

of the diffusion coefficients. The main difference of this technique from Chu *et al*'s is in the idea that the distribution function H be calculated from the derivative of the relaxation function, *i.e.* from eq. (3), but not from eq. (1). It should be pointed out that this technique, just like the histogram method of Chu *et al*¹⁹, can also be applied to the calculation of the distribution of the diffusion coefficients in solution.

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Kinetic Studies on Bromine-Exchange Reactions of Antimony Tribromide with α -Phenyl-n-butyl and α -Phenyl-i-butyl Bromides in Nitrobenzene †

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The rate of bromine-exchange reaction between antimony tribromide and α -phenyl-n-butyl bromide in nitrobenzene has been determined, using antimony tribromide labelled with Br-82. The results indicate that the exchange reaction follows the first-order kinetics with respect to the organic bromide, and either the second- or first-order kinetics with respect to antimony tribromide depending on its concentration. The third-order rate constant obtained was $7.50 \times 10^{-2} \text{ l}^2\text{mol}^{-2}\text{s}^{-1}$ at 28°C. Similar study on the bromine-exchange reaction between antimony tribromide and α -phenyl-i-butyl bromide has also been carried out. The results of the study show the same kinetic orders as the ones observed with α -phenyl-n-butyl bromide. The third-order rate constant observed was $2.40 \times 10^{-2} \text{ l}^2\text{mol}^{-2}\text{s}^{-1}$ at 28°C. The activation energy, the enthalpy of activation and the entropy of activation for the two exchange reactions mentioned above have been determined. The reaction mechanisms for the exchange reactions are discussed.

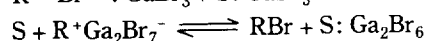
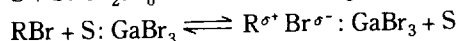
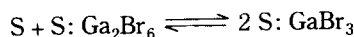
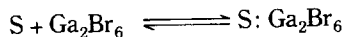
Introduction

In the previous papers of this series,¹⁻⁶ we reported the results of kinetic studies on the bromine-exchange reactions between gallium bromide and alkyl bromides in nitrobenzene. The alkyl bromides (RBr) examined were methyl, ethyl, n-propyl, i-propyl, n-butyl and i-butyl bromides. From the results of these studies, it was concluded that all the bromine-exchange reactions followed the second-order kinetics with

respect to gallium bromide and the first-order kinetics with respect to the alkyl bromides examined.

$$\text{Rate} = k_3[\text{GaBr}_3]^2[\text{RBr}]$$

It was assumed that the exchange reactions between gallium bromide and the alkyl bromides took place through the following reaction schemes (S denotes the solvent molecule):



† Based on the Ph. D. thesis of Sok Hwan Rhyu, Sogang University, Seoul, 1987. Presented at the Asian Chemical Congress '87 Seoul, June 29-July 3, 1987.

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The breaking of the carbon-bromine bond in the polarized molecules of the addition compounds of gallium bromide with alkyl bromides was assumed to be the slowest step among various reaction steps. This mechanism could lead to the kinetic expression written above.

We extended the studies to the systems of antimony tribromide with benzyl,⁷ *p*-xylyl,⁸ α -phenylethyl,⁹ and α -phenyl-*n*-propyl¹⁰ bromides in nitrobenzene. The results of these studies indicated that all the bromine-exchange reactions followed the first-order kinetics with respect to the organic bromides(RBr), and either the second- or first-order kinetics with respect to antimony tribromide depending on its concentration.

$$\text{Rate} = k_3[\text{SbBr}_3]^2[\text{RBr}]$$

(at higher SbBr₃ concentrations)

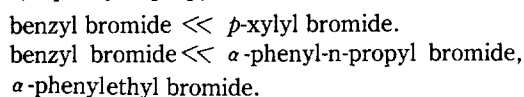
$$\text{Rate} = k_2[\text{SbBr}_3][\text{RBr}]$$

(at lower SbBr₃ concentrations)

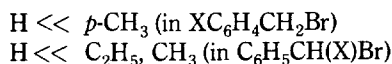
Thus it was concluded that the kinetic expressions for the bromine-exchange reactions observed in the region of higher SbBr₃ concentrations were similar to those obtained on the systems with gallium bromide. Hence, we proposed that the bromine-exchange reactions at higher SbBr₃ concentrations might proceed through the reaction schemes similar to those written above for the systems with gallium bromide.

Since entirely different situations were observed at lower SbBr₃ concentrations, we proposed the reaction schemes for the bromine-exchange reactions at lower SbBr₃ concentrations in different reaction schemes. Thus, in our previous papers we proposed two different reaction schemes for the bromine-exchange reactions between antimony tribromide and organic bromides, depending on the concentrations of antimony tribromide.

