$$+4\eta^2-\eta^3)\varepsilon_0-2(2-\eta)(2+\eta)(4+\eta)]$$
$$(2p)^{\eta}\}\omega^3, \text{ if } p \rangle\rangle 1. \tag{6}$$

The circular dichroism in the extreme critical region behaves $\sim\omega^3(n_0\xi\omega)^\eta$, whereas the circular dichroism of a fluid satisfying the Ornstein–Zernike theory shows logarithmic divergence, $\sim\omega^3$ in $(n_0\xi\omega)$.

The optical rotation, $\phi(\omega)$ may be separated into three parts

$$\phi(\omega)=\frac{1}{2}\omega\, Re[n_L(\omega)-n_R(\omega)]$$
$$=\phi_0(\omega)+\phi_1'(\omega)+\phi_2'(\omega). \tag{7}$$

The first term, ϕ_0 is due to the molecular contribution and has been given in I. The second term, ϕ_1' is

$$\phi_1'(\omega)=-(81\pi^2)^{-1}(4-\varepsilon_0)(\varepsilon_0+2)\beta_0\rho_0(k_BT\chi/\xi^3)$$
$$[(\frac{\xi}{\alpha})^{1+\eta}\psi(\eta,\alpha_0\rho_0)-\frac{\pi}{2}\frac{(\varepsilon_0-1)^2}{\varepsilon_0}$$
$$\psi(1+p^2)^{\frac{\eta}{2}}]\omega^2, \text{ if } \alpha\ll\xi, \tag{8}$$

with

$$\psi(\eta,\alpha_0\rho_0)=\int dx\, x^\eta\frac{\theta(x)^2}{1+\theta(x)}. \tag{9}$$

When $\xi=0$, ψ has been given in ref. 3 and is of the order 1 for $0\leqslant\alpha_0\rho_0\leqslant 1$. The function, $\psi(\eta,\alpha_0\rho_0)$ is also of the order 1 for $0\leqslant\alpha_0\rho_0\leqslant 1.5$ and $0<\eta<1$. Owing to the condition $a\ll\xi$, the first part is dominant over the second term in the bracket of the right-handed side of eq.(8). The last term in eq.(7) is

$$\phi_2'(\omega)=\phi_2(\omega)(1+p^2)^{\frac{\eta}{2}}, \tag{10}$$

where $\phi_2(\omega)$ has been given in eq.(1,4,15). As discussed in I, ϕ_1' dominates over ϕ_2' in the case of $p\ll 1$. As the system approaches to the critical point, ϕ_2' becomes more important. If $1\ll p\ll|t|^{-1}$, we have

$$\phi_2'(\omega)\simeq[\frac{1}{3}(\varepsilon_0+2)(\varepsilon_0-1)]^2(k_BT\chi/16\pi\,\varepsilon_0\xi^2)$$
$$\omega^2p^{1+\eta}\,|t|. \tag{11}$$

The magnitude of ϕ_2' may be comparable to or larger than ϕ_1'. In the extreme case of $p|t|\gg 1$, ϕ_2' becomes

$$\phi_2'(\omega)\simeq[\frac{1}{3}(\varepsilon_0+2)(\varepsilon_0-1)]^2(k_BT\chi/32\varepsilon_0\xi^2)\omega^2p^\eta. \tag{12}$$

The above result independent of β_0 may be comparable to or larger than ϕ_0. We refer to I for the detailed discussion of the results.

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Kinetic Study on Bromine-Exchange Reaction of Antimony Tribromide with α-Phenylethyl Bromide in Nitrobenzene

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The kinetic study on the bromine-exchange reaction of antimony tribromide with α-phenylethyl bromide in nitrobenzene has been carried out, using Br-82 labelled antimony tribromide. The results show that the exchange reaction is first order with respect to α-phenylethyl bromide, and either second or first order with respect to antimony tribromide depending on its concentration. It is also concluded that α-phenylethyl bromide exchanges bromine atom with antimony tribromide much faster than other organic bromides previously examined. Reaction mechanisms for the exchange reaction are discussed.

Introduction

Previously we reported the resulte of the kinetic studies on the bromine-exchange reactions between some metal bromides and various organic bromides in nitrobenzene solution.[1-8] The systems of antimony tribromide with benzyl and *p*-xylyl bromides in nitrobenzene solution were studied for the bromine-exchange reactions,[7,8] using radioactive tracer techniques similar to those utilized in the systems of gallium bromide with various organic bromides.[1-6] The results of the studies on the systems of antimony tribromide with organic bromides indicated that the rates of the exchange reactions were first order with respect to the organic bromides, and either second or first order with respect to antimony tribromide depending on its concentrations. The experimental results also revealed that *p*-xylyl bromide exchanged bromine atom with antimony tribromide much faster than benzyl bromide. Hence, it was thought that

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the methyl group in the organic bromide molecules enhanced the rate of the exchange reactions.

It appeared of interest to extend the study to the system of antimony tribromide with α-phenylethyl bromide, $C_6H_5CH(CH_3)Br$, in the hope of better understanding of the effect of methyl group in the organic bromide molecules on the rates of the exchange reactions. Thus, the present study was undertaken on the system of antimony tribromide with α-phenylethyl bromide in nitrobenzene.

Experimental Part

Materials. The solvent used in the present study, nitrobenzene, was purified by the method described in the previous paper[7]. By the use of usual fractionation technique α-phenylethyl bromide (Extra pure grade, TCI, Japan) was purified.

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.

Experimental Procedures for Kinetic Studies. The experimental procedures for kinetic study of the bromine-exchange reaction were the same as those described in the previous paper[7]. The rate of the exchange reaction was calculated by the following equation[9]:

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

In this equation a denotes the molar concentration of antimony tribromide, b that of α-phenylethyl bromidce, 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:

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

where A_{total} denotes the total radioactivity present in both organic and aqueous layers. Then, the values of $\log\{(A_\infty - A_t)/(A_\infty - A_0)\}$ were plotted against time t. From the slope of the plots, the rate of the exchange reaction was calculated by equation (1).

TABLE 1: Rates of Bromine Exchange between Antimony Tribromide and α-Phenylethyl Bromide in Nitrobenