benzenesulfinic Acid. In Aqueous Ethanol. (a) Treatment of ArSSAr with $ArSO_2H$. A 50 mM (36 μL, 0.04905 g) solution of *p*-fluorophenyl disulfide in 2.0 mL of EtOH was mixed with 2.0 mL of H_2O. The disulfide was only partially soluble as most of the oil settled to the bottom of the tube. To this was added 50 mM (0.23050 g) *p*-fluorobenzenesulfinic acid. No reaction occurred.

(b) Stability of ArS(O)SAr to Disproportionation. A sample of *S*-*p*-fluorophenyl *p*-fluorobenzenethiosulfinate was dissolved in 4.0 mL of aqueous ethanol to give a solution which exhibited the following ^{19}F NMR signals: δ 114.72 (0.06, ArSSAr), 107.92 and 109.95 (2.4 each, ArS(O)SAr), and 103.03 and 107.90 (0.04 each, $ArSO_2SAr$). After heating at 60 °C for 30 min, there was very little change: δ 114.76 (0.2, ArSSAr), 107.99 and 110.04 (2.6 each, ArS(O)SAr), and 103.10 (0.11 each, $ArSO_2SAr$).

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Supplementary Material Available: ^1H NMR spectra of ethyl *p*-fluorobenzenesulfinate (2 pages). Ordering information is given on any current masthead page.

Effects of Mass Transfer and Extraction of Quaternary Salts on a Substitution Reaction by Phase-Transfer Catalysis

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The substitution reaction of hexachlorocyclotriphosphazene with 2,2,2-trifluoroethanol using quaternary ammonium salts as the phase-transfer catalysts in an organic solvent/alkaline solution has been investigated. The pseudo-first-order reaction rate constant of the two-phase reaction and the rate constant ratios of the sequential substitution reaction in the organic phase were obtained. The hydration number of the catalyst, $QOCH_2CF_3$, is determined from the experimental data. The reaction reactivity is influenced by the content of the acids, which include water and alcohol in the aqueous phase. For an extraction mechanism, the reactivities of all kinds of catalysts in the organic phase with the same kind of solvent are the same. The effects of mass transfer and the extraction of quaternary ammonium salts on the conversion are used to explain the experimental data. The obtained results can be used as a reference for selecting the appropriate solvent and catalyst as well as for determining the appropriate content in the aqueous phase. Meanwhile, the desired distributed products, including the intermediate and final products, can be obtained by the appropriate choice of reaction conditions.

Introduction

The problems of two-phase reactions were not solved until Jarrouse[1] discovered the catalyzing effect of quaternary ammonium salt in the aqueous–organic phase reaction system. The quaternary ammonium salt, which served as a phase-transfer catalyst in the two-phase reaction system, was then studied by many chemists.[2–4] At this time, it has been extensively applied to the synthesis of special organic chemicals by displacement, alkylation, arylation, elimination, condensation, oxidation, reduction, and free-radical polymerization. The most advantageous uses of phase-transfer catalysis to synthesize organic chemicals are fast reaction rate, high selectivity of product, moderate operating temperature, and applicability to industrial-scale production.

In recent years, scientists have paid great attention to the development of inorganic cyclic compounds and high polymers for material applications.[5–8] In the past, poly(trifluoroethoxycyclotriphosphazene) was synthesized by reacting metallic sodium (or sodium hydride) with phosphazene.[9] Unfortunately the yield was too low even though the experiment was carried out at a high temperature for a long time.[10] Allcock[11] used tetra-*n*-butylammonium chloride as a phase-transfer catalyst to study the substitution of mono-$OC_6H_{14}NO_2$-P from chloride in chloropentaphenoxylcyclotriphosphazene. Further, Carr and Nichols[12] synthesized phosphazene esters by using phase-transfer catalysis. However, the effects of mass transfer and extraction of catalyst in the organic phase during conversion were not investigated.

In general, there are three main topics which need to be clarified in studying the phase-transfer catalytic reaction, i.e., the selection of an appropriate catalyst, and solvent, and the determination of an appropriate content in the aqueous phase. In the present study, the effects of mass transfer and extraction of quaternary ammonium salts on the substitution reaction of hexachlorocyclotriphosphazene with 2,2,2-trifluoroethanol by phase-transfer catalysis (PTC) are studied in detail. The objective of this paper is to employ the experimental data in studying the effects of mass transfer and extraction of quaternary ammonium salts on the conversion in order to give a reasonable explanation of the phenomenon.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$; 2,2,2-trifluoroethanol ($HOCH_2CF_3$; ROH); tetra-*n*-butylammonium

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bromide (($(C_4H_9)_4N^+Br^-$; QBr); and the other quaternary ammonium salts are all G.R. grade chemicals.