The experimental results of our previous studies also revealed that benzyl bromide exchanged bromine atom with antimony tribromide much more slowly than *p*-xylyl bromide, α -phenyl-*n*-propyl bromide and α -phenylethyl bromide:



Thus, it was concluded that the substitution of alkyl groups for H-atoms in the benzyl bromide molecule enhanced the rate of bromine-exchange reactions,



Since it was observed that the existence of additional methyl or ethyl groups in the organic bromide molecules enhanced the rate of bromine-exchange reactions, α -phenylethyl bromide was anticipated to exchange bromine atom with antimony tribromide more slowly than α -phenyl-*n*-propyl bromide. But the experimental observations were exactly the reverse.

It appeared important to extend the studies to the systems of antimony tribromide with α -phenyl-*n*-butyl bromide (C₆H₅CH(*n*-C₃H₇)Br) and α -phenyl-*i*-butyl bromide (C₆H₅CH(*i*-C₃H₇)Br) in the hope of better understanding of the effect of additional alkyl groups in the organic bromide molecules on the rate of the bromine-exchange reactions. Thus, the present study was undertaken on the systems of antimony tribromide with α -phenyl-*n*-butyl and α -phenyl-*i*-butyl bromides in nitrobenzene.

Experimental Part*

Materials. Nitrobenzene (>99.5%, puriss grade, Fluka, Switzerland), the solvent used in the present study, was purified by the method described in the previous paper of this series.⁷ α -phenyl-*n*-butyl bromide was prepared by the reaction of *n*-butyl benzene (>99%, purum grade, Fluka, Switzerland) with N-bromosuccinimide in the presence of catalytic amount of benzoyl peroxide in carbon tetrachloride,¹¹ and purified by the method of fractional distillation under vacuum. Similarly, α -phenyl-*i*-butyl bromide was prepared from *i*-butyl benzene (>99%, purum grade, Fluka, Switzerland) and N-bromosuccinimide, and purified by fractional distillation under vacuum. Radioactive antimony tribromide labelled with Br-82 was prepared by the method reported previously,⁷ using radioactive ammonium bromide produced in the nuclear reactor, TRIGA-III, of the Korea Advanced Energy Research Institute.

Determination of Exchange Rates. The kinetic studies of the bromine-exchange reactions were carried out by the procedures described in the previous paper.⁷ The rate of the bromine-exchange reactions was calculated by the following equation:¹²

$$\text{Rate} = -2.303 \left(\frac{3ab}{3a+b} \right) \frac{d}{dt} \log \frac{(A_\infty - A_t)}{(A_\infty - A_0)} \quad (1)$$

In this equation, *a* denotes the molar concentration of antimony tribromide, *b* that of organic bromide, and *A*₀, *A*_t and *A*_∞ the radioactivities of the organic layer at time zero, at time *t* and at time of the completion of the exchange reaction, respectively.

The values of *A*_∞ were obtained by the following equation:

$$A_\infty = \frac{b}{3a+b} \times A_{total}$$

where *A*_{total} denotes the total radioactivity present in both organic layer and aqueous layer. Then the values of log(*A*_∞ - *A*_t)/(*A*_∞ - *A*₀) were plotted against time, *t*. From the slope of the plots, the rate of the exchange reaction was calculated by equation (1).

Results

Bromine-Exchange Reaction of Antimony Tribromide with α -Phenyl-*n*-butyl Bromide in Nitrobenzene. The rates of bromine exchange between antimony tribromide and α -phenyl-*n*-butyl bromide in nitrobenzene were measured at several temperatures with various concentrations of both antimony tribromide and α -phenyl-*n*-butyl bromide. In each run of the experiments, good linearity was observed between log(*A*_∞ - *A*_t)/(*A*_∞ - *A*₀) and *t*. From the slopes of the plots and the molar concentrations of antimony tribromide and α -phenyl-*n*-butyl bromide, the exchange rate was calculated by equation (1). The experimental results are summarized in Table 1.

The rate of the exchange reaction may be expressed by the following equation:

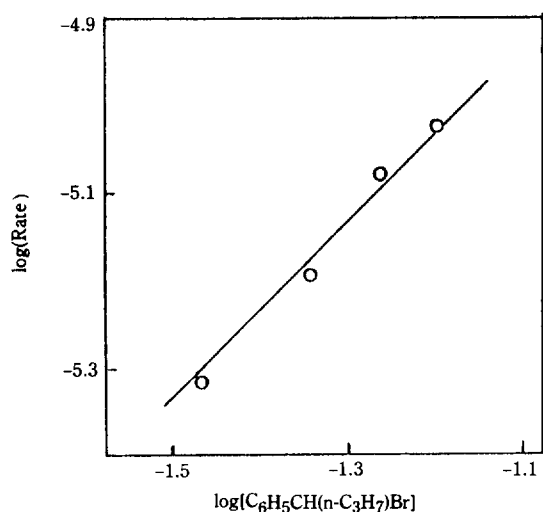
$$\text{Rate} = k[\text{SbBr}_3]^m[\text{C}_6\text{H}_5\text{CH}(n\text{-C}_3\text{H}_7)\text{Br}]^n$$

