# Kinetics of the Reaction of Hexachlorocyclotriphosphazene with 2,2,2-Trifluoroethanol by Phase-transfer Catalysis

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The kinetics of the series substitution reaction between hexachlorocyclotriphosphazene and 2,2,2-trifluroethanol by tetrabutylammonium bromide as a phase-transfer catalyst in a two-phase organic solvent/alkaline solution was investigated. The kinetic data of this reaction gave a good fit to a second-order equation up to 90–100% of the complete reaction. The intrinsic reaction rate constants of the series substitution reaction in the organic phase were determined. The corresponding activation energy and activation entropy of the series substitution reaction were also obtained. The electronic density effect and the steric effect were both used to explain the relative reactivity of the six substituted reactions. The information would be valuable for an initial analysis of related reactions.

Phase-transfer catalysis (PTC) has been considered to be one of the most effective tools in the synthesis of organic chemicals from two immiscible reactants.[1–3] Quaternary salts are the most common ones used as phase-transfer catalysts. A generally accepted mechanism is that the catalyst will transfer between the two phases. The greatest advantage of synthesis of an ether in a Williamson reaction by PTC is, first, that the sodium phenoxide is synthesized *in situ* directly by reaction of phenol with cheap sodium hydroxide in the aqueous phase. During the reaction, the inorganic salt by-product, which is water soluble, is very easily removed from the products. The applications of PTC to the synthesis of phosphazenes has also been reported.[4–6]

The synthesized organophosphazenes can be used as pressurized working fluids, flame retardants and lubricants.[7] In recent years, only a few studies devoted to the investigation of the reaction kinetics of $(NPCl_2)_3$ have been published.[4,8,9] In the present study, hexakis(trifluoroethoxy)cyclotriphosphazene was synthesized by reaction of 2,2,2-trifluoroethanol with hexachlorocyclotriphosphazene by PTC in a mixture of an organic solvent and alkaline solution. The purpose of the present study was to understand the reactivity and the degree of the substitution reaction of chloride from phosphazene by the trifluoroethoxy group in the organic phase and to identify the substitution mechanism occurring in PTC.

## Experimental

*Materials.*—Hexachlorocyclotriphosphazene $[(NPCl_2)_3]$, 2,2,2-trifluoroethanol (ROH), tetrabutylammonium bromide (TBAB, QBr) and other reagents are all G.R.-grade chemicals.

*Procedures.*—(A) *Product separation by column chromatography.*[4] In this study, the product $N_3P_3(OCH_2CF_3)_6$ was first separated by cooling and crystallization. Crystalline $N_3P_3(OCH_2CF_3)_6$ of very high purity was obtained. The five other intermediate products, $N_3P_3Cl_{6-y}(OCH_2CF_3)_y$, $y$ = 1–5, were then separated by column chromatography. A pressurized control flow rate enhanced the separation effect.

Gas chromatography was carried out using a Shimadzu GC-9A instrument. A 7G 3.2 mm × 3.1 m glass column which contained 5% SE-30 on 80–100 mesh Chromosorb WAW-DMSC (Applied Supelco, Inc.) was used to separate the components and to analyse them experimentally. Mass spectra were obtained from a JEOL JMS-100 mass spectrometer at ionization potentials of 75 and 12 eV. $^{31}P$ NMR spectra were observed in deuteriated acetone on a JEOL 100 MHz. FT-NMR spectrometer. The m.p. was measured on a Model-MELTEP apparatus and is uncorrected.

(B) *Kinetic measurement of the two-phase reaction.* The reactor was a 125 cm³ four-necked Pyrex flask, allowing us to agitate the solution, insert the thermometer, take samples and feed substrate. The reactor was submerged in a constant-temperature water-bath in which the temperature could be controlled to within ±0.1 °C. To start a kinetic run, known quantities of sodium hydroxide, trifluoroethanol and TBAB were prepared and introduced into the reactor which was thermostatted at the desired temperature. Measured quantities of phosphazene reactant, $(NPCl_2)_3$, chlorobenzene (or diethyl ether) and pentadecane (internal standard for GC), which were also at the desired temperature, were then added to the reactor. An aliquot was withdrawn from the reaction solution at the chosen time. The sample (0.5 cm³) was immediately added to hydrochloric acid (3 cm³) to quench the reaction and then the contents of the organic phase were analysed quantitatively by GC using internal standards.

