Kinetics of the Nucleophilic Substitution of Benzyl-tributylammonium Bromide with Allyl, Butyl, and Benzyl Chlorides and with Benzyl Acetate and Benzyl Ether

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ABSTRACT

In this study, we investigated the kinetics of the nucleophilic substitutions, $RX + (BzBu_3NBr) \rightleftharpoons RBr + (BzBu_3NX)$, where R = allyl, Bu and Bz, when X = Cl; and X = AcO and BzO when R = Bz. The forward and backward rate constants in addition to the activation energies for R = allyl and Bu were also determined. However, only the rate constants at 35°C were determined for the benzyl compounds with toluene as the solvent to reduce the reaction rate. Moreover, the effects of the structures of the groups R and the leaving groups X on the reactivity were compared. Results in this study can provide valuable information for future studies involving the phase transfer catalyzed displacements. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The typical L–L phase transfer catalyzed displacement is expressed as [1]

$$\text{org.} \quad RX + (QY) \longrightarrow RY + (QX)$$
$$\text{aq.} \quad X^- + (QY) \longleftarrow Y^- + (QX)$$
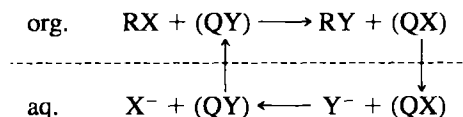
The ion pairs (QX) produced in the organic phase transfer back to the aqueous phase and the pairs (QY) transfer from the aqueous phase to the organic phase. Therefore, RX can be completely substituted by (QY). Nevertheless, the reaction is often reversible.

The intrinsic chemical reaction rate constant and activation energy and the mass transfer parameters (i.e., the mass transfer coefficients and the specific interfacial area) can not be simultaneously determined by only measuring the overall rate of formation of the product RY. The apparent rate constant and activation energy can be determined if the overall rate is under the reaction control and the mass transfer parameters are known [2,3]. However, the rate constant and the activation energy thus determined are still not the actual forward rate constant and activation energy owing to the reaction's reversibility. Therefore, the intrinsic reaction kinetics can only be studied without the interfacial mass transfer. Obtaining further information of the intrinsic kinetics is essential to thoroughly understand the behaviors of the phase transfer catalyzed displacement reaction system. However, only limited attention has been given to separation of the organic phase from the aqueous phase so that the complexity caused by interfacial mass transfer can be avoided [4,5]. Among those studies, Dermeik and Sasson [4] dissolved methyltributylammonium fluoride in excess n-octyl chloride and obtained the activation energy as 19.0 kcal/mol in the temperature range of 90–100°C. Also, Bar et al. [5] obtained the rate constant by analyzing the initial rate data. However, their method could only be applied when the extraction constant $K_{x/y}$ was less than 1 and when the catalyst cations Q^+ were not poisoned by anions other than Y^-.

Benzyltributylammonium salts are effective phase transfer catalysts [3]. In this study, we investigate the intrinsic kinetics of the reactions of the salts with halides, $RCl + (BzBu_3NBr) \rightleftharpoons RBr + (BzBu_3NCl)$ and $BzX + (BzBu_3Br) \rightleftharpoons BzBr + (BzBu_3NX)$, where R = allyl, butyl, and benzyl; and X = Cl, CH_3COO, and BzO. The reactivities of the groups R and X are compared to provide valuable kinetic information for the phase transfer catalyzed displacements.
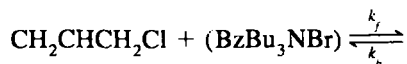
DETERMINATION OF THE RATE CONSTANTS

The Reaction with Soluble Quaternary Ammonium Salts
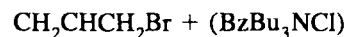
As generally accepted, the reaction

$$RX + (QY) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RY + (QX)$$
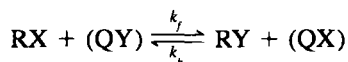
is a reversible second-order nucleophilic substitution

reaction S_N2 [6]. When (QY) is soluble in RX as in the case of the reaction

$$CH_2CHCH_2Cl + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$

$$\quad (1) \qquad\qquad (2)$$

$$\qquad\qquad CH_2CHCH_2Br + (BzBu_3NCl)$$

$$\qquad\qquad (3) \qquad\qquad (4)$$

and the initial concentrations of species (3) and (4) are zero and the amount of species (1) is in large excess, the integrated rate equation can be derived as

$$\ln \frac{(C_1 + b + a)(b - a)}{(C_4 + b - a)(b + a)} = 2ak_b t \qquad (1)$$

where

$$a = \frac{1}{2}\left[\left(\frac{k_f}{k_b}\right)^2 C_1^2 + \frac{k_f}{k_b} C_{2i} C_1\right]^{1/2} \qquad (2)$$

$$b = \frac{1}{2}\frac{k_f}{k_b} C_1 \qquad (3)$$

In addition, if $k_f C_1 C_2$ is significantly greater than $k_b C_4^2$ during the reaction's initial period, then eq. (1) can be reduced to

$$C_4 = C_{2i}[1 - \exp(-k_f C_1 t)] \qquad (4)$$

Then the forward rate constant k_f can be determined from eq. (4) by performing regression analysis of the experimental data of C_4 vs. the reaction time t. In contrast, if the backward reaction rate is sufficiently fast, eq. (4) does not hold. However, the reaction reaches equilibrium within a relatively long reaction period. The equilibrium constant k_f/k_b is subsequently determined, and the parameters a and b are simultaneously calculated from eqs. (2) and (3). If the errors of the determined rate constants are sufficiently small, the relation between $\ln\{(C_4 + b + a) (b - a)/[(C_4 + b - a)(b + a)]\}$ and the reaction time t is a straight line passing through the origin as shown by eq. (1).