Procedures. (A) Product Separation by Column Chromatography. In this study, the product of $N_3P_3(OCH_2CF_3)_6$ is first separated by cooling crystallization. A very high purity of white $N_3P_3(OCH_2CF_3)_6$ crystal is obtained. The other five intermediate products, $N_3P_3Cl_{6-y}(OCH_2CF_3)_y$, $y = 1–5$, are then separated by column chromatography.[13,14] A presurized control flow rate will enhance the separation effect.[15]

A glass chromatography column 50 cm in length and 3.8 cm in diameter serves as the separation column. Some glass wool is packed at the bottom of column. Then, 40–60 mesh sand is filled from the bottom of the column to a 0.3-cm height. An appropriate quantity of silica gel and eluent solvent (a mixture of hexane and dichloromethane) are mixed by agitation until no existance of bubbles is seen. This is then added into the column. Then, this packed material is packed more tightly with pressurized air in order to keep the height of packed material at a constant level. In addition, a little sand is further added to the bed. The sample to be analyzed (i.e., 10 g of distributed product mixed with 10 mL of eluent) is then poured into the column. The column wall, to which a little distributed product may cling, is then washed with the eluent. The liquid level should be kept at the same or higher level than the packed material. Then, the upper end of the column is connected to an eluent reservoir. The sample is collected by test tubes batchwise. The sample in every test tube is analyzed by GC, and those samples which have the same strong single absorbance by GC, indicating the same single component, are collected together. After removal of the solvent from the collected samples, a product of very high purity is then obtained. By this procedure, it appears that some test tubes contain more than one component. For this reason, the samples are further collected together and then treated by column chromatography two or three times.

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 a 80–100 mesh Chromosorb WAW-DMSC (Applied Supelco, Inc.) was used to separate the components and to analyze then experimentally. Mass spectra were obtained from a JEOL JMS-100 mass spectrometer at the ionization potentials of 75 and 12 eV. ^{31}P NMR spectra were observed in deuterated acetone on a JEOL 100 MHz FT-NMR. The melting point was measured by the laboratory device Model-MELTEP.

(B) Kinetic Measurement of the Two-Phase Reaction. The reactor is a 125-mL four-neck Pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding feed. The reactor is submerged into a constant-temperature water bath in which the temperature can be controlled to within ±0.1 °C. To start a kinetic run, a known quantity of sodium hydroxide, trifluoroethanol, and tetra-*n*-butylammonium bromide (or other kind of quaternary ammonium salt) is prepared and introduced into the reactor which is thermostated at the desired temperature. A measured quantity of phosphazene reactant, $(NPCl_2)_3$, chlorobenzene (or other kind of solvent), and *n*-pentadecane (internal standard for GC), which are also at the desired temperature, are then added to the reactor. An aliquot sample is withdrawn from the reaction solution at the chosen time. The sample (0.5 mL) is immediately added to 3 mL of hydrochloric acid to quench the reaction and then the organic-phase contents are analyzed quantitatively by GC using the method of internal standard.

(C) Measurement of Quaternary Cation Concentration. Known quantities of catalyst, sodium hydroxide (3 g), 2,2,2-trifluoroethanol (7 g), organic solvent (50 mL), and water (20 mL) are prepared and introduced into a 125 mL flask. The flask is submerged into a constant temperature water bath in which the temperature can be controlled to within ±0.2 °C. The mixed solution is agitated for a long time, and the reagents are allowed to uniformly distribute between the two phases. At the final equilibrium state the sample is withdrawn and analyzed by the titration method.

The concentration of the quaternary cation (R_4N^+ or Q^+) was determined by the extractive titration method using sodium tetraphenylborate (TPB: $Na(C_6H_5)_4B$) as the titrant and the tetrabromophenolphthalein ethyl ester potassium salt ($C_{22}H_{13}Br_4KO_4$) as the indicator.[16] The indicator (Ind) is insoluble in water, but gives a yellow solution in 1,2-dichloroethane. The quaternary cation is extracted as a blue ion pair with the dye from the aqueous phase to the 1,2-dichloroethane phase. When the quaternary cation is titrated with sodium tetraphenylborate solution, the R_4N^+TPB is formed in the organic layer, and the reaction which follows at the end point is

$$\underset{\text{blue}}{[R_4N^+Ind^-]_{org}} + H^+ + [TPB^-]_{aq} \rightarrow [R_4N^+TPB^-]_{org} + \underset{\text{yellow}}{[Ind]_{org}}$$

The color change is quite sharp at the end point. A complete stirring is important to avoid overtitration. Thus, $C_{22}H_{13}Br_4KO_4$ was first dissolved in ethanol Quaternary ammonium salt solution (10 mL), phosphate baffer solution (5 mL, pH 6.6), 1,2-dichloroethane (5 mL) and $C_{22}H_{13}Br_4KO_4$ solution (2–3 drops, 0.1%) were placed in flask. The mixture was then titrated with 0.002 M sodium tetraphenylborate solution with shaking by the stirrer.

Mathematical Model

In the S_N2 mechanism of organic reactions by phase-transfer catalysis, the substrate and the nucleophile react directly via a transitition state to product.[3,17] By plotting ln $[(NPCl_2)_3]_o$ vs time from experimental data in the present study, a straight line is obtained. Thus, the system, which was originally described by the second-order reaction with constant concentration of $QOCH_2CF_3$ in the organic phase, is reduced to a first-order reaction and can be expressed as[3]

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

where

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

The fixed value of $k_{0,app}$ is called the pseudo-steady-state first-order reaction rate constant. Some preliminary studies[18,19] have shown that the substitution reaction between hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and sodium 2,2,2-trifluoroethoxide ($NaOCH_2CF_3$) follows the S_N2 mechanism. Therefore, the series reaction of the organic phase in the present study can also be described by the S_N2 mechanism. The reaction expressions can be written as

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

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

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

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

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

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

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The reaction rate expressions are, thus,