## The Mathematical Model

Based on the experimental data, a generalized approach to describe the phase-transfer catalysed reaction system is to use a pseudo-first-order reaction [eqn. (1)],[1] where eqn. (2) holds,

$$-\frac{d[(NPCl_2)_3]_o}{dt} = k_{0,app}[(NPCl_2)_3]_o \qquad (1)$$

$$k_{0,app} = k[QOCH_2CF_3]_o \qquad (2)$$

where the subscript 'o' denotes the characteristics in the organic phase. The fixed value of $k_{0,app}$ is called the pseudo-steady-state first-order reaction rate constant.

Some preliminary studies[9,10] have shown that the substitution reaction between hexachlorocyclotriphosphazene and sodium 2,2,2-trifluoroethoxide follows an $S_N2$ mechanism. Therefore, the series reaction of the organic phase in the present study can also be described by an $S_N2$ mechanism. The reactions can be written as eqns. (3)–(8).

$$(NPCl_2)_3 + QOCH_2CF_3 \xrightarrow{k_0} N_3P_3Cl_5(OCH_2CF_3) + QCl \qquad (3)$$

$$N_3P_3Cl_5(OCH_2CF_3) + QOCH_2CF_3 \xrightarrow{k_1} N_3P_3Cl_4(OCH_2CF_3)_2 + QCl \qquad (4)$$

$$N_3P_3Cl_4(OCH_2CF_3)_2 + QOCH_2CF_3 \xrightarrow{k_2} N_3P_3Cl_3(OCH_2CF_3)_3 + QCl \quad (5)$$

$$N_3P_3Cl_3(OCH_2CF_3)_3 + QOCH_2CF_3 \xrightarrow{k_3} N_3P_3Cl_2(OCH_2CF_3)_4 + QCl \quad (6)$$

$$N_3P_3Cl_2(OCH_2CF_3)_4 + QOCH_2CF_3 \xrightarrow{k_4} N_3P_3Cl(OCH_2CF_3)_5 + QCl \quad (7)$$

$$N_3P_3Cl(OCH_2CF_3)_5 + QOCH_2CF_3 \xrightarrow{k_5} [NP(OCH_2CF_3)_2]_3 + QCl \quad (8)$$

The reaction rate expressions are therefore given by eqn. (9)–(14), where the dimensionless variables and parameters are

$$\frac{dy_1}{dy_0} = -1 + k_1^* \frac{y_1}{y_0} \quad (9)$$

$$\frac{dy_2}{dy_0} = -k_1^* \frac{y_1}{y_0} + k_2^* \frac{y_2}{y_0} \quad (10)$$

$$\frac{dy_3}{dy_0} = -k_2^* \frac{y_2}{y_0} + k_3^* \frac{y_3}{y_0} \quad (11)$$

$$\frac{dy_4}{dy_0} = -k_3^* \frac{y_3}{y_0} + k_4^* \frac{y_4}{y_0} \quad (12)$$

$$\frac{dy_5}{dy_0} = -k_4^* \frac{y_4}{y_0} + k_5^* \frac{y_5}{y_0} \quad (13)$$

$$\frac{dy_6}{dy_0} = -k_5^* \frac{y_5}{y_0} \quad (14)$$

defined as

$$y_0 = \frac{[(NPCl_2)_3]_o}{[(NPCl_2)_3]_o^0}, y_1 = \frac{[N_3P_3Cl_5(OCH_2CF_3)]_o}{[(NPCl_2)_3]_o^0},$$

$$y_2 = \frac{[N_3P_3Cl_4(OCH_2CF_3)_2]_o}{[(NPCl_2)_3]_o^0}, y_3 = \frac{[(N_3P_3Cl_3(OCH_2CF_3)_3]_o}{[(NPCl_2)_3]_o^0},$$