The Reaction with Slightly Soluble Quaternary Ammonium Salts

On the other hand, when (QY) is difficult to dissolve in RX as the following reaction

$$C_4H_9Cl + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$

(1)   (2)

$$C_4H_9Br + (BzBu_3NCl)$$

(3)   (4)
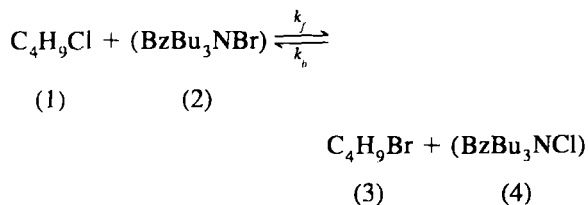
and species (1) is in large excess and a sufficient amount of species (2) is added to exceed saturation, and species (3) and (4) are not initially present. That is, the initial conditions are $C_1 = C_{1i}$, $C_2 = C_{2s}$ and $C_{3i} = C_{4i} = 0$. Consequently, the integrated rate equation can be derived as:

$$\ln \frac{1 + \sqrt{k_2}\,C_4}{1 - \sqrt{k_2}\,C_4} = 2\sqrt{k_2}\,k_1\,t \tag{5}$$

or

$$C_4 = \frac{\exp(2\sqrt{k_2}\,k_1\,t) - 1}{\sqrt{k_2}\,[\exp(2\sqrt{k_2}\,k_1\,t) + 1]} \tag{6}$$

where

$$k_1 = k_f C_1 C_{2s} \tag{7}$$

and

$$k_2 = k_b/k_1 \tag{8}$$

The concentration of $BzBu_3NCl$ is extremely low because it is barely soluble in n-butyl chloride. Therefore the reaction rate is considerably slow. Thus, during the initial period, the concentration of the product, butyl bromide, is too low to be determined by gas chromatography. However, the concentrations of the quaternary ammonium salts $BzBu_3NCl$ and $BzBu_3NBr$ can be determined accurately to as low as 10^{-5} N by conductometry. Consequently, the rate constants can be determined by the following method.

The relation between the concentration and the corresponding specific conductance is

$$C_j V_s = \frac{\chi_j}{\Lambda_j} V_w \tag{9}$$

When the concentration of the salt species j is very dilute, its molar conductance Λ_j is nearly equal to that at infinite dilution.

Slightly Soluble Quaternary Ammonium Salts and Negligible Backward Rate During Initial Period: If

the backward rate constant is insufficient, the forward rate is exceedingly greater than the backward rate during the initial reaction period, i.e., the reaction rate can be expressed as

$$\frac{dC_4}{dt} = k_f C_1 C_{2s} \tag{10}$$

By substituting eq. (9) into eq. (10) and integrating the consequential equation, the specific conductance contributed by species (4) χ_4 can be expressed by the following equation:

$$\frac{\chi_4 - \chi_{4o}}{\chi_{2s}} = \frac{\Lambda_4}{\Lambda_2} k_f C_1 (t - t_o) \tag{11}$$

where t_o is the time required for the solution to be saturated with species (2).

When the solution is very dilute, the solution's conductivity is equal to the sum of the conductivities contributed by the various salts in the solution. Thus, when the solution is saturated with species (2), its conductivity is

$$\chi = (\Lambda_4/\Lambda_2)\chi_{2s}k_f C_1(t - t_o) + \chi_{2s} + \chi_{4o} \tag{12}$$

If t_o is very small, then χ_{4o} is also very small and equation (12) can be simplified to

$$\chi = (\Lambda_4/\Lambda_2)\chi_{2s}k_f C_1 t + \chi_{2s} \tag{13}$$

Thus, the forward rate constant k_f can be determined according to the slope of the straight line of χ vs. t. The forward rate is equal to the backward rate at equilibrium, i.e.,

$$k_f C_1 C_{2e} = k_b C_{3e} C_{4e} \tag{14}$$

The backward rate constant k_b is then calculated by eq. (14) since k_f has been determined.

Slightly Soluble Quaternary Ammonium Salts and Comparable Backward Rate During Initial Period: For another case, if $k_f C_1 C_{2s} \gg k_b C_3 C_4$ does not hold during the initial period of the reaction as below

$$BzX + BzBu_3NBr \underset{k_b}{\overset{k_f}{\rightleftharpoons}} BzBr + BzBu_3NX,$$

(1)   (2)   (3)   (4)
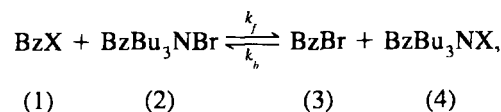
$$X = Cl, AcO, \text{ and } BzO$$

then k_f can only be roughly estimated by eq. (12). In addition, from the reversible rate equation $dC_4/dt =$

$k_f C_1 C_{2s} - k_b C_4^2$, k_b can be estimated by the equation below

$$k_b = \frac{k_f C_1 C_{2s}(t - t_o) - (C_4 - C_{4o})}{\int_{t_o}^{t} C_4^2 \, dt} \qquad (15)$$

Thus, the approximate values of the parameters k_1 and k_2 can be calculated by eqs. (7) and (8), respectively. Here, the estimated k_2 is used as the reference value for obtaining the plots of $\ln[(1 + \sqrt{k_2} \, C_4)/(1 - \sqrt{k_2} \, C_4)]$ vs. t with k_2 as the parameter. The value of k_2, such that the plot is a straight line passing through the origin, is recognized as the true value of k_2 since it satisfies eq. (5). The slope of the straight line is $2\sqrt{k_2} \, k_1$. Finally, the true value of k_1 is determined.