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

$$\frac{dy_2}{dy_0} = k_1^*\frac{y_1}{y_0} - k_2^*\frac{y_2}{y_0} \tag{10}$$

$$\frac{dy_3}{dy_0} = k_2^*\frac{y_2}{y_0} - k_3^*\frac{y_3}{y_0} \tag{11}$$

$$\frac{dy_4}{dy_0} = k_3^*\frac{y_3}{y_0} - k_4^*\frac{y_4}{y_0} \tag{12}$$

$$\frac{dy_5}{dy_0} = k_4^*\frac{y_4}{y_0} - k_5^*\frac{y_5}{y_0} \tag{13}$$

$$\frac{dy_6}{dy_0} = k_5^*\frac{y_5}{y_0} \tag{14}$$

where the dimensionless variables and parameters are defined as

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

$$y_2 = \frac{[\mathrm{N_3P_3Cl_4(OCH_2CF_3)_2}]_o}{[(\mathrm{NPCl_2})_3]_o^0},\ y_3 = \frac{[(\mathrm{NPCl_3(OCH_2CF_3)_3}]_o}{[(\mathrm{NPCl_2})_3]_o^0}$$

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

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

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

In general, eq 9–14 can be solved with the following initial conditions of y_i.

$$y_0 = 1,\ y_1 = y_2 = y_3 = y_4 = y_5 = y_6 = 0 \tag{15}$$

The solutions are

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

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

From eqs 16 and 17, the concentrations of the distributed products, $\mathrm{N_3P_3Cl_{6-y}(OCH_2CF_3)_y}$, $y = 1$–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 nonlinear least-square method.

Results and Discussion

A difficult problem in the kinetics of phase-transfer-catalyzed reactions is to sort out the rate effects due to equilibria and anion-transfer mechanism for transfer of anions from the aqueous to the organic phase. That is, the concentration of $\mathrm{QOCH_2CF_3}$ would remain constant if $\mathrm{Q^+}$ concentration in the organic phase remained constant throughout the entire course of a kinetic run and the equilibrium constant K for

$$\mathrm{QOCH_2CF_3}_{\,\mathrm{org}} + \mathrm{Cl^-}_{\mathrm{aq}} \overset{K}{\rightleftharpoons} \mathrm{QCl_{org}} + {}^-\mathrm{OCH_2CF_3}_{\,\mathrm{aq}} \tag{18}$$

is very small. In the present study, many experimental runs were carried out to examine the $\mathrm{Q^+}$ values and K values. More than 99.5% of $\mathrm{Q^+}$ stay in the organic phase and K value is calculated to be less than 1.0×10^{-2}. Therefore, the concentration of $\mathrm{QOCH_2CF_3}$ in the organic phase remains constant. Based on this experimental evidence, those factors affecting the reaction are discussed in the following.

(i) Effect of Mass Transfer. Usually, it is recognized that the rate-determining step is controlled by the chemical reaction in the organic phase under the PTC condition. For a fast mass-transfer rate of catalyst between two phases, the influence of mass transfer on the reaction can be neglected. However, as shown in Table I, the apparent reaction rate constant, $k_{0,\mathrm{app}}$ is changed by changing the concentration of $(\mathrm{NPCl_2})_3$ reactant in the organic phase. In addition, the value of $k_{0.5/2}$, defined as the ratio of the $k_{0,\mathrm{app}}$ value using 0.5 g of $(\mathrm{NPCl_2})_3$ to the $k_{0,\mathrm{app}}$ value using 2 g of $(\mathrm{NPCl_2})_3$, is increased for increasing reaction temperature. Thus, it is obvious that the present reaction system is both controlled by chemical kinetics and mass transfer.

(ii) Influence of the Quaternary Cation under the PTC Condition. In assessing the relative efficacies of the various quaternary ions, as given in Table II, three dominated factors should be considered. First, the quaternary ions must be able to carry trifluoroethoxide ions from the aqueous phase to the organic phase. Second, the reactivity of the quaternary ions may be dependent upon the natural aggregation between the quaternary ions and the trifluoroethoxide ions. Third, the quaternary ions will also be able to pick up other molecules of the nucleophile in order to return to the aqueous phase from the organic phase.

In general, the functional groups of the quaternary cation will affect the dissolution of the catalyst in the organic phase. Further, the phase transfer of the anion will also affect the reaction rate in the two-phase reaction. Therefore, a proper choice of phase-transfer catalyst is very important in promoting the reaction rate. Unfortunately, a universal guideline is unavailable for selecting the proper phase-transfer catalyst to enhance the reaction rate. Thus, commonly commercial phase-transfer catalysts, such as tetra-*n*-butylammonium bromide, etc., are employed in the present study. The experimental results of the conversion of $(\mathrm{NPCl_2})_3$ vs time for different kinds of phase-transfer catalysts in the two-phase reaction system are shown in Table II. The order of the reactivity for these phase-transfer catalysts is TBAHS > BTEAOH > TBAI > BTBAB > TBAB > BTEAC > Aliquot 336 > CTMAB > BTMAC > TEAC.