$$y_4 = \frac{[N_3P_3Cl_2(OCH_2CF_3)_4]_o}{[(NPCl_2)_3]_o^0}, y_5 = \frac{[N_3P_3Cl(OCH_2CF_3)_5]_o}{[(NPCl_2)_3]_o^0},$$

$$y_6 = \frac{[[NP(OCH_2CF_3)_2]_3]_o}{[(NPCl_2)_3]_o^0}$$

and

$$k_1^* = \frac{k_1}{k_0}, k_2^* = \frac{k_2}{k_0}, k_3^* = \frac{k_3}{k_0}, k_4^* = \frac{k_4}{k_0}, k_5^* = \frac{k_5}{k_0}$$

where $[(NPCl_2)_3]_o^0$ represents the initial concentration of reactant $(NPCl_2)_3$ in the organic phase, and $k_0^* = 1$.

In general, eqns. (9)–(14) can be solved with the initial conditions of $y_i$ given in eqn. (15).

$$y_0 = 1, y_1 = y_2 = y_3 = y_5 = y_6 = 0 \quad (15)$$

The solutions are given in eqns. (16) and (17).

$$y_{n+1} = \sum_{l=0}^{n+1} \frac{\left(\prod_{i=0}^{n} k_i^*\right) y_0^{k_l^*}}{\prod_{\substack{i=0\\ i\neq l}}^{n+1} (k_i^* - k_l^*)}; \; n = 0, 1, 2, 3, 4; \; y_0 \neq 0 \quad (16)$$

$$y_6 = \sum_{l=0}^{5} \frac{k_5^*\left(\prod_{i=0}^{4} k_i^*\right)(y_0^{k_l^*} - 1)}{k_l^* \prod_{\substack{i=0\\ i\neq l}}^{5} (k_i^* - k_l^*)}; \; y_0 \neq 0 \quad (17)$$

From eqns. (16) and (17), the concentrations of the distributed products, $N_3P_3Cl_{6-y}(OCH_2CF_3)_y$, $y$ = 1–6, including the intermediate and final products, are thus determined. Meanwhile, the parameters $k_i^*$, $i$ = 1–5, can be estimated from the experimental data by using the non-linear least-squares method.

## Results and Discussion

The system chosen for study was the reaction of trifluoroethanol with hexachlorocyclotriphosphazene, with TBAB as the phase-transfer catalyst in an organic solvent/alkaline solution. The application of PTC had a dramatic accelerating effect on the reaction. It was found that the stirring rate did not influence the reaction when the agitation rate exceeded 800 rpm.[4] Therefore, the agitation rate was set at 950 rpm in order to allow us to study the kinetic phenomena in the present reaction. Despite the complexities of a two-phase system of water and organic solvent, the reaction followed good second-order kinetics at different temperatures.

(i) *Ratio of Reactant Rate Constants for Different Products.*—In the organic phase, the reaction mechanism of the reaction of $(NPCl_2)_3$ with $QOCH_2CF_3$ can be expressed by eqns. (3)–(8). The expression cannot be solved directly to give compositions as a function of time because the magnitude of the individual rate constants is not known (only their ratios are known). These rate-expression equations [eqns. (9)–(14)], along with the mass balance, can be solved for the desired yields of the products in terms of the amount of $(NPCl_2)_3$ which reacted (by eliminating time as a variable).

By applying eqns. (9)–(14), the relationships between six distributed products and the reactant can be obtained. By use of at least 12 sets of experimental data with a non-zero value of $y_0$ and by employing the method of non-linear least-squares, the $k_i^*$, $i$ = 1–5, were thus determined, *i.e.*, the $k_i^*$-values (at 40 °C) were $k_1^*$ 1.16, $k_2^*$ 0.70, $k_3^*$ 0.33, $k_4^*$ 0.20, $k_5^*$ 0.06. Using the above obtained values for $k_i^*$, the trajectories of the six products and the reactant are plotted in terms of the ratio of moles consumed of $HOCH_2CF_3/(NPCl_2)_3$. The estimated trajectories are also shown in Fig. 1. In general, the precision of the concentration measurements is within 3%. The largest error between experimental data and the estimated value is within 10%. Based on the above results, an $S_N2$-type reaction mechanism can be used to describe this series substitution reaction.