EXPERIMENTAL

Chemicals

Allyl bromide, allyl chloride, n-butyl chloride, benzyl bromide, benzyl chloride, triethylamine, benzyl alcohol, benzyl acetate, benzyl ether, and toluene were purchased from Merck (Germany). The above compounds' purities were all above 99%. Benzyltributylammonium bromide and benzyltributylammonium chloride were prepared in our laboratory as follows: One mole of tributylamine and one mole of benzyl chloride or benzyl bromide were added into a 500 ml three-necked bottle adapted with a stirrer and a con-

denser. The system was maintained at 50°C by a thermostat. The product crystallized during the reaction. The slurry was transferred into a funnel and then filtered when the liquid part was reduced to roughly a quarter of its original amount. The filter cake was washed by stirring in a beaker containing 100 ml benzene. The suspension was again filtrated and washed with benzene, the cake was then dried under vacuum at 60°C for 8 h. The salts' purities exceeded 99%, as determined by analyzing the bromide or chloride ions with the Mohr method.

Apparatus for the Kinetic Experiments

The reactor used in the kinetic studies was a 250 ml three-necked bottle immersed in a Lauda RC 20 thermostat with the temperature controlled within $\pm 0.1°C$. The bottle's central neck was fitted with a teflon stirrer; one of the side necks was adapted with a condenser and the other was plugged with glass stopper.

Experimental Procedure

The Ion Chromatography Calibration Curves of Mass-Ratio vs. Area-Ratio for the Halide Ions: The calibration curves (Fig. 1) were prepared with an ion chromatograph of Dionex IC 4500i. The analytic conditions were anion analytic column HPIC-AS4A, precolumn HPIC-AG4A, conductivity detector II CDM, nitrate ions as internal standard, eluent 5.0 mM $NaB_4O_7 \cdot 10H_2O$ with a flow rate of 2 ml/min and re-
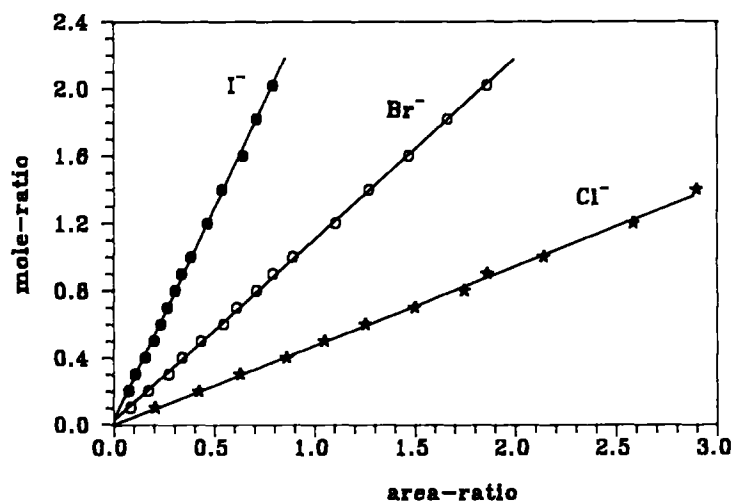

Figure 1 The calibration curves of mass-ratio vs. area-ratio for Cl^-, Br^-, and I^- with NO_3^- as the internal standard. Anion analytic column HPIC-AS4A, precolumn HPIC-AG4A, conductivity detector II CDM, eluent 5.0 mM $NaB_4O_7 \cdot 10H_2O$ with a flow rate of 2 ml/min and regeneration solution 25 mM H_2SO_4 with a flow rate of 5 ml/min.
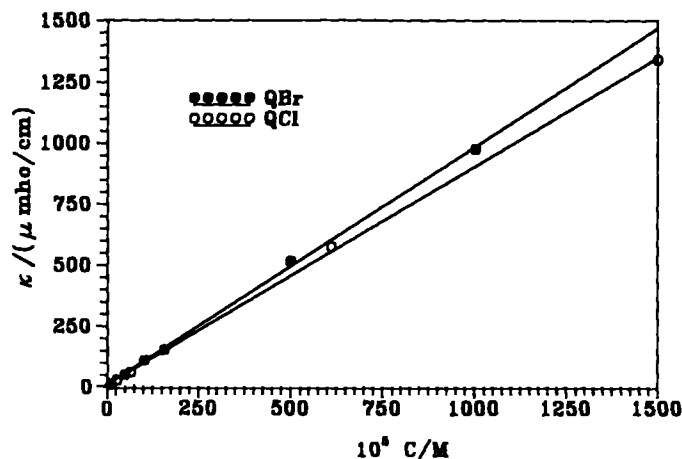
Figure 2 The calibration curves of conductivity vs. concentration for the aqueous solutions of QBr and QCl (Q = $BzBu_3N$), respectively.

generation solution 25 mM H_2SO_4 with a flow rate of 5 ml/min.

The Conductometry Calibration Curves of Conductivity vs. Concentration for the Quaternary Ammonium Salts: A 100 ml solution was made from 2.738g benzyltributylammonium bromide or 1.775g benzyltributylammonium chloride and distilled water. The conductivity of the solution was then measured via a Suntex SC-15 conductivity meter. The conductivity due to the salt was the difference of the measured value subtracted by that of the distilled water. A portion of the solution was withdrawn and diluted to the wanted concentration; the conductivity was then measured again. The procedure was repeated until the concentration fell below 10^{-5} N. Thus, the calibration curves of conductivity vs. concentration were obtained (Fig. 2). In this figure, the molar conductances Λ (defined as $\Lambda = \chi/C$) are the slopes of the straight lines. The values are 89.2 and 98.1 mho cm^2 mol^{-1} for $BzBu_3NBr$ and $BzBu_3NCl$, respectively.