The k_i^* values of the sequential substituting reactions are given in Table II. The results of $k_1^* > 1$ and $k_{i+1}^* < k_i^*$, $i = 1$–4 for those catalysts employed in a chloro-

Table I. Effects of Mass Transfer on the Reaction System[a]

temp, °C	$k_{0,\text{app}}$, min^{-1} mass of reactant, $(NPCl_2)_3$, g 2.0	1.5	1.0	0.5	$k_{1.5/2}$	$k_{1/2}$	$k_{0.5/2}$
20	0.17	0.21	0.27	0.36	1.24	1.59	2.11
30	0.24	0.31	0.40	0.58	1.29	1.67	2.42
40	0.31	0.52	0.75	0.87	1.67	2.42	2.81

[a] Reaction conditions: 0.0059 mol of $(NPCl_2)_3$, 7 g of $HOCH_2CF_3$, 9.6×10^{-5} mol of TBAB, 3 g of NaOH, 50 mL of chlorobenzene, 20 mL of water.

Table II. Effects of Catalysts on the Ratios of Reaction Rate Constants

PTC[b]	$k_{0,\text{app}}$, min^{-1}	k_{rel}[a]	k_1*	k_2*	k_3*	k_4*	k_5*
TBAHS	0.19	1.12	1.32	0.74	0.29	0.16	0.045
BTEAOH	0.19	1.12	1.32	0.74	0.29	0.16	0.045
TBAI	0.18	1.06	1.32	0.74	0.32	0.16	0.045
BTBAB	0.18	1.06	1.32	0.74	0.29	0.16	0.045
TBAB	0.17	1.00	1.32	0.74	0.29	0.16	0.045
BTEAC	0.16	0.94	1.32	0.74	0.32	0.16	0.045
Aliq336	0.14	0.82	1.32	0.74	0.29	0.16	0.045
CTMAB	0.14	0.82	1.15	0.64	0.27	0.14	0.040
BTMAC	0.038	0.22	1.17	0.63	0.27	0.14	0.04
TEAC	0.015	0.09	1.32	0.74	0.29	0.16	0.045
CROWN6	0.030	0.17	1.32	0.74	0.29	0.16	0.045

[a] Relative to TBAB. [b] TBAHS: tetrabutylammonium hydrogen sulfate. BTEAOH: benzyltriethylammonium hydroxide (10% in water). TBAI: tetrabutylammonium iodide. BTBAB: benzyltributylammonium bromide. TBAB: tetrabutylammonium bromide. BTEAC: benzyltriethylammonium chloride. Aliq336: trioctylmethylammonium chloride. CTMAB: cetyltrimethylammonium bromide. BTMAC: benzyltrimethylammonium chloride. TEAC: tetraethylammonium chloride. CROWN6: crown ether/18-Crown-6. Reaction conditions: 0.0059 mol of $(NPCl_2)_3$, 7 g of $HOCH_2CF_3$, 3 g of NaOH, 9.6×10^{-5} mol of PTC, 50 mL of chlorobenzene, 20 mL of water, 20 °C.

Table III. Effects of Catalysts on the Relative Reactivities

	$k_{0,\text{app}}$,[a] min^{-1}							
	$(NPCl_2)_3$, g							
PTC	2.0	1.5	1.0	0.5	relative reactivity, $k_{0.5/2}$	Q^+ in chlorobenzene with adding ROH,[b] %	Q^+ in chlorobenzene without adding ROH,[c] %	apparent extraction constants for no adding ROH, E_{app}[d]
BTBAB	0.18	0.22	0.29	0.39	2.16	100	31	51
TBAB	0.17	0.21	0.27	0.36	2.1	100	18	18
BTEAC	0.16	0.19	0.23	0.28	1.75	19.2	0	0
Aliq336	0.14	0.19	0.25	0.32	2.3	100	100	∞
CTMAB	0.14	0.17	0.19	0.26	1.86	100	4.1	3.7
BTMAC	0.033	0.034	0.038	0.039	1.18	4.67	0	0
TEAC	0.022	0.033	0.022	0.022	1.0	trace	0	0

[a] 0.0059 mol of $(NPCl_2)_3$, 7 g of $HOCH_2CF_3$, 3 g of NaOH, 9.6×10^{-5} mol of PTC, 50 mL of chlorobenzene, 20 mL of water, 20 °C. [b] 7 g of $HOCH_2CF_3$, 3 g of NaOH, 9.6×10^{-5} mol of PTC, 50 mL of chlorobenzene, 20 mL of water, 20 °C. [c] 3 g of NaOH, 9.6×10^{-5} mol of PTC, 50 mL of chlorobenene, 20 mL of water, 20 °C. [d] $E_{\text{app}} = [QY]_o/[Q^+]_a[Y^-]_a$.

benzene/NaOH aqueous solution reaction indicate that the substitution of the second chloride by trifluoroethoxide is more reactive than that of the first one, and that the sequential substitutions of more chlorides by trifluoroethoxides become increasingly more difficult. In addition, the ratios of the second-order reaction rate constants of the intermediate products, k_i*, $i = 1$–5 are almost the same for those tested catalysts, except for the CTMAB and BTMAC catalysts. In general, the catalysts, CTMAB and BTMAC, with methyl groups around the cationic center have less reactivity than other catalysts. Based on the experimental data listed in Table II and on the observation of experiments, the reaction mechanism using the CTMAB and BTMAC catalysts is a micelle reaction.[3] Except for these two kinds of catalysts, the reaction mechanism is an extraction mechanism of quaternary cations. This result clarifies and confirms quantitatively the already proposed concept[20,21] that the effectiveness of a phase-transfer catalyst depends highly on the organophilicity. The pseudo-first-order reaction rate constants, $k_{0,\text{app}}$, for those tested catalysts in a chlorobenzene/NaOH aqueous solution reaction are also depicted in Table II. The reactivities of the catalysts relative to the TBAB catalyst differ by several orders of magnitude due to the variation of the quaternary cation structure. The estimated $k_{0,\text{app}}$ value can be used as a criterion for selecting an appropriate catalyst in the two-phase reaction.