(ii) *Effect of Temperature.*—As shown in Table 1, both the intrinsic reaction rate constants and apparent pseudo-first-order reaction rate constants increased when the reaction temperature increased. The relative reaction rate constants for six distributed products at various temperatures were determined using the previous method and are given in Table 1. The inverse increase of $k_1^*$ and $k_2^*$ is more significant, due to the change in the difference in the reaction temperature. In order to find the relative reaction rate constants at various temperatures, the Arrhenius equation is rewritten for $k_0$ and $k_i$, $i$ = 1, 2, 3, 4 and 5, *i.e.*, eqns. (18) and (19), where $E_{i,0} = E_i - E_0$.

$$\log k_0 = \log k_{0,0} - \frac{E_0}{2.303RT} \quad (18)$$

**Table 1** The reaction rate constants *vs.* temperature in the chlorobenzene/alkaline solution by PTC

| $T$/°C | $k_{0,\mathrm{app}}$/min$^{-1}$ | $k_0$/dm$^3$ mol$^{-1}$ min$^{-1\,a}$ | $k_1^*$ | $k_2^*$ | $k_3^*$ | $k_4^*$ | $k_5^*$ |
|---|---|---|---|---|---|---|---|
| 2 | 0.066 | 159 | 1.60 | 0.85 | 0.26 | 0.14 | 0.034 |
| 20 | 0.171 | 293 | 1.32 | 0.74 | 0.29 | 0.16 | 0.045 |
| 30 | 0.237 | 509 | 1.23 | 0.71 | 0.31 | 0.18 | 0.052 |
| 40 | 0.309 | 763 | 1.16 | 0.70 | 0.33 | 0.20 | 0.060 |

Reaction conditions: Chlorobenzene (50 cm$^3$), ($NPCl_2$) (0.0059 mol), NaOH (3 g), $HOCH_2CF_3$ (7 g), water (20 cm$^3$), TBAB (9.6 × $10^{-5}$ mol).
$^a$ Ref. 11.

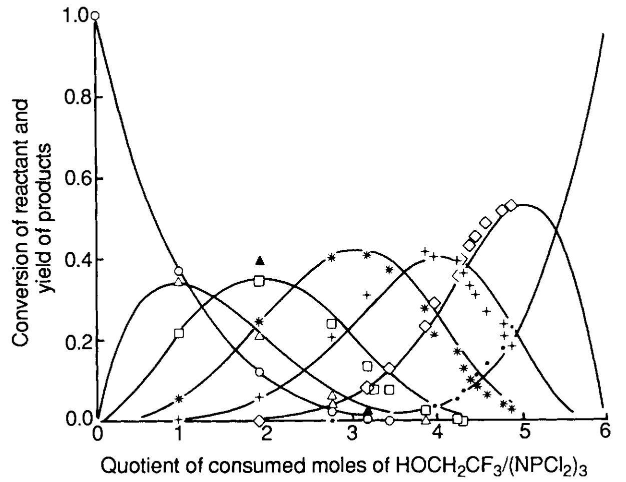

**Fig. 1** Yields of the six distributed products and reactant as a function of the reactant $HOCH_2CF_3/(NPCl_2)_3$ consumption ratio for the reaction of chlorobenzene (50 cm$^3$), with $(NPCl_2)_3$ (0.0059 mol), NaOH (3 g), $HOCH_2CF_3$ (7 g), water (20 cm$^3$) and TBAB (9.6 × $10^{-5}$ mol) at 950 rpm, 40 °C. ○, $N_3P_3Cl_6$; △, $N_3P_3Cl_5(OCH_2CF_3)$; □, $N_3P_3Cl_4(OCH_2CF_3)_2$; *, $N_3P_3Cl_3(OCH_2CF_3)_3$; +, $N_3P_3Cl_2(OCH_2CH_3)_4$; ◇, $N_3P_3Cl(OCH_2CF_3)_5$; ●, $N_3P_3(OCH_2CF_3)_6$.