The Reaction of Allyl Chloride with Benzyltributylammonium Bromide: One hundred ml allyl chloride was poured in a 250 ml three-necked bottle and heated with stirring to the desired temperature. Next, 1.6 g benzyltributylammonium bromide at the same temperature was added to carry out the reaction. About 0.2 g sample was taken at a suitable time interval and analyzed by ion chromatography.

The Reaction of n-Butyl Chloride with Benzyltributylammonium Bromide: A 250 ml three-necked bottle containing 150 ml of n-butyl chloride was heated to the desired temperature. Benzyltributylammonium bromide of a suitable amount greater than that of saturation was added to proceed with the reac-

tion. About 1 ml sample was withdrawn at a suitable time interval and analyzed by conductometry.

The Reaction of BzX (X = Cl, CH_3COO, and BzO) with benzyltributylammonium Bromide: The direct reaction of benzyl chloride with benzyltributylammonium bromide was too fast to be measured by an ordinary reactor. Therefore, a substantial amount of toluene was added to reduce the reaction rate [7]. Thus, the binary solution of volume 200 ml and mole-ratio of BzX/toluene 1/10 was placed in the 250 ml bottle and heated to 35°C. Next, a suitable amount of benzyltributylammonium bromide at the same temperature was added. The sample drawn from the reaction mixture was also analyzed by conductometry.

Sample Analysis

Ion Chromatography: One hundred ml water of a known amount of internal standard (NO_3^-) was used to extract the salts' content in about 0.2 g sample. The extract was analyzed by ion chromatography. The area-ratio of Cl^- or Br^- to NO_3^- was determined by an integrator connected to the ion chromatograph. The mass-ratio was then determined by the ion chromatography calibration curves (Fig. 1).

Conductometry: One ml of the sample drawn from the reaction mixture was poured in a funnel containing 30 ml of distilled water and 2 ml of toluene. The mixture was shaken vigorously to allow the organics be extracted into the toluene layer and the salts be extracted into the water layer. The water layer was separated and its conductivity was measured. The salts'
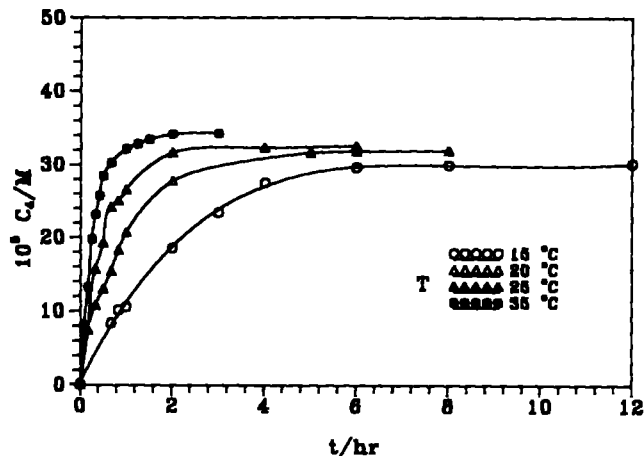
Figure 3 The concentration of $BzBu_3NCl$, C_4, vs. the reaction time, t, for the reaction $CH_2CHCH_2Cl + (BzBu_3NBr) \rightleftharpoons CH_2CHCH_2Br + (BzBu_3NCl)$, with initial conditions of 100 ml of allyl chloride and 1.6 g of benzyltributylammonium bromide.

concentrations were determined by the conductome-
try calibration curves (Fig. 2).

RESULTS AND DISCUSSION

The Reaction Kinetics

$$CH_2CHCH_2Cl + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$

(1)   (2)

$$CH_2CHCH_2Br + (BzBu_3NCl)$$
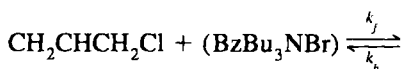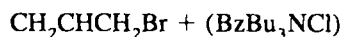
(3)   (4)

Under the initial conditions of 100 ml of allyl chlo-
ride and 1.6 g of benzyltributylammonium bromide,

Figure 3 shows the concentration of the product ben-
zyltributylammonium chloride vs. the reaction time at
the temperatures of 15, 20, 25, and 35°C, respec-
tively. In this figure, the equilibrium constants k_f/k_b
are determined according to the equilibrium concen-
tration data. The parameters a and b are then cal-
culated by eqs. (2) and (3), respectively. Figure 4
shows the relation of $\ln\{[(C_4 + b + a)\ (b - a)]/[(C_4 + b - a)\ (b + a)]\}$ vs. t. The lines in this figure
are linear and pass through the origin as predicted by
eq. (1). As indicated by the equation, the slopes of the
lines are $2\ ak_b$. Thus, the backward rate constants k_b
are determined, and the forward rate constants are
subsequently obtained from the equilibrium con-
stants. Figure 5 presents the Arrhenius plot of the re-
action. The forward and backward activation energies
are determined as 15.1 and 10.3 kcal/mol, respec-

Figure 4 The plot showing the second-order reversible reaction behavior of the reaction in Fig-
ure 3.