In general, the reaction, which is controlled by purely chemical reaction kinetics, will be independent of the mass of the reactant, $(NPCl_2)_3$, on the conversion. The effect of the mass of $(NPCl_2)_3$ on the conversion is shown in Table III. The only case for chemical reaction kinetic control is to use the TEAC catalyst in the two-phase reaction. Other reactions with different kinds of catalysts are both controlled by chemical reaction kinetics and mass transfer. A higher value of $k_{0.5/2}$ implies a higher effect of mass transfer on the reaction rate.

At equilibrium, the percentage of quaternary ions in the organic phase of the chlorobenzene/NaOH aqueous system with or without adding $HOCH_2CF_3$ is also measured. The results are also given in Table III. Based on the reaction mechanism, either the catalyst QOR or QX may stay within the organic phase or the aqueous phase. The competition of QOR with QX to stay within the organic phase is influenced by the addition of $HOCH_2CF_3$. It is obvious that the addition of the organophilic substance, $HOCH_2$-

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Table IV. Effects of Solvents on the Ratios of Reaction Rate Constants

solvents	$k_{0,\mathrm{app}}$, min^{-1}	k_{rel}[a]	k_1*	k_2*	k_3*	k_4*	k_5*
1,2-dichloroethane	0.30	1.76	1.01	0.52	0.24	0.11	–
chlorobenzene	0.17	1.00	1.32	0.74	0.32	0.16	0.045
dichloromethane	0.14	0.82	0.90	0.42	0.19	0.09	0.031
benzene	0.071	0.41	1.30	0.70	0.23	0.13	0.035
toluene	0.070	0.41	1.30	0.70	0.19	0.11	0.030
chloroform	0.043	0.22	1.29	0.77	0.35	0.18	–
hexane	0.040	0.23	3.80	3.0	1.35	1.2	0.6

[a] Relative to chlorobenzene. Reaction conditions: 0.0059 mol of $(NPCl_2)_3$, 7 g of $HOCH_2CF_3$, 3 g of NaOH, 9.6 × 10^{-5} mol of TBAB, 50 mL of solvent, 20 mL of water, 20 °C.

Table V. Effects of Solvents on the Relative Reactivities[a]

	$k_{0,\mathrm{app}}$, min^{-1}								
	$(NPCl_2)_3$, g				relative reactivity	no PTC rxn 4 h consumed	$HOCH_2CF_3$ extracted in	dielectronic constant	apparent extract constant
solvent	2.0	1.5	1.0	0.5	$k_{0.5/2}$	$(NPCl_2)_3$, %	solvent	(temp, °C)	E_{TBAB}[25]
1,2-dichloroethane	0.30	0.45	0.59	0.82	2.73	5	+	10.36 (25)	6.1
chlorobenzene	0.17	0.21	0.27	0.36	2.10	8	–	5.6 (25)	<0.1
dichloromathane	0.14	0.19	0.26	0.36	2.57	5	+	9.08 (20)	35
benzene	0.071	0.08	0.09	0.11	1.55	2	+	2.28 (20)	<0.001
tolune	0.07	0.095	0.11	0.14	2.00	4	+	2.37 (25)	<0.001
hexane	0.04	0.041	0.046	0.045	1.10	0	+	1.89 (20)	<0.001
chloroform	0.043	0.047	0.059	0.066	1.53	2	+	4.8 (20)	47

[a] $E_{\mathrm{TBAB}} = [QBr]_o/[Q^+]_a[Br^-]_a$. Reaction conditions: solvent = 50 mL, H_2O = 20 mL, NaOH = 3 g, $HOCH_2CH_3$ = 7 g, TBAB = 9.6 × 10^{-5} mol, temp = 20 °C.

CF_3, will make the quaternary cation move into the organic phase. Thus, the preferential extraction of $^-OCH_2CF_3$ into the organic phase by the quaternary cation catalyst is responsible for the efficiency of the reaction. The apparent extraction constant, E_{app} $(=[QY]_o/([Q^+]_a[Y^-]_a)$, is thus an index for reflecting the mass transfer effect, i.e., a larger value of E_{app} implies that the two-phase reaction is dominated by the effects of mass transfer.

(iii) Effects of Solvents. The reactions by phase-transfer catalysis are, in general, dominated by the reactions in the organic and aqueous phases, the two-phase transfer steps, and the distribution of the catalyst between the two phases. The organic solvent will directly affect the distribution of the catalyst between the two phases. In order to find the effect of the solvent on the conversion of the reactant, $(NPCl_2)_3$, seven kinds of solvents, including polar or nonpolar solvents, are examined. The results are shown in Table IV. The order of relative activities of the solvents is dichloroethane > chlorobenzene > dichloromethane > benzene > toluene > chloroform > hexane. The ratios of the second-order reaction rate constants are shown in Table IV.