In order to estimate the value of *n*, the log(Rate) values obtained at given SbBr₃ concentration (Table 1) were plotted

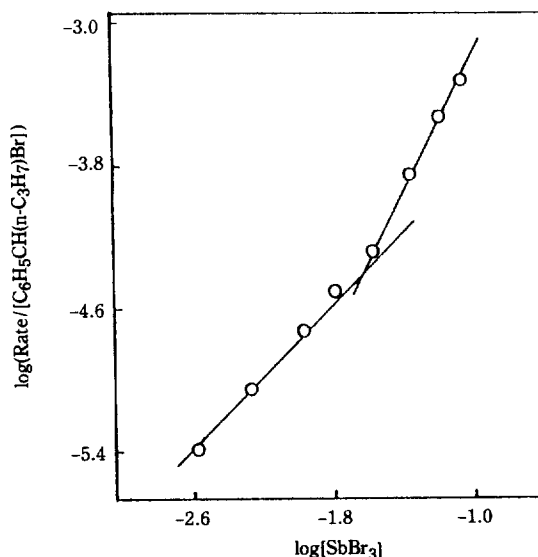
* For further details, refer to the Ph. D. thesis of Sok Hwan Rhyu, Sogang University Library, Seoul.

Table 1. Exchange Rates and Rate Constants of the Bromine-Exchange Reaction between Antimony Tribromide and α -Phenyl-*n*-butyl Bromide in Nitrobenzene

Temp °C	[SbBr ₃] × 10 ² mol·l ⁻¹	[C ₆ H ₅ CH(<i>n</i> -C ₃ H ₇)Br] × 10 ² , mol·l ⁻¹	Rate × 10 ⁶ mol·l ⁻¹ ·s ⁻¹	k ₃ × 10 ² l ² ·mol ⁻² ·s ⁻¹
15	3.94	4.56	1.75	2.47
15	5.25	4.56	3.17	2.52
15	6.56	4.56	4.83	2.46
				2.5 (av.)
18	5.47	2.58	2.39	3.10
18	5.47	3.87	3.82	3.29
18	5.47	6.46	7.01	3.63
				3.3 (av.)
24	5.27	3.42	4.85	5.10
24	5.27	4.56	6.40	5.05
24	5.27	5.47	8.28	5.50
24	5.27	6.38	9.47	5.34
				5.3 (av.)
28	0.263	4.47	0.184	
28	0.527	4.47	0.408	
28	1.05	4.47	0.831	
28	1.58	4.47	1.37	
28	2.63	4.47	2.30	7.44
28	4.21	4.47	6.20	7.83
28	6.32	4.47	13.0	7.28
28	8.43	4.47	20.9	6.58
28	3.13	1.68	1.22	7.41
28	3.13	2.52	2.05	8.33
				7.5 (av.)
32	5.40	2.28	5.88	8.84
32	5.40	3.42	9.08	9.10
32	5.40	4.56	13.3	10.0
				9.3 (av.)

**Figure 1** The effect of [C₆H₅CH(*n*-C₃H₇)Br] on the rate of bromine exchange between antimony tribromide and α -phenyl-*n*-butyl bromide in nitrobenzene at 24°C (0.0527 M SbBr₃).

against log[C₆H₅CH(*n*-C₃H₇)Br]. The plots showed good linearity as shown in Figure 1. Since the slope of the straight line was approximately equal to 1, we concluded that $n = 1$.

**Figure 2.** The effect of [SbBr₃] on the rate of bromine exchange between antimony tribromide and α -phenyl-*n*-butyl bromide in nitrobenzene at 28°C (0.0447 M C₆H₅CH(*n*-C₃H₇)Br).

$$\text{Rate} = k[\text{SbBr}_3]^m[\text{C}_6\text{H}_5\text{CH}(\textit{n}\text{-C}_3\text{H}_7)\text{Br}]$$

In order to evaluate the value of m , the values of $\log(\text{Rate}/[\text{C}_6\text{H}_5\text{CH}(\textit{n}\text{-C}_3\text{H}_7)\text{Br}])$ obtained at given C₆H₅CH(*n*-C₃H₇)Br concentration (Table 1) were plotted against $\log[\text{SbBr}_3]$. The plots did not show simple linear relation between $\log(\text{Rate}/[\text{C}_6\text{H}_5\text{CH}(\textit{n}\text{-C}_3\text{H}_7)\text{Br}])$ and $\log[\text{SbBr}_3]$ (Figure 2). It would be concluded, however, that the slope of the plots seemed to be equal to 2 at relatively high SbBr₃ concentrations, and be close to 1 in the region of lower SbBr₃ concentration. Hence, it seemed reasonable to conclude that the rate of exchange reaction could be expressed by the following two equations:

$$\text{Rate} = k_3[\text{SbBr}_3]^2[\text{C}_6\text{H}_5\text{CH}(\textit{n}\text{-C}_3\text{H}_7)\text{Br}] \quad (2)$$

(at higher SbBr₃ concentrations)

$$\text{Rate} = k_2[\text{SbBr}_3][\text{C}_6\text{H}_5\text{CH}(\textit{n}\text{-C}_3\text{H}_7)\text{Br}] \quad (3)$$

(at lower SbBr₃ concentrations)

Bromine-Exchange Reaction of Antimony Tribromide with α -Phenyl-*i*-butyl Bromide in Nitrobenzene.

