-1}$ | Method B.3 $k_0$ $(M \cdot min)^{-1}$ |
|---|---|---|---|---|---|
| $CH_2Cl_2$ | 10 | 2323 | 17.2 | 2225 | 2349 |
| | 20 | 3712 | 22.8 | 3685 | 4000 |
| | 30 | 5563 | 30.6 | 5624 | 5720 |
| | 35 | 6337 | 36.0 | 6290 | 6245 |
| $ClC_6H_5$ | 10 | 122 | 72.0 | 113 | 108 |
| | 20 | 279 | 66.7 | 279 | 276 |
| | 30 | 586 | 37 | 578 | 580 |
| | 40 | 1340 | 29 | 1350 | 1200 |
| | 50 | 2747 | 20.7 | 2598 | 2579 |

Reaction conditions: $H_2O$ = 50 mL; NaOH = 45 mmol; $C_6H_5OH$ = 37 mmol; solvent = 50 mL; $(NPCl_2)_3$ = 2.9 mmol.

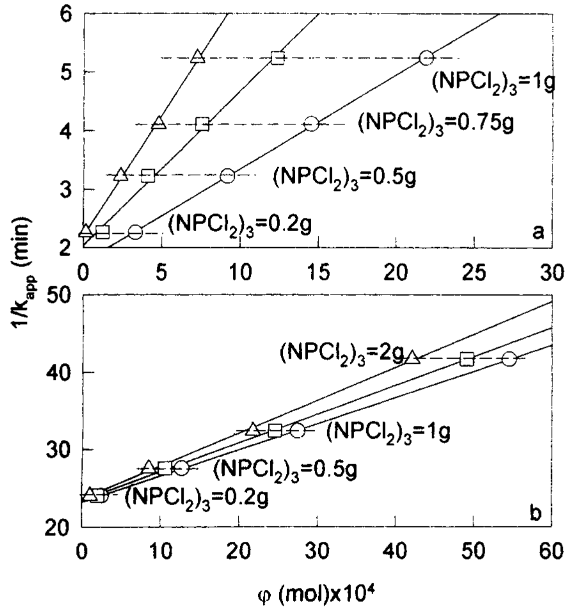


**Figure 6. Relation between apparent reaction-rate constant and amount of reactant $(NPCl_2)_3$ on various reaction times.**

(a) Dichloromethane; (b) chlorobenzene.

**Table 5. Six Intrinsic Reaction-Rate Constants and Overall Mass-Transfer Coefficient by Phase-Transfer Catalysis**

| Solvent | $k_0$ $(M \cdot min)^{-1}$ | $k_1$ $(M \cdot min)^{-1}$ | $k_2$ $(M \cdot min)^{-1}$ | $k_3$ $(M \cdot min)^{-1}$ | $k_4$ $(M \cdot min)^{-1}$ | $k_5$ $(M \cdot min)^{-1}$ |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 3712 | 665 | 25 | 0.71 | $1.31 \times 10^{-2}$ | $1.68 \times 10^{-4}$ |
| $ClC_6H_5$ | 279 | 27.6 | 1.08 | 0.0345 | $9.4 \times 10^{-4}$ | $9.4 \times 10^{-6}$ |
| $ClC_6H_5^*$ | 293 | 387 | 217 | 85 | 47 | 13 |

*Quoted from the report of Wang and Wu (1991a) for the reaction of $(NPCl_2)_3$ and $CF_3CH_2OH$.
Reaction conditions: $H_2O$ = 50 mL; NaOH = 45 mmol; $C_6H_5OH$ = 37 mmol; solvent = 50 mL; $(NPCl_2)_3$ = 2.9 mmol; temperature = 20°C.

the changing concentration of the aqueous solution, that is, the increase in the chloride ion concentration in Eq. 24. Figure 7 shows the results of plotting the intercept distance and slope of straight lines vs. time obtained from Figure 6. Straight lines are obtained for both intercept distance vs. time and slope vs. time plots. The reaction system obeyed the pseudo-first-order kinetic approximation for $t > 0$ min. Hence, we can extrapolate time to zero in order to omit the effect of the changing environment (concentration) of the reaction. From Eq. 29, the intercept $(\bar{V}/k_0 Q_i)$ and the slope $(\bar{V}/(K_{QX} A Q_i))$ are 1.74 and 283 and 23 and 97 for dichloromethane and chlorobenzene, respectively. The substituted reaction-rate constant $k_0$ and the overall mass-transfer coefficient $K_{QX}A$ are obtained first. Therefore, the six reaction-rate constants and overall mass-transfer coefficients are given their entirety in Table 5. As shown in Figure 6, the two extreme limits of values in the present study are $\phi = 0.034$ and $\phi = 0.72$. The corresponding $Da_{QX}$ values are 5.5 and 117, respectively. They are more than 0.02. The calculation made earlier confirms that the chemical reaction and mass-transfer dominate the reaction in this study.