It has been proposed that a higher dielectric constant of solvent will lead to faster conversion of the reactant $(NPCl_2)_3$ in a homogeneous condition.[18] This phenomenon is also the same for a two-phase reaction without using a phase-transfer catalyst. As shown in Table V, the consumption of the reactant, $(NPCl_2)_3$, after 4 h of reaction is correlated with the dielectric constant of the solvent, except for chlorobenzene. Almost all of the trifluoroethanol stays in the aqueous phase because of its insolubability in a chlorobenzene solvent. Therefore, a larger driving force in the concentration gradient of $HOCH_2CF_3$ across the aqueous–organic interphase will cause a faster reaction (8% of yield). In principle, a higher polarity of solvent will lead to an increase in the dissociation of nucleophilic molecules (QOR), and the catalyst (QOR) will be ready to associate with the organic solvent in a two-phase reaction. Therefore, the reaction rate is enhanced by using a polar solvent. As shown in Table V, however, a higher dielectric constant solvent does not correlate to a higher reaction rate for a two-phase reaction. For example: the dielectric constant of dichloromethane is greater than that of chlorobenzene, whereas the reaction rate when using chlorobenzene is larger than that when using dichloromethane. The situations are the same for using benzene or toluene as the solvent. Therefore, there must be some additional factors concerned with the solvent as well as the dielectric constant of the solvent affecting the relative reactivity. First, trifluoroethanol is soluble in all solvents except chlorobenzene. It is appropriate for one to choose a solvent which will not dissolved trifluoroethanol. Second, a smaller value of the apparent extraction constant, E_{TBAB} $(=[QBr]_o/([Q^+]_a[^-Br]_a)$, will lead to the existence of QBr mostly in the aqueous phase. Hence, the reaction rate is enhanced. Therefore, relating a smaller value of E_{TBAB} to a larger value of the dielectric constant and the insoluble $HOCH_2CF_3$ of the solvent will enhance the reaction rate.

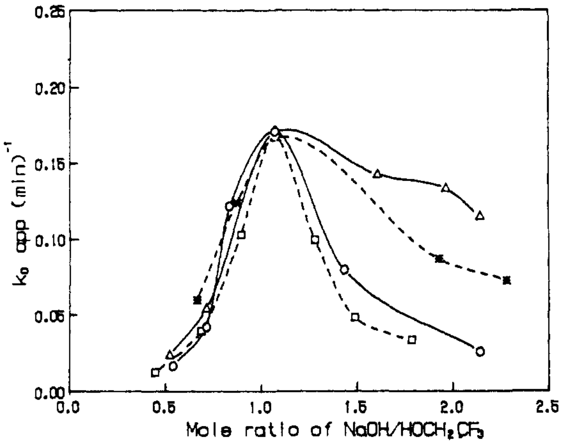


Figure 1. The apparent reaction rate constants vs mole ratios of $NaOH/HOCH_2CF_3$: 0.0059 mol of $(NPCl_2)_3$, 9.6 × 10^{-5} mol of TBAB, 50 mL of chlorobenzene, 20 mL of H_2O, 20 °C; and (△) 0.07 mol of $HOCH_2CF_3$, (*) 0.058 mol of $HOCH_2CF_3$, (○) 0.075 mol of NaOH, (□) 0.063 mol of NaOH.

Table V also shows the dependence of the pseudo-first-order reaction rate constant on the mass of the reactant, $(NPCl_2)_3$, for using the TBAB catalyst with several kinds of solvents. This indicates that the mass transfer of QOR affects the reaction rate. A larger value

Table VI. Influence of [NaOH] - [HOCH$_2$CF$_3$] to the Ratios of Reaction Rate Constants

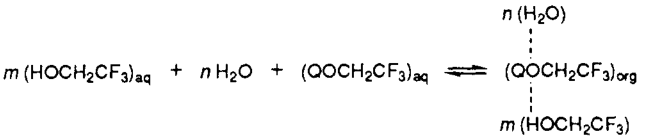
[NaOH], M	[HOCH$_2$CF$_3$], M	[NaOH] - [HOCH$_2$CF$_3$], M	$k_{0,\mathrm{app}}$, min^{-1}	k_1*	k_2*	k_3*	k_4*	k_5*
8.13	3.50	4.63	0.11	1.95	1.33	0.55	0.32	0.1
6.68	2.92	3.76	0.071	1.85	1.25	0.50	0.28	0.085
5.63	2.02	2.71	0.087	1.70	1.12	0.45	0.24	0.072
5.63	3.50	2.13	0.141	1.65	1.08	0.42	0.23	0.068
4.38	2.92	1.46	0.094	1.60	1.02	0.40	0.22	0.065
3.75	3.50	0.25	0.171	1.32	0.74	0.29	0.16	0.045
2.55	2.92	-0.37	0.124	1.15	0.63	0.24	0.13	0.035
1.88	2.92	-1.04	0.057	0.95	0.48	0.18	0.09	0.025

[a] Reaction conditions: $(NPCl_2)_3$ = 0.0059 mol, chlorobenzene = 50 mL,H_2O = 20 mL, TBAB = 9.6×10^{-5} mol, temp = 20 °C.

of $k_{0.5/2}$ implies a significant influence of the mass transfer on the reaction rate.