Figure 5   The Arrhenius plot of the reaction in Figure 3.

tively. Table I lists the values of the rate constants, the equilibrium constants, the activation energies and the relative standard deviations of C_4, $\sigma/\overline{C_4}$. The magnitudes of the equili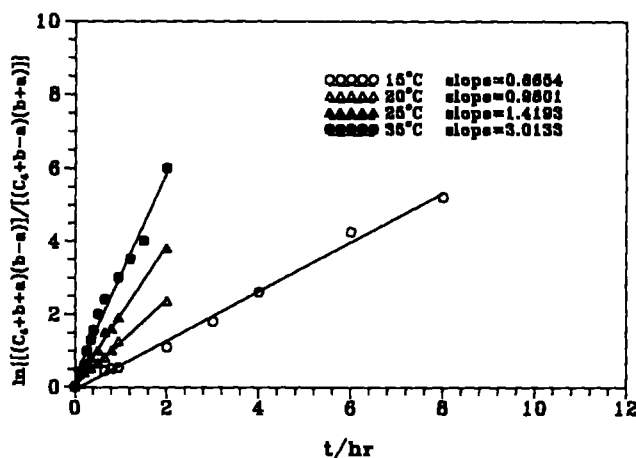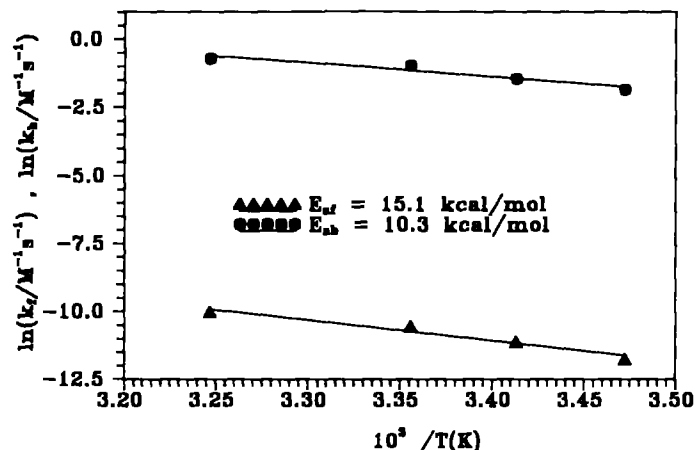brium constants k_f/k_b are of the order of 10^{-4}. A factor favoring the backward rate constant is that the basicity of leaving group Br$^-$ is stronger than that of Cl$^-$ [8]. Another factor is that, owing to the smaller size of Cl$^-$, the free energy of

transfer of Cl$^-$ from a more polar solvent to a less polar solvent is greater than Br$^-$; therefore, in a less polar solvent, the activation energy for (BzBu$_3$NCl) is relatively lower than (BzBu$_3$NBr) [9,10]. The factor of basicity causes the allyl bromide to be more reactive than allyl chloride. Moreover, the factor of free energy of transfer causes BzBu$_3$NCl to be more reactive than BzBu$_3$NBr in solvents of lower polarity.

Table I   Kinetic Information of the Reaction

$$RX + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RBr + (BzBu_3NCl)$$

		(1)	(2)	(3)	(4)			
R	X	$\dfrac{T}{K}$	$\dfrac{10^5 k_f}{M^{-1}s^{-1}}$	$\dfrac{10^3 k_b}{M^{-1}s^{-1}}$	$\dfrac{10^5 k_f}{k_b}$	$\dfrac{E_{a,f}}{k\text{cal mol}^{-1}}$	$\dfrac{E_{a,b}}{k\text{cal mol}^{-1}}$	$\dfrac{100\sigma}{C_4}$
		308	4.29	487	8.81			6.27
Allyl	Cl	298	2.53	368	6.87	15.1	10.3	3.60
		293	1.44	227	6.36			2.96
		288	0.758	152	4.98			3.10
		348	1.66	3.73	441			3.32
Butyl	Cl	343	0.760	1.93	394	18.6	16.0	6.31
		338	0.522	1.42	369			3.69
		333	0.481	1.34	360			2.92
		308	0.049^a	0.188^a				
	Cl	308	4.35	1.60	2718			2.56
Benzyl^b	AcO	308	2.30	1.22	1885			4.99
	BzO	308	2.7	0.0552	48913			11.1

^{a} The rate constants at 308 K are calculated by the Arrhenius law.

^{b} Toluene of mole-ratio to the benzyl compound 10/1 was added to reduce the reaction rate.

The Reaction Kinetics

$$CH_3CH_2CH_2CH_2Cl + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$

$$(1) \qquad\qquad (2)$$

$$CH_3CH_2CH_2CH_2Br + (BzBu_3NCl)$$

$$(3) \qquad\qquad (4)$$

Figure 6 shows the conductivity of the sample analyzed by the above conductometry vs. the reaction time when the initial volume of n-butyl chloride is 150 ml, and the initial amount of benzyltributylammonium bromide corresponding to the reaction temperatures of 75, 70, 65, and 60°C is 1.5, 1.35, 1.20, and 1.10 g, respectively. Owing to the fact that the salt's initial amount is slightly more than that required for saturation, the conductivity increases abruptly at the beginning of the reaction until the solution is saturated with the dissolution of benzyltributylammonium bromide. The conductivity then increases linearly with the reaction time during the initial period. The increase in conductivity is due to the formation of benzyltributylammonium chloride; meanwhile, benzyltributyl ammonium bromide remains saturated. The linearity implies that the reaction's backward rate is negligible. The rate of increase for the conductivity gradually slows down after the initial period, and becomes zero during the stage when the solution is saturated with both of the salts. The conductivity is next reduced because the product, benzyltributylammonium chloride, crystal-