To verify the accuracy of the intrinsic reaction-rate constant calculated by methods B.1 and B.2, we allow chloropentaphenoxycyclotriphosphazene $(N_3P_3Cl(OC_6H_5)_5)$ to react with tetra-*n*-butyl ammonium phenolate in a homogeneously organic phase. The $k_5$ value is easily found from the second-order reaction equation. The intrinsic reaction-rate constant $k_0$ is calculated from $k_0 = k_5/k_5^*$. Table 4 summarizes the results. The error in the first intrinsic reaction-rate constant in methods B.1–B.3 is less than 10%. This occurrence therefore verifies that the pseudo-steady-state LLPTC model, and the extrapolation method can be used to obtain the intrinsic reactant constant when the phase-transfer catalytic reaction is influenced by mass-transfer resistance.

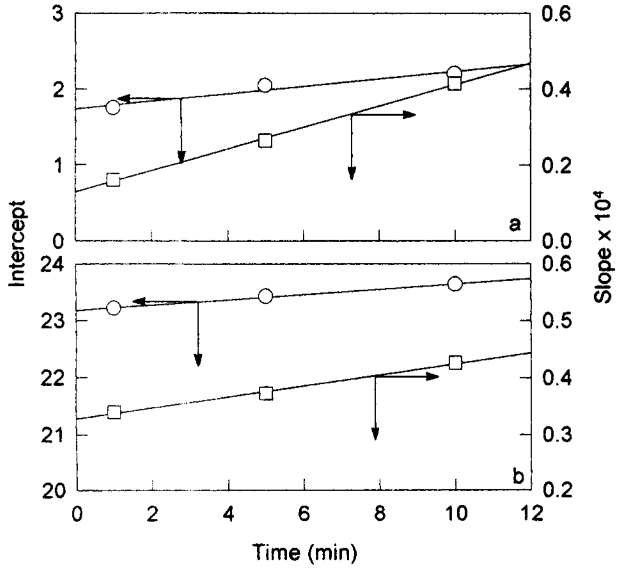


**Figure 7. Intercept distance and slope vs. time from Figure 6.**

(a) Dichloromethane; (b) chlorobenzene.

In Table 5, the reactivity of the series reaction of hexachlorocyclotriphosphazene with phenol in dichloromethane is larger than that in chlorobenzene. Wang and Wu (1991b) demonstrated that the electronic effect is more important than the steric effect in the first or the second substitution reaction during PTC. Nevertheless, the final substitution reaction is dominated by steric effects. In this study, the values of $k_i^*$ ($i = 1$–$4$) are all less than 0.01. Therefore, the steric effect is more important than the electronic effect. The increasing degree of the substitution reaction increases the activation energy in Tables 2 and 3. If this rate decrease is the result of phenoxy groups supplying electrons to the ring, an $S_N1$-type mechanism is precluded, since the electron supply would enhance the ionization of P-Cl to $P^+ Cl^-$, thus increasing the rate. Also, second-order kinetics (first order in both phosphazene and the phenoxy group) are observed. Hence, this result suggests an $S_N2$-type mechanism.

## Acknowledgment

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## Notation

$A$ = interfacial area between the organic and aqueous phase, $m^2$
$Da_{QX}$ = mass-transfer factor of $QX$
$Da_{QY}$ = mass-transfer factor of $QY$
$h$ = Planck's constant,
$H_i$ = activation enthalpy
$k$ = reaction-rate constant $(min^{-1})$
$k_i$ = rate constant for the $i$th substitution reaction in the organic phase, $(M \cdot min)^{-1}$
$k_B$ = Boltzmann's constant
$K_{QY}$ = overall mass-transfer coefficient of $QY$, $l \cdot min^{-1}$
$m_{QX}$ = distribution coefficient of $QX$ $(\overline{[QX]}/[QX])$
$m_{QY}$ = distribution coefficient of $QY$ $(\overline{[QY]}/[QY])$
$Q_i$ = total quantity of onium salts (mol)
$QX, QY$ = onium salts
$R$ = gas constant
$RY$ = chemical product
$t$ = reaction time, min
$T$ = temperature, K
$V$ = volume of aqueous phase, L
$\bar{V}$ = volume of organic phase, L
$X^-$ = anions in the aqueous phase

$y_0$ = fraction of reactant, $N_3P_3Cl_6$, unconverted
$Y^-$ = anions in the aqueous phase
$\alpha$ = volume ratio ( $= V_0/V_a$ )

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