The rates of bromine exchange between antimony tribromide and α -phenyl-*i*-butyl bromide in nitrobenzene were also measured at several temperatures with various concentrations of both reactants. The results are summarized in Table 2.

By plotting the values of $\log(\text{Rate})$ obtained at given SbBr₃ concentration against $\log[\text{C}_6\text{H}_5\text{CH}(\textit{i}\text{-C}_3\text{H}_7)\text{Br}]$ (Figure 3) and those of $\log(\text{Rate}/[\text{C}_6\text{H}_5\text{CH}(\textit{i}\text{-C}_3\text{H}_7)\text{Br}])$ against $\log[\text{SbBr}_3]$ (Figure 4), it was concluded that the exchange rates were first order with respect to α -phenyl-*i*-butyl bromide, and either second or first order with respect to antimony tribromide depending on its concentration. These results were similar to those obtained on the systems with α -phenyl-*n*-butyl bromide. Thus, the rate of the exchange reaction could be expressed by the following equations:

$$\text{Rate} = k_3[\text{SbBr}_3]^2[\text{C}_6\text{H}_5\text{CH}(\textit{i}\text{-C}_3\text{H}_7)\text{Br}] \quad (4)$$

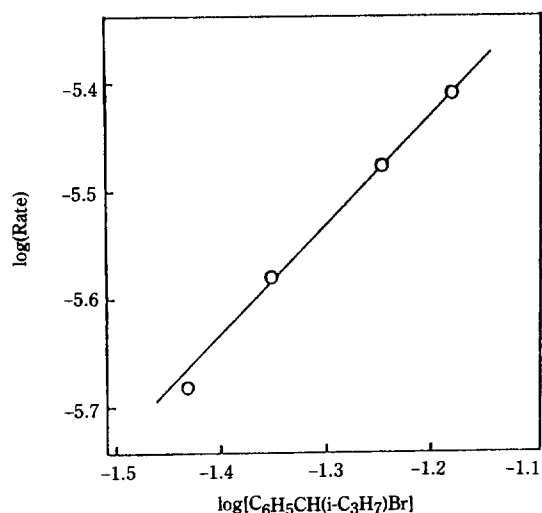
(at higher SbBr₃ concentrations)

$$\text{Rate} = k_2[\text{SbBr}_3][\text{C}_6\text{H}_5\text{CH}(\textit{i}\text{-C}_3\text{H}_7)\text{Br}] \quad (5)$$

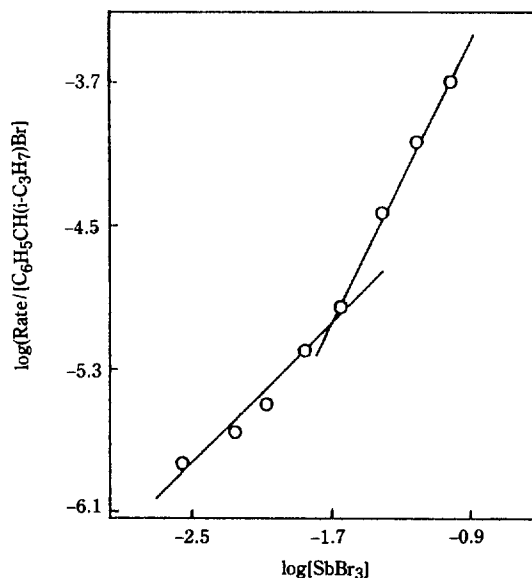
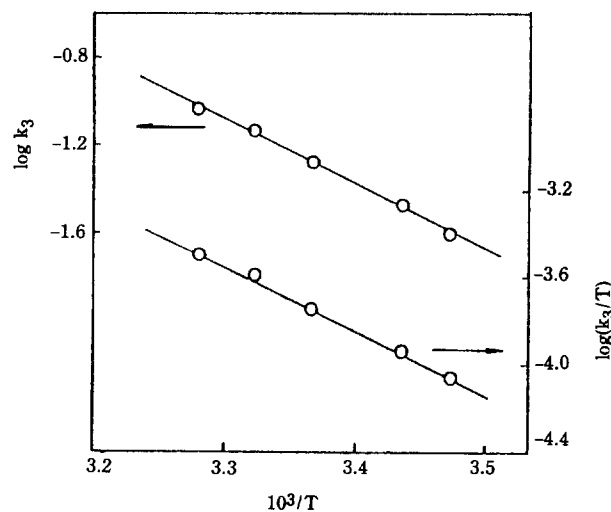
(at lower SbBr₃ concentrations)