lizes out and the concentration of the reactant, benzyltributylammonium bromide, falls below its saturation value as the reaction proceeds toward equilibrium. Moreover, when the reaction reaches equilibrium, the salt concentration is not reduced further and the conductivity is maintained constant. The straight lines obtained by the linear regression of the data of initial period are expressed as $\chi = mt + \chi_{2s}$, χ and χ_{2s} in μmho cm^{-1} and t in h. The values of (m, χ_{2s}) at 75, 70, 65, and 60°C are (18.8, 29.9), (6.99, 24.2), (3.93, 19.8), and (3.08, 16.9), respectively. The slopes of the straight lines are $\chi_2 k_f C_1 \Lambda_4/\Lambda_2$ as shown by eq. (13). The molar conductances Λ_4 and Λ_2 are equal to the slopes of their corresponding conductometry calibration curves (Fig. 2). Those conductances are evaluated as $\Lambda_4 = 98.1$ mho cm^2 mol^{-1} and $\Lambda_2 = 89.2$ mho cm^2 mol^{-1}. The forward rate constant, k_f, is then obtained, and the backward rate constant, k_b, is subsequently determined by the equilibrium relation, $k_b(C_{2a} - C_{2e})C_{4s} = k_f C_1 C_{2e}$. Where C_{2e} and C_{4s} can be calculated by eq. (9) with the data of the conductivities at equilibrium, $\chi_e = \chi_{2e} + \chi_{4s}$, and at plateau stage, $\chi_p = \chi_{2s} + \chi_{4s}$. Figure 7 shows the Arrhenius plot. The forward and backward activation energies are then determined as $E_{af} = 18.6$ kcal/mol and $E_{ab} = 16.0$ kcal/mol. Table I presents the kinetic information and relative standard deviation of C_4. The reciprocals of the equilibrium constants k_b/k_f are around 250. Since the rate constants have been obtained, the parameter k_2 can be simultaneously calculated by eqs. (6) and (7). Figure 8 shows the relation between $\ln[(1 + \sqrt{k_2} \ C_1)/(1 - \sqrt{k_2} \ C_1)]$ and the reaction time. The relations

Figure 6 The conductivity of the treated sample vs. t for the reaction $CH_2CH_2CH_2CH_2Cl + (BzBu_3NBr) \rightleftharpoons CH_2CH_2CH_2CH_2Br + (BzBu_3NCl)$, initial volume of butyl chloride 150 ml and initial amount of the bromide, corresponding to the reaction temperature 75, 70, 65, and 60°C, 1.50, 1.35, 1.20, and 1.10 g.
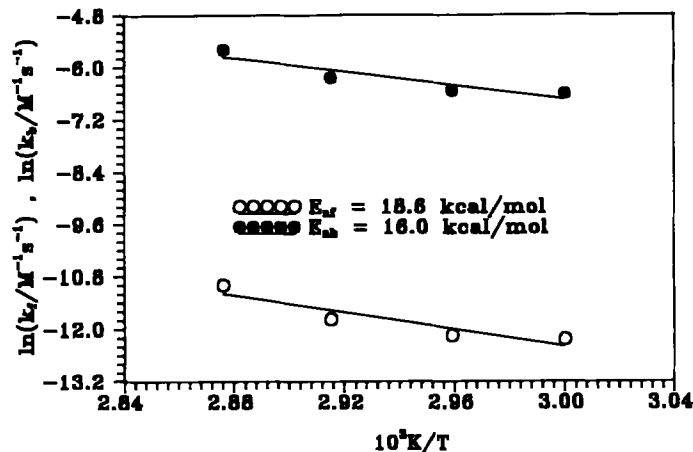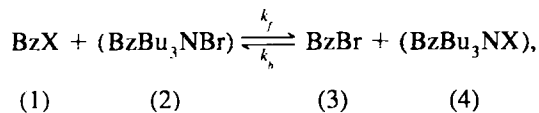
Figure 7   The Arrhenius plot of the reaction in Figure 6.

can be expressed by the straight lines passing nearly through the origin. This finding correlates with eq. (5).

The Reaction's Rate Constants

$$BzX + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} BzBr + (BzBu_3NX),$$

(1)   (2)   (3)   (4)

$$X = Cl, AcO, \text{ and } BzO$$

Under the initial conditions of mole-ratio of BzX to toluene 1/10, solution volume 200 ml, reaction temperature 35°C, and amount of $BzBu_3NBr$ corresponding to X = Cl, AcO, and BzO 2.50, 2.40 and 2.25 g, Figure 9 shows the conductivity of the treated sample vs. the time, t. After the solution is saturated

with $BzBu_3NBr$, the relations between χ and t obtained by the linear regression of the data of the initial period are expressed as $\chi = mt + \chi_{2s}$. The pairs (m, χ_{2s}) for X = Cl, AcO, and BzO are (3.07, 16.8), (1.20, 17.3), and (0.85, 7.41), respectively. Where χ and χ_{2s} are in μmho cm^{-1} and t is in h.

Figure 9 also shows that the linearities are not as obvious as those of Figure 6, implying that the backward reaction rate can not be omitted. Under this circumstance, a previous section describes the method for obtaining the forward and backward rate constants.