(iv) Extraction of QOCH$_2$CF$_3$ from the Aqueous Phase into the Organic Phase. A plot of $k_{0,\mathrm{app}}$ vs the mole ratio of [NaOH]/[HOCH$_2$CF$_3$] is shown in Figure 1. A maximum reaction rate occurs at a ratio of [NaOH]/[HOCH$_2$CF$_3$] = 1.07 for all experimental runs operated at various concentrations of NaOH or HOCH$_2$CF$_3$. The reaction rates are insensitive to the change of ratio of [NaOH]/[HOCH$_2$CF$_3$] for different concentrations of NaOH$_2$CF$_3$ when the ratio of [NaOH]/[HOCH$_2$CF$_3$] is less than 1.07. Nevertheless, the reaction rates diversify with the variation of NaOH or HOCH$_2$CF$_3$ concentrations when the ratio of [NaOH]/[HOCH$_2$CF$_3$] is greater than 1.07. This phenomenon is explained in the following.

In general, there will be several molecules of water surrounding the formed catalyst QX or QOCH$_2$CF$_3$ in the aqueous phase. Schmutz and Allcock[19] in 1975 found the existence of trifluoroethanol in the purification of sodium trifluoroethoxide. This implied the formation of a very strong hydrogen bond between sodium trifluoroethoxide and trifluoroethanol. Further, the catalyst QOCH$_2$CF$_3$ forms a hydrogen bond not only with water but also with trifluoroethanol to reach an equilibrium state in the aqueous phase, i.e.,



$$m(HOCH_2CF_3)_{aq} + nH_2O + (QOCH_2CF_3)_{aq} \rightleftharpoons \underset{m(HOCH_2CF_3)}{\overset{n(H_2O)}{(QOCH_2CF_3)_{org}}} \quad (19)$$

The corresponding rate equation for QOCH$_2$CF$_3$ reacting with (NPCl$_2$)$_3$ is

$$-\frac{d[(NPCl_2)_3]_o}{dt} = k[QOCH_2CF_3]_o[H_2O]_o^n[HOCH_2CF_3]_o^m[(NPCl_2)_3]_o \quad (20)$$

or

$$k_{0,\mathrm{app}} = k[QOCH_2CF_3]_o[H_2O]_o^n[HOCH_2CF_3]_o^m \quad (21)$$

As indicated in the above equation, the two solvation factors of the complex number of water molecules and the complex number of acids affect the reaction rate. Usually, the reaction rate is decreased when the complex number is increased. In addition, the report of Landini et al.[22] indicated that the capability of solvation between the catalyst and water would decrease by increasing the concentration of NaOH. However, the present results for [NaOH]/[HOCH$_2$CF$_3$] > 1.07 contradict the results of Landini et al.[22] This inconsistency is explained by the formation of a hydrogen bond between QOCH$_2$CF$_3$ and H$_2$O in the aqueous phase. Therefore, the catalyst QCl (or QBr) will mostly stay in the organic phase when QCl (QBr) competes with QOCH$_2$CF$_3$. Hence, the reaction rate decreases when the concentration of NaOH is increased.

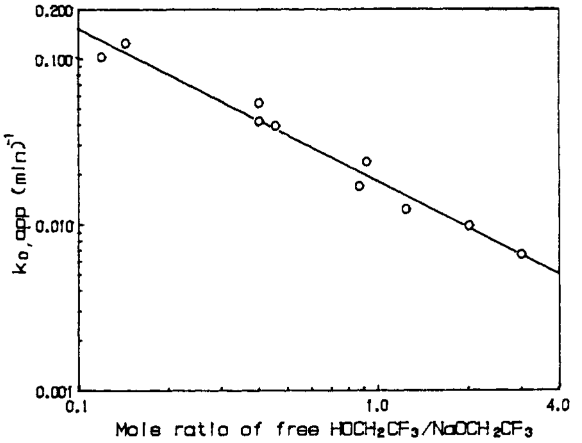


Figure 2. The apparent reaction rate constants vs mole ratios of free HOCH$_2$CF$_3$ to NaOCH$_2$CF$_3$; Reaction conditions are the same as given in Figure 1.

In the aqueous phase, the catalyst QOCH$_2$CF$_3$ forms a hydrogen bond not only with water but also with HOCH$_2$CF$_3$. Therefore, it is difficult to transport QOCH$_2$CF$_3$ from the aqueous phase to the organic phase by increasing the concentration of HOCH$_2$CF$_3$. This is due to the hydration of QOCH$_2$CF$_3$. Thus, the reactivity of the nucleophilic reaction[23,24] decreases when the concentration of HOCH$_2$CF$_3$ is increased for the case of [NaOH]/[HOCH$_2$CF$_3$] < 1.07.

A replot of $k_{0,\mathrm{app}}$ vs the mole ratio of free HOCH$_2$CF$_3$/NaOCH$_2$CF$_3$ from Figure 1 for [NaOH]/[HOCH$_2$CF$_3$] less than 1.07 is shown in Figure 2. A straight line with slope −0.94 is obtained. Under this situation, sodium hydroxide is almost run out by reacting 2,2,2-trifluoroethanol in excess amount. Therefore, there are free molecules of HOCH$_2$CF$_3$ in the reacting system. The results also reflect that the $k_{0,\mathrm{app}}$ is decreased by increasing the amount of HOCH$_2$CF$_3$. By taking a logarithm for eq 21, the slope of the straight line, shown in Figure 2, indicates the number of hydration for QOCH$_2$CF$_3$, i.e., the number of hydration is approximated as 1. Schmutz and Allcock[19] obtained 2 for the number of hydration for NaOCH$_2$CF$_3$.