Table 2. Exchange Rates and Rate Constants of the Bromine-Exchange Reaction between Antimony Tribromide and α -Phenyl-*i*-butyl Bromide in Nitrobenzene

Temp °C	$[\text{SbBr}_3] \times 10^2$ mol·l ⁻¹	$[\text{C}_6\text{H}_5\text{CH}(\text{i-C}_3\text{H}_7)\text{Br}]$ $\times 10^2$, mol·l ⁻¹	Rate $\times 10^6$ mol·l ⁻¹ ·s ⁻¹	$k_3 \times 10^2$ l ² ·mol ⁻² ·s ⁻¹
15	3.94	4.96	0.574	0.745
15	5.25	4.96	1.02	0.746
15	6.56	4.96	1.61	0.754
				0.75(av.)
17.5	1.26	4.84	0.0949	1.24
17.5	2.35	4.84	0.272	1.02
17.5	4.71	4.84	1.08	1.01
17.5	7.84	4.84	3.19	1.07
17.5	12.55	4.84	8.44	1.11
				1.1 (av.)
23.5	5.85	3.72	2.08	1.63
23.5	5.85	4.46	2.63	1.72
23.5	5.85	5.70	3.33	1.71
23.5	5.85	6.69	3.90	1.70
				1.7 (av.)
28	0.281	4.96	0.0739	
28	0.562	4.96	0.110	
28	0.843	4.96	0.160	
28	1.40	4.96	0.326	
28	2.25	4.96	0.553	2.20
28	3.87	4.96	1.86	2.50
28	6.20	4.96	4.63	2.43
28	9.30	4.96	10.3	2.40
				2.4 (av.)
32	5.40	2.48	2.03	2.81
32	5.40	3.72	3.63	3.35
32	5.40	4.96	4.94	3.43
				3.2 (av.)

**Figure 3.** The effect of $[\text{C}_6\text{H}_5\text{CH}(\text{i-C}_3\text{H}_7)\text{Br}]$ on the rate of bromine exchange between antimony tribromide and α -phenyl-*i*-butyl bromide in nitrobenzene at 23.5°C (0.0585 M SbBr_3).

Activation Parameters of the Bromine-Exchange Reactions. In order to calculate the values of various activation parameters of the exchange reactions, it was re-

**Figure 4.** The effect of $[\text{SbBr}_3]$ on the rate of bromine exchange between antimony tribromide and α -phenyl-*i*-butyl bromide in nitrobenzene at 28°C (0.0496 M $\text{C}_6\text{H}_5\text{CH}(\text{i-C}_3\text{H}_7)\text{Br}$).**Figure 5.** Temperature dependence of $\log k_3$ and $\log(k_3/T)$ of the bromine-exchange reaction of antimony tribromide with α -phenyl-*n*-butyl bromide in nitrobenzene.

quired to obtain the values of the rate constant at different temperatures. Unfortunately, it was difficult to calculate the exact values of the rate constants because of the complexity of the kinetic orders with respect to antimony tribromide. The values of the third-order rate constant (k_3) were estimated, by dividing the observed rates of exchange by $[\text{SbBr}_3]^2 [\text{C}_6\text{H}_5\text{CH}(\text{n-C}_3\text{H}_7)\text{Br}]$ or $[\text{SbBr}_3]^2 [\text{C}_6\text{H}_5\text{CH}(\text{i-C}_3\text{H}_7)\text{Br}]$, assuming the rate equations (2) and (4), and using the experimental data obtained at relatively high concentrations of SbBr_3 . The average values of k_3 thus obtained at different temperatures are included in Tables 1 and 2.

The values of $\log k_3$ and $\log(k_3/T)$ were plotted against $1/T$ (Figures 5 and 6). From the slopes and the intercepts of the linear plots, the activation parameters of the exchange reactions, such as activation energy E_a , frequency factor A , enthalpy of activation ΔH^\ddagger , and entropy of activation ΔS^\ddagger , were calculated by the following equations.