Figure 10 plots the optimum k_2 such that the reaction satisfies the second-order reversible kinetics. In this figure, the deviations of the intercepts for X = AcO and BzO (both 0.13) are greater than that of X = Cl (0.08). This occurrence seems to be caused by the errors in evaluating the molar conductances of aqueous $BzBu_3NX$, X = AcO, and BzO.
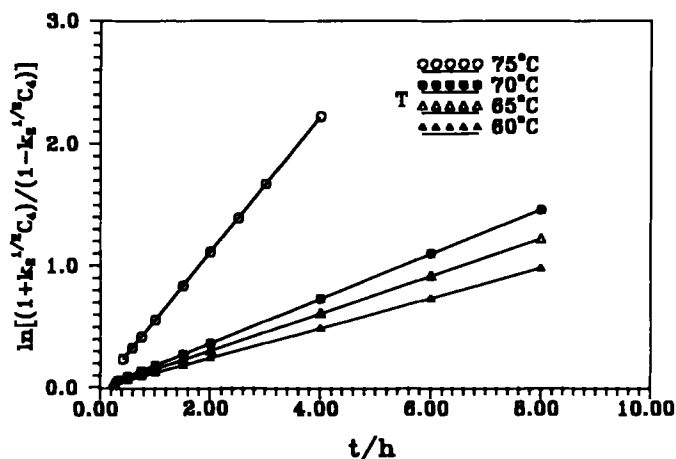

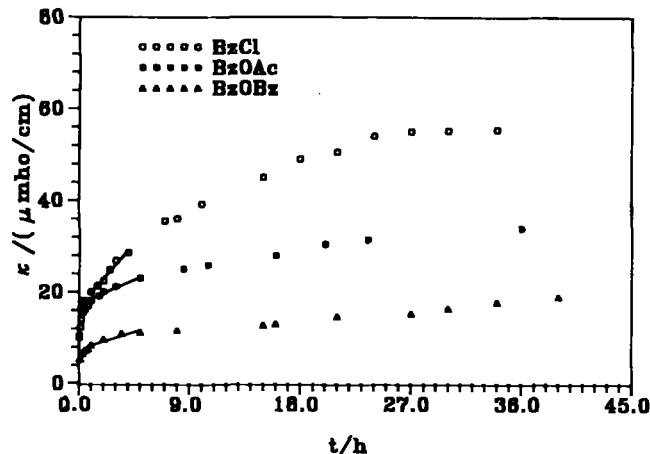**Figure 8**   The plot showing the second-order reversible reaction behavior in Figure 6.

Figure 9 The conductivity of the treated sample vs. time for the reaction of BzX + (BzBu$_3$NBr) $\rightleftharpoons$ BzBr + (BzBu$_3$NX), X = Cl, AcO and BzO, initial conditions: mole-ratio of BzX/toluene 1/10, solution volume of 200 ml, reaction temperature of 35 °C and BzBu$_3$Br corresponding to X = Cl, AcO and BzO 2.80, 2.40 and 2.25 g.

Since k_2 is already determined, k_1 can be calculated from the value of the slope of the line in Figure 10 (eq. (5)). The rate constants k_f and k_b are then calculated by eqs. (7) and (8), respectively. Moreover, Table I lists the values of the rate constants.

Summary and Comparison of the Kinetic Information

The kinetic information of the reactions

$$RX + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RBr + (BzBu_3NX)$$
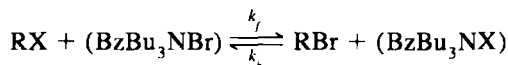
where R = allyl, Bu and Bz when X = Cl; and X = AcO and BzO when R = Bz, is summarized

as Table I for the convenient comparison of the reactivities.

The Relative Reactivity of Allyl/Bu/Bz of the Halides: For the chlorides in the forward reactions at 308 K, the ratio of the forward rate constants of allyl /Bu/Bz is about 1:0.011:1. On the other hand, for the backward reaction at the same temperature, the ratio is about 300:0.12:1. Those findings indicate that the relative reactivity among allyl, butyl, and benzyl groups of halides depends not only on their own structures but also on the sizes of the leaving groups (the X$^-$ from RX). When Cl of the halides is replaced by Br, the reactivity ratio mentioned above changes from 1:0.011:1 to 300:0.12:1. Apparently, the increase in the size of the leaving group significantly favors the reactivity of the smaller groups R of
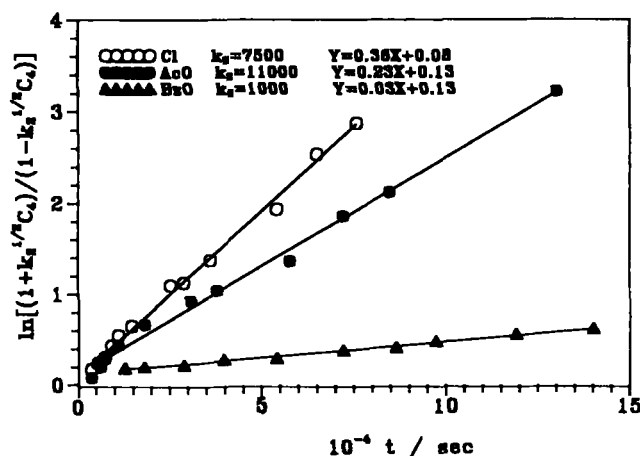

Figure 10 The plot with the optimum k_2 such that the reaction in Figure 9 satisfies the second-order reversible kinetics.