The data in Table VI show that the ratios of the second order reaction rate constant k_i*, i = 1–5, increase by increasing the concentration difference of NaOH and HOCH$_2$CF$_3$. This tendency is the same for the variation

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Table VII. Influence of [NaOH] − [$HOCH_2CF_3$] to the Relative Reaction Rate Constants

[NaOH], M	[$HOCH_2CF_3$], M	[NaOH] − [$HOCH_2CF_3$], M	k_1/k_0	k_2/k_1	k_3/k_2	k_4/k_3	k_5/k_4
8.13	3.50	4.63	1.95	0.65	0.41	0.58	0.31
6.68	2.92	3.70	1.85	0.67	0.40	0.56	0.30
5.63	2.92	2.71	1.70	0.66	0.40	0.53	0.30
5.63	3.50	3.13	1.65	0.65	0.39	0.55	0.30
4.38	2.92	1.46	1.60	0.64	0.39	0.55	0.30
3.75	3.50	0.25	1.32	0.56	0.39	0.55	0.28
2.55	2.92	−0.37	1.15	0.55	0.38	0.54	0.27
1.88	2.92	−1.04	0.95	0.50	0.37	0.50	0.26

[a] Reaction conditions: same as given in Table VI.

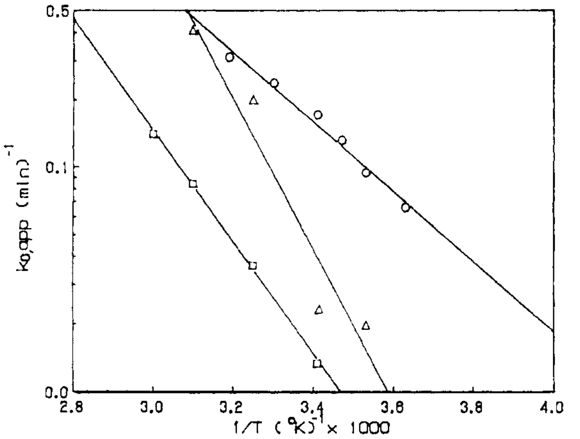

Figure 3. The apparent reaction rate constants vs temperature; 0.0059 mol of $(NPCl_2)_3$, 9.6×10^{-5} mol of TBAB, 50 mL of chlorobenzene, 20 mL of H_2O; and (○) 7 g of $HOCH_2CF_3$, 3 g of NaOH, (△) 7 g of $HOCH_2CF_3$, 7 g of NaOH, (□) 14 g of $HOCH_2CF_3$, 2.5 g of NaOH.

of k_{i+1}/k_i, i = 0–4, which is shown in Table VII. The influence of k_1/k_0 and k_2/k_1 is more significant due to the change of the [NaOH] − [$HOCH_2CF_3$] concentration difference. Thus, the first and second substitutions of chloride by trifluoroethoxide are dramatically influenced by a larger value of ([NaOH] − [$HOCH_2CF_3$]). Figure 3 shows the plot of $k_{0,\mathrm{app}}$ vs $1/T$ for different initial concentration ratios of NaOH and $HOCH_2CF_3$. The activation energy, E_a, is obtained from the Arrhenius equation and is given in the following:

NaOH	$HOCH_2CF_3$	E_a
3 g	7 g	7.14 kcal/mol
7 g	7 g	19 kcal/mol
2.5 g	14 g	11.4 kcal/mol

It is obvious that the effects of mass transfer and chemical reaction kinetics on the conversion depend highly on the reactant concentrations of NaOH and $HOCH_2CF_3$.

Based on the experimental data, the retarding effect of free acids on the normal PTC substitution process can be attributed to the masking of the anion and the deactivation of the anion via hydrogen bonding. Increasing the concentration of NaOH will decrease the capability of solvation between catalyst and acid. The reaction rate is promoted.

Conclusion

Kinetic data of nucleophilic substitutions with the 2,2,2-trifluoroethoxy group in hexachlorocyclotriphosphazene catalyzed by quaternary ammonium salts under phase-transfer catalysis have been measured. The reactions were carried out in an organic solvent/alkaline solution. The same ratios of reaction rate constants for the series reactions are obtained for the various quaternary ammonium salts, except for the CTMAB and BTMAC catalysts with a methyl group. It is confirmed that the reactivities of all kinds of catalysts in the organic phase with the same kind of solvent are the same for an extraction mechanism. The reaction system is both controlled by chemical reaction kinetics and mass-transfer effects. Increasing the apparent extraction constant of the quaternary ammonium halide, which accounts for the mass-transfer effect, will lead to a decrease in the reaction rate. In the present system, free acids, present in the reaction system, not only inhibit transport of the active catalyst, QOR, from the aqueous phase to the organic phase, but also affect the reactivity of the nucleophilic reaction. The reactivities of reaction were also investigated for various ratios of sodium hydroxide to trifluoroethanol. The activation energy of the reaction is highly dependent on the concentrations of sodium hydroxide and trifluoroethanol. From this experimental analysis, the number of hydration for $QOCH_2CF_3$ is about 1.

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Registry No. TBAHS, 32503-27-8; BTEAOH, 1836-42-6; TBAI, 311-28-4; BTBAB, 25316-59-0; TBAB, 1643-19-2; BTEAC, 56-37-1; Aliq 336, 5137-55-3; CTMAB, 57-09-0; BTMAC, 56-93-9; TEAC, 56-34-8; CROWN6, 17455-13-9; $(NPCl_2)_3$, 940-71-6; $HOCH_2CF_3$, 75-89-8; NaOH, 1310-73-2.