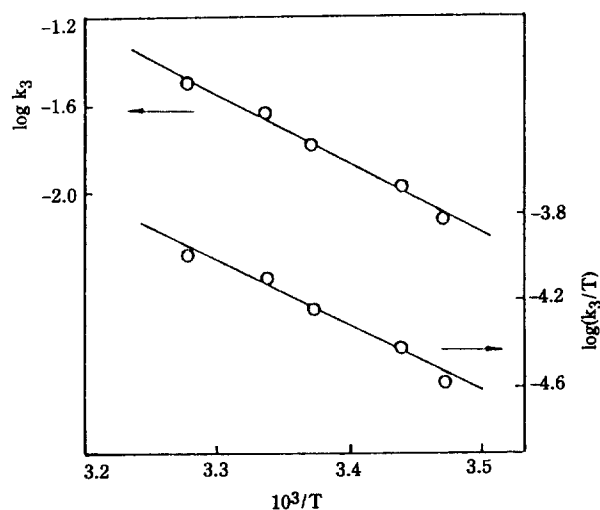


Figure 6. Temperature dependence of $\log k_3$ and $\log(k_3/T)$ of the bromine-exchange reaction of antimony tribromide with α -phenyl-*i*-butyl bromide in nitrobenzene.

Table 3. Activation Parameters of the Bromine-Exchange Reactions of Antimony Tribromide with α -Phenyl-*n*-butyl bromide and α -Phenyl-*i*-butyl Bromide in Nitrobenzene

Item	α -Phenyl- <i>n</i> -butyl bromide	α -Phenyl- <i>i</i> -butyl bromide
E_a (Kcal/mol)	14 ± 0.6	15 ± 0.5
$\log A$	8.8 ± 0.5	9.3 ± 0.4
ΔH^\ddagger (Kcal/mol)	13 ± 0.5	15 ± 0.5
ΔS^\ddagger (e.u.)	-20 ± 1.5	-18 ± 1.8

$$k_3 = A \exp(-E_a/RT)$$

$$k_3/T = (k/h) \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$$

In these equations k denotes the Boltzmann constant and h the Plank constant. The results of the calculation of the activation parameters are listed in Table 3.

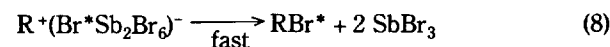
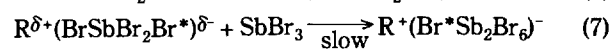
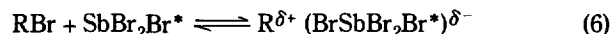
Discussion

As a result of the present investigation, the bromine-exchange reactions of antimony tribromide with α -phenyl-*n*-butyl and α -phenyl-*i*-butyl bromides show simple, first-order kinetics with respect to the organic bromides, but complicated kinetic orders with respect to antimony tribromide. The experimental results seem to indicate that the exchange reactions follow the second-order kinetics with respect to antimony tribromide at relatively higher SbBr_3 concentrations

and the first-order kinetics with respect to antimony tribromide at lower SbBr_3 concentrations.

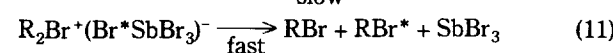
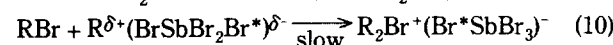
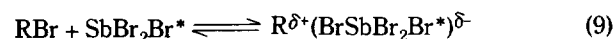
These results are similar to those observed previously on the systems of antimony tribromide with organic bromides.⁷⁻¹⁰ On the basis of the reaction mechanisms reported previously,⁸ we now propose the following two reaction schemes for the bromine-exchange reactions of antimony tribromide with organic bromides.

(a) In the case of relatively high SbBr_3 concentrations, it is assumed that the bromine-exchange reactions proceed through the following reaction steps.



In the reaction step (7), we assume that the carbon-bromine bond in the polarized molecule of the addition compounds of antimony tribromide with organic bromides, $\text{R}^{\delta+}(\text{BrSbBr}_2\text{Br}^*)^{\delta-}$, is broken with the aid of another molecule of antimony tribromide. Assuming the reaction step (7) is the slowest step among various reaction steps, the third-order kinetic expression (2) or (4) could be obtained, as was shown in the previous papers of this series.^{8,9}

(b) In the case of lower SbBr_3 concentrations, it is assumed that the bromine-exchange reactions proceed through the following reaction steps:



In the reaction step (10), it is assumed that the carbon-bromine bond in the polarized molecule of the addition compounds, $\text{R}^{\delta+}(\text{BrSbBr}_2\text{Br}^*)^{\delta-}$, is broken with the aid of another molecule of the organic bromides, forming bromonium ion. Among the various reaction steps, the reaction step (10) is assumed to be the slowest step of the exchange reaction, which will satisfy the kinetic expression (3) or (5), as was shown in the previous papers of this series.^{8,9}

The results of the present studies are now compared with the results of previous studies on similar systems with other organic bromides (Table 4).⁷⁻¹⁰ It can be seen from Table 4 that the third-order rate constants (k_3) for the bromine exchange increase in the following order of alkyl substituents at the benzylic position of the organic bromides:

$$\text{X: } \text{H} \ll \text{i-C}_3\text{H}_7 < \text{C}_2\text{H}_5 < \text{n-C}_3\text{H}_7 < \text{CH}_3$$

$$k_3(\text{X})/k_3(\text{H}): \quad 1 \quad 1100 \quad 1700 \quad 3600 \quad 5700$$