the halides RX. In the above reactions, allyl chloride is roughly 100 times more reactive than butyl chloride. The reason for such a high reactivity is that when the nucleophile approaches sufficiently to the partially formed allyl carbonium ion [6,11], the reaction would proceed with S_N2' (bimolecular nucleophilic substitution with arrangement) mechanism. If the nucleophile is an anion, the mechanism proposed by Bergman [12] is
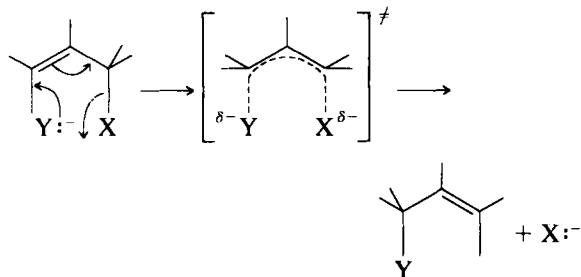
In our case, the nucleophilic is an ion pair, and the mechanism is proposed as
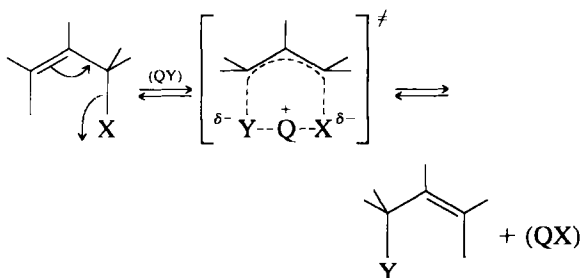
As indicated in the above mechanism, the energy of the activated complex is markedly lower than that without a resonance structure. In toluene, the reactivity of benzyl chloride is approximately equal to that of allyl chloride. With itself as the solvent, benzyl chloride would be significantly more reactive than allyl chloride [6,7] since the partially formed benzyl carbonium ion may possess the various resonance structures as [6]
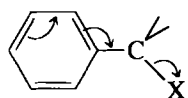

As indicated in the above structures, the leaving group X more easily departs from the benzyl activated complex than from the allyl activated complex.

The Relative Reactivities of Cl^-, AcO^-, BzO^-, and Br^- of the Halides and the Quaternary Ammonium Ion Pairs: A previous section has already accounted for why the leaving group Br^- of halides is more reactive than Cl^- and the anion Br^- of the quaternary ammonium ion pair is less reactive than Cl^- in solvents of lower polarity.

The last row of Table I reveals that the forward rate constants of Cl^-, AcO^-, and BzO^- of the benzyl compounds are of the same order (1.9:1:1.2). This is because that the favors of basicity in S_N2 for AcO^- and BzO^- are counterbalanced by their own steric hindrances. This table also indicates that the backward rate constants of Cl^- and AcO^- of the quaternary ammonium ion pairs are also of the same order and considerably greater than that of BzO^- (i.e., the ratio of the backward rate constants is 1.3:1:0.045). Comparing the two ratios reveals that the value 0.0552×10^{-3} M^{-1} s^{-1} is not the correct backward rate constant. Since BzO^- is a very strong base, its quaternary ammonium ion pairs can be easily de-composed by E2 elimination [2,12]. Simultaneously, most of the salt $BzBu_3NBzO$ produced by the forward reaction decomposed. This occurrence accounts for why Figure 9 shows that the equilibrium of the reaction $BzOBz$ + $(BzBu_3NBr) \rightleftharpoons BzBr + (BzBu_3NBzO)$ can apparently not be reached.

CONCLUSION

The reaction

$$RX + (BzBu_3NBr) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RBr + (BzBu_3NX)$$
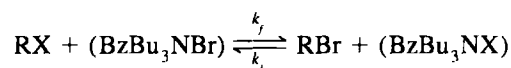
where R = allyl, butyl and benzyl when X = Cl; and X = AcO and BzO when R = benzyl, are reversible. The ratios k_b/k_f for RX = allyl chloride, BuCl and BzCl are 1.6×10^4, 2.5×10^2, and 3.7×10^1, respectively. The reason for why the ratios are all significantly greater than 1 is that RBr is more reactive than RCl; moreover, $BzBu_3NCl$ is more reactive than $BzBu_3NBr$ in solvents of lower polarity. The ratio of reactivity of allyl chloride/BuCl is about 91/1. The reactivity of BzCl in mixed solvent of mole-ratio of toluene /BzCl 10/1 is roughly equal to that of allyl chloride with itself as the solvent. The superior reactivities of allyl and benzyl groups are due to the resonance stabilization of their partially formed carbonium ions at the instant of forming activated complex.

For the chlorides in the forward reactions, the ratio of the forward rate constants of allyl/Bu/Bz is about $1:0.011:1$. However, for the bromides in the backward reaction, the ratio of the backward rate constants is about $300:0.12:1$. This finding suggests that the increase in the size of the leaving group (X^- from RX) strongly favors the reactivity of the smaller group R of the halide RX.

When RX are the benzyl compounds, the forward rate constants are of the same order of magnitude although the order of basicity is $BzO^- \gg AcO^- \gg Cl^-$. This is owing to the fact that the favors of basicity in S_N2 for BzO^- and AcO^- are counterbalanced by their own steric hindrances.

SYMBOLS

a   The parameter defined by eq. (2).

b   The parameter defined by eq. (3).

c_j The molar concentration of species j.

c_{ja} The apparent value of c_j defined as c_{ja} = moles of species j added/volume of solution (1).

c_{je} The equilibrium value of c_j.

c_{ji} The initial value of c_j.

c_{js} The saturated value of c_j.

$\overline{C_j}$ The mean value of c_j.

k_b Backward rate constant.

k_f Forward rate constant.

k_1 The parameter defined by eq. (7).

k_2 The parameter defined by eq. (8).

t   Reaction time.

t_o The time required for the solution to be saturated with the salt $BzBu_3NBr$.

V_s The volume of sample taken from the reaction solution.

V_w The volume of water used for diluting the sample.

Greek Letters

χ The specific conductance of solution.

χ_j The specific conductance contributed by species j.

χ_{jo} The value of χ_j at the time t_o.

χ_{js} The saturate value of χ_j.

χ_p The specific conductance of the solution during the plateau stage.

Λ_j The molar conductance contributed by species j.

σ The standard derivation of C_4.

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