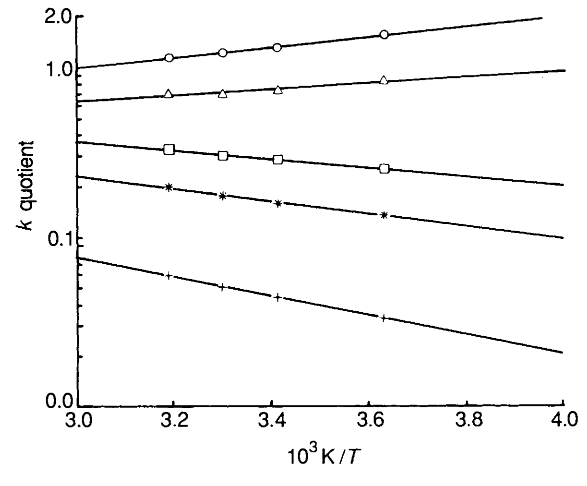

**Fig. 2** The temperature effect on the quotient of the intrinsic reaction rate constants. The operating conditions are the same as those given for Fig. 1. ○, $k_1^*$; △, $k_2^*$; □, $k_3^*$; *, $k_4^*$; †, $k_5^*$.

and

$$\log\frac{k_i}{k_0} = log\frac{k_{i,0}}{k_{0,0}} - \frac{E_{i,0}}{2.303RT} \tag{19}$$

From Table 1 and eqns. (18) and (19), one can easily obtain the $k$-ratios which are shown in Fig. 2 and the difference in activation energies. The corresponding activation entropies and frequency factors are given in Table 2. The ratio of frequency factors for the series substitution reaction is increased on increasing the reaction temperature. The order of increase for the Arrhenius activation energy and entropy of activation is that both are first decreased and then increased with incremental substitution reaction from one to six chlorine atoms. This implies that the high activation energy is more sensitive in a high-temperature reaction.

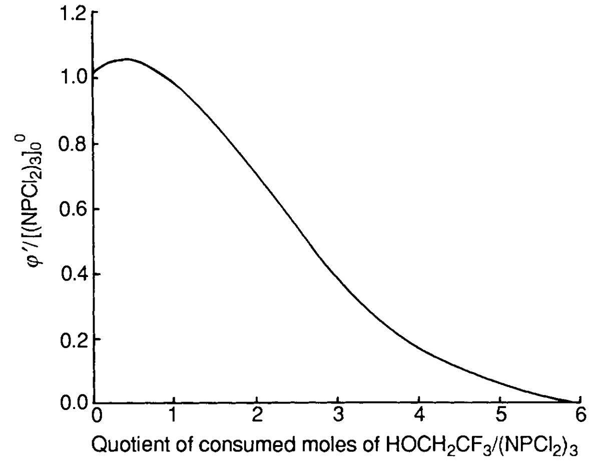

**Fig. 3** The relation between $[(NPCl_2)_3]_0$ and $(HOCH_2CF_3)$

(iii) *Reaction Path by PTC*.—Schmutz and Allcock[10] observed that the reaction of hexachlorocyclotriphosphazene with 2,2,2-trifluoroethanol followed a *trans*-geminal pathway. In the present study,[4] the products analysed by NMR spectroscopy were also consistent with the work of Schmutz and Allcock.[10] As shown in Fig. 1, the evidence is consistent with an $S_N2$-type reaction mechanism during replacement of chlorine atoms by the trifluoroethoxy group.

Table 1 shows the data for $k_1^* > 1$ and $k_i^* < 1$, $i = 2, 3, 4$ and 5. The results indicate that the reactivity of $N_3P_3Cl_5(OCH_2CF_3)$ is larger than that of the reactant $(NPCl_2)_3$.