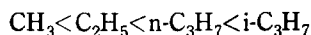
Table 4. Summary of Data Obtained for the Bromine-Exchange Reactions between Antimony Tribromide and Organic Bromides in Nitrobenzene *

Organic bromide	Kinetic order observed	$k_3 \times 10^4$ $\text{l}^2\text{mol}^{-2}\text{s}^{-1}$	E_a Kcal/mol	$\log A$	ΔH^\ddagger Kcal/mol	ΔS^\ddagger e.u.	ref.
Benzyl	3, 2	0.21(29°C)	16 ± 2.0	6.7 ± 1.4	15 ± 2.0	-30 ± 6.5	7
α -Phenyl- <i>i</i> -butyl	3, 2	240	15 ± 0.5	9.3 ± 0.4	15 ± 0.5	-18 ± 1.8	
α -Phenyl- <i>n</i> -propyl	3, 2	350	17 ± 1.4	11 ± 1.0	16 ± 1.4	-13 ± 4.5	10
α -Phenyl- <i>n</i> -butyl	3, 2	750	14 ± 0.6	8.8 ± 0.5	13 ± 0.5	-20 ± 1.5	
α -Phenylethyl	3, 2	1200	19 ± 0.6	13 ± 0.4	19 ± 0.6	-1.3 ± 1.9	9

* The k_3 values were obtained at 28°C unless otherwise indicated.

The comparison of the relative values of k_3 among various organic bromides reveals that the alkyl-substituted benzyl bromides exchange bromine atoms with antimony tribromide 10^3 times or more rapidly than benzyl bromide itself. It seems that the alkyl-substituted benzyl bromides may form the ion pairs, $\text{R}^+(\text{Br}^*\text{Sb}_2\text{Br}_6)^-$, more readily than benzyl bromide, and hence, may lower the activation energy of the exchange reactions.

On the basis of this assumption it can be said that the more readily the alkyl groups tolerate positive charge to the adjacent carbon atom, the faster the exchange reaction might proceed. Thus, the relative rates of the exchange reactions of the alkyl-substituted benzyl bromides with antimony tribromide are anticipated to increase in the following order of the alkyl substituents:



Contrary to the expectations, however, the substitution of CH_3 group indicates much faster exchange reaction. Thus, α -phenylethyl bromide exchanges bromine atoms with antimony tribromide much faster than the other alkyl-substituted benzyl bromide examined. This result may be rationalized by considering that the methyl group of α -phenylethyl bromide can stabilize the transition state of the exchange reaction by hyperconjugation. Among various alkyl groups, methyl group is known to be the best to stabilize an adjacent positive charge through hyperconjugation.¹³

By comparing the k_3 values for various alkyl-substituted benzyl bromides, it can be seen that the $\text{i-C}_3\text{H}_7$ -substituted benzyl bromide exchanges bromine atom with antimony tribromide much more slowly than the other alkyl-substituted benzyl bromides. This result is contrary to the expectation that i-propyl group may tolerate a positive charge to the adjacent carbon atom at the benzylic position more readily than the other normal alkyl groups such as methyl, ethyl, and n-propyl , and hence, lead to the increase in exchange rate. It is speculated that the decrease of exchange rate may arise from the steric hindrance that restricts the polarized addition compound to be attacked by antimony tribromide molecules. In general, the branched alkyl substituents are considered to give greater steric hindrance than normal alkyl substituents.

The reaction mechanisms proposed in the present study are slightly different from those reported in the previous papers.^{8,9} Interactions of antimony tribromide with solvent molecules previously assumed are neglected in the present paper. This may give reasonable explanation for the negative values of entropy of activation observed for the exchange reactions (Table 4). The rate determining step (7) may result in a negative value of ΔS^\ddagger , since it indicates an association process.

As mentioned above, the increasing order of third-order rate constants can be ascribed to some substituent effects such as inductive effect, hyperconjugation effect, and steric effect, assuming that those effects influence the stability of the transition state and the exchange rate is related to the stability of the transition state.

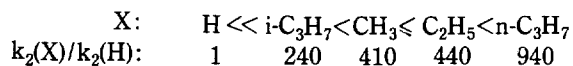
As a result of the present study it is concluded that the bromine-exchange reactions of antimony tribromide with the organic bromides examined reveal the first order kinetics with respect to antimony tribromide if its concentration is relatively low. The systems with low SbBr_3 concentrations, however, has not been thoroughly studied because of possi-

Table 5. The $k_2(28^\circ\text{C})$ Values Obtained for the Bromine-Exchange Reactions between Antimony Tribromide and organic Bromides in Nitrobenzene

Organic bromide	$k_2 \times 10^4$ $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
Benzyl	0.018*
α -Phenyl-i-butyl	4.4
α -Phenylethyl	7.3
α -Phenyl-n-propyl	7.9
α -Phenyl-n-butyl	17