If we define $\varphi'$ as in eqn. (20), where $\varphi'/[(NPCl_2)_3]_0^0$ is

$$\begin{aligned}\varphi' = {} & k_0^*[(NPCl_2)_3] + k_1^*[N_3P_3Cl_5(OCH_2CF_3)] + \\ & k_2^*[N_3P_3Cl_4(OCH_2CF_3)_2] + k_3^*[(N_3P_3Cl_3(OCH_2CF_3)_3] + \\ & k_4^*[N_3P_3Cl_2(OCH_2CF_3)_4] + \\ & k_5^*[N_3P_3Cl(OCH_2CF_3)_5]\end{aligned} \tag{20}$$

the quotient of the total reactivity of the series reaction to the initial reactivity of $(NPCl_2)_3$. As shown in Fig. 3, a maximum in reactivity was found during the course of replacement of all of the chlorine atoms.

In general, the series reaction rate constants are affected by electronic and steric effects. The mobility of the chlorine atoms should be facilitated by an increase in the electron density on the phosphorus atoms. The phosphorus atoms become progressively more shielded when additional chlorine atoms are replaced by the trifluoroethoxy groups. Schmutz and Allcock[10] suggested that nucleophilic attack by an $S_N2$ process occurs at the least hindered side of the ring in a homogeneous phase. The

**Table 2** Kinetic parameters of the reaction of $(NPCl_2)_3$ derivatives with 2,2,2-trifluoroethanol by PTC

| | | | *i* | | | | |
|---|---|---|---|---|---|---|---|
| | | *a* | 1 | 2 | 3 | 4 | 5 |
| Activation energy | $E_{i,0}$/kcal mol$^{-1}$ [b] | 6.95 | −1.42 | −0.87 | 1.00 | 1.65 | 2.57 |
| Entropy of activation | $\Delta S^{\neq}_{i,0}$ [c]/cal mol$^{-1}$ K$^{-1}$ | −33.62 | −4.29 | −3.57 | 1.26 | 1.99 | 2.61 |
| Frequency factor | $k_{i,0}/k_{0,0}$ | | 0.12 | 0.17 | 1.90 | 2.75 | 3.63 |

[a] The intrinsic kinetic parameters of the reactant $(NPCl_2)_3$. [b] 1 cal = 4.184 J. [c] $\Delta S^{\neq}_{i,0} = \Delta S^{\neq}_i - \Delta S^{\neq}_0$, at 20 °C.

**Table 3** *k*-Values of the reaction rate constants *vs.* temperature in the diethyl ether/alkaline solution

| Temperature ($T$/°C) | $k^*_1$ | $k^*_2$ | $k^*_3$ |
|---|---|---|---|
| 10 | 0.99 | 0.35 | 0.13 |
| 20 | 0.95 | 0.36 | 0.15 |
| 30 | 0.90 | 0.38 | 0.19 |

Reaction conditions: diethyl ether (50 cm$^3$), $(NPCl_2)_3$ (0.0059 mol), NaOH (3 g), $HOCH_2CF_3$ (7 g), water (20 cm$^3$).

kinetic data for the two-phase reaction by PTC are shown in Tables 1 and 2. The Arrhenius activation energies $E_{i,0}$, $i = 1, 2$ are negative. Increasing the replacement of chlorine atoms of $(NPCl_2)_3$ by the trifluoroethoxy group results in a decrease in the relative reaction ratio ($k^*_i$). The electronic effect will be 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.

The synchronous bimolecular type of mechanism is well known in the chemistry of tetraco-ordinate phosphorus. The mechanism is characterized by the formation of a trigonal bipyramidal transition state from which the displaced anion leaves axially from the opposite side of the complex to the attacking group. For this, second-order or pseudo-first-order kinetics may be expected for a single-step $S_N2$-type mechanism. On the other hand, an $S_N1$-type process would involve the prior dissociation of chloride ion from the phosphorus, followed by rapid trifluoroethoxide attack on the cation thus formed. Such a mechanism would be characterized by first-order kinetics. Nevertheless, an analysis of the experimental data should provide a clue to the reaction path. For this, let us consider the evidence based on the pattern of chlorine replacement. If the substitution follows a simple $S_N2$-type mechanism, replacement of one chlorine atom on phosphorus by $OCH_2CF_3$ should decrease the tendency of a second $OCH_2CF_3$ moiety to attack at the same phosphorus atom. Steric hindrance by bulky $OCH_2CF_3$ groups would also be expected to inhibit the approach of the nucleophile to the phosphorus atom. Thus, non-geminal substitution should be observed.