* 29°C

ble magnification of experimental errors at low concentrations of the reactants. Using the data obtained at the lower region of antimony tribromide concentrations, the approximate values of the second-order rate constants (k_2) can be calculated by dividing the observed exchange rate by $[\text{SbBr}_3][\text{RBr}]$. The average values of k_2 thus obtained at 28°C are listed in Table 5. It can be seen from Table 5 that the second-order rate constant for the bromine-exchange reaction between antimony tribromide and organic bromides increases in the following order of the alkyl groups substituted at the benzylic position of the organic bromides:



This order of increasing exchange rate differs from the order observed for the third-order rate constants. The position of the CH_3 group relative to other groups is quite different. As mentioned above, the hyperconjugation effect of CH_3 group is considered to play important role on the third-order rate constant of the exchange reaction. If the exchange reaction in the lower SbBr_3 concentration region proceeds through the bromonium ion intermediate, $\text{R}_2\text{Br}^+(\text{BrSbBr}_3)^-$, the hyperconjugation effect of CH_3 group will be no longer important.

The smaller value of k_2 obtained for the $\text{i-C}_3\text{H}_7$ -substituted benzyl bromide may explained by steric effect of the substituent by analogy with the case of k_3 . An association-type reaction is subject to more steric hindrance by branched alkyl group ($\text{i-C}_3\text{H}_7$) than normal alkyl groups (CH_3 , C_2H_5 , $\text{n-C}_3\text{H}_7$).

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Reaction Conditions and Mechanism of Electrolytic Reduction of Dibenzoylmethane †

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Electrochemical reduction of dibenzoylmethane was studied on mercury electrode by means of cyclic voltammetry, polarography and potentiostatic measurements in ethanol-water system. In acidic solutions monomeric pinacol was produced by irreversible two-electron process while monomeric and dimeric pinacol were competitively produced by the same process in neutral solution. However, in basic solution the dimeric pinacol was mostly produced through radical by irreversible one-electron transfer process. Mechanisms of the reduction of dibenzoylmethane are deduced from Tafel slope, pH dependance and reaction order with respect to the concentration of dibenzoylmethane in the solution of various pH.

Introduction

Previous investigators¹⁻⁷ have studied the electrochemical reduction of 1,3-diphenyl-1,3-propanedione (or dibenzoylmethane, DBM) by polarographic and coulometric experiments. Evans and Woodbury³ reported that dibenzoylmethane could be reduced in ethanol-water to three kinds of product, via one, two or four electron transfer per a molecule, depending upon the pH of the solutions and the electrode potential. The one-electron product at the first polarographic wave was the dimeric pinacol (1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol) and the two-electron product at the second, the cyclic tetrol (1,2,4,5-tetraphenyl-1,2,4,5-cyclohexanetetrol), however the four-electron product at the third wave was the monomeric diol (1,3-diphenyl-1,3-propanediol).

On the other hand it was recently reported by Chon⁸ that the dimeric and the monomeric pinacols could be obtained by two consecutive one-electron transfer processes on mercury film electrode in basic ethanol-water solvents.

In this paper polarography, cyclic voltammetry and kinetic measurements of the electrochemical reduction of dibenzoylmethane in various pH range of ethanol-water solutions were made in order to elucidate the reduction mechanism against the reaction conditions.

Experimental

Chemicals. Reagent grade dibenzoylmethane (Fisher) was checked for purity by measurements of the melting point, IR and NMR spectra and used without further purification.

†Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.

Dibenzoylmethane used in this investigation was found to exist almost entirely in the enol form on comparison with the melting point and the standard spectral data⁹⁻¹¹. All electrolyte solutions were prepared from reagent grade absolute ethanol (James Burrough) and distilled water (50% by volume) with sulfuric acid or citrate buffers as the electrolytes for acidic or moderate solutions and with sodium hydroxide or carbonate buffers for basic solutions. Ionic strength of the solutions were adjusted to 0.10M. All inorganic compounds used herein were reagent grade of Junsei. They were used as received and checked for purity by measurements of the background polarograms.

Apparatus and Measurements. The electrochemical measurements for cyclic voltammetry and polarography were performed with a Princeton Applied Research (PAR) model 264A polarographic analyzer/stripping voltammeter equipped with a PAR 303A static mercury drop electrode (SMDE) and cell system. This cell is suited for sample volume of about 10ml, and the top of the cell allows for introduction of the counter, reference probe, deaeration tube, and a working electrode. The working electrode was SMDE and HMDE which set up by using triply-distilled mercury. The counter electrode was a platinum wire immersed in the test solution, hence it was not separated from the working compartment. The amount of product formed at the counter electrode during a measurement was so small that its presence did not affect the subsequent measurements.

The reference electrode was encased in a bridge tube which made contact with the test solution by means of a fine porosity frit-tip. A Ag/AgCl (sat'd KCl) reference electrode was used and all the potential data given here are referred to this electrode.