In the present system, the reaction of hexachlorocyclotriphosphazene with 2,2,2-trifluoroethanol followed a *trans*-non-geminal pathway.[4] As shown in Tables 1 and 2, the reaction rate decreases in the order $N_3P_3Cl_5(OCH_2CF_3) > N_3P_3Cl_4(OCH_2CF_3)_2 > N_3P_3Cl_3(OCH_2CF_3)_3 > N_3P_3Cl_2(OCH_2CF_3)_4 > N_3P_3Cl(OCH_2CF_3)_5$ with the activation energy increasing in the order −1.42, −0.87, 1.00, 1.65, 2.57 kcal mol$^{-1}$.* For this phenomenon, second-order kinetics are observed and this suggests an $S_N2$-type mechanism. This statement is consistent with the work of Allcock,[7] Sorokin and Latov[9] and Schmutz and Allcock.[10]

In general, there is only one single step without an intermediate being involved for the $S_N2$-type reaction mechanism. For this type of mechanism, the reaction follows second-order kinetics. Nevertheless, a stable pentaco-ordinate phosphorus intermediate will probably be formed during the reaction. For this type of reaction, the two-step, addition–elimination process is involved. Both the one-step, $S_N2$ reaction mechanism and the two-step, addition–elimination process give rise to the same kinetics, *i.e.*, second-order kinetics. Therefore, it is possible that the reaction mechanism is a two-step, addition–elimination process in the replacement of chlorine from the phosphorus atom by the $OCH_2CF_3$ groups. Hence it is difficult to identify the reaction mechanism simply from the kinetic data only. However, it seems that our postulate of a single-step, $S_N2$ reaction mechanism is likely to be acceptable.

(iv) *Reaction without addition of Phase-Transfer Catalyst.*—Sodium trifluoroethoxide is not soluble in chlorobenzene. The consumption of the reactant $(NPCl_2)_3$ was less than 10% after 4 h reaction time when no catalyst was added, despite the fact that the reaction is enhanced by addition of a small quantity of catalyst. However, if the organic solvent is diethyl ether, the solubility of sodium trifluoroethoxide in the organic phase increases. The reaction could occur then even when no catalyst was added. Nevertheless, the reaction rate was dramatically enhanced by addition of a catalyst.

When the organic solvent was diethyl ether and no catalyst was added, the relative reaction rate constants were determined by using the previous method. The results are given in Table 3. In this reaction system, the largest error between the experimental data and estimated values was >10%. However, the error in estimating the three former relative reaction rate constants ($k^*_1$–$k^*_3$) was within 5% and the fitted error between experimental data and the estimated values could be <10%. The estimated data are shown in Table 3. The first ($k_1$) value of the reactant constant decreases upon an increase in reaction temperature. In other words, the second and third quotients of the reaction both increase. This tendency is similar to that in the reaction system in chlorobenzene by PTC studied in this paper.

*Conclusions.*—In the present paper, the results of the reaction of hexachlorocyclotriphosphazene with 2,2,2-trifluoroethanol in a two-phase organic solvent/alkaline solution by tetrabutylammonium bromide are presented. A second-order equation could be used to describe the kinetics of this series reaction. This evidence is consistent with an $S_N2$-type mechanism during replacement of the chloride atoms by trifluoroethoxy groups using PTC. The quotients of intrinsic reaction rate constants of the distributed products were determined by the non-linear

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* 1 cal = 4.184 J.

least-squares method. Increasing replacement of the chlorine atoms of $(NPCl_2)_3$ by trifluoroethoxy groups resulted in a sharp decrease in both the activation energy and the activation entropy. Furthermore, the electronic density effect and the steric effect were also employed to explain the relative reaction reactivities of the six distributed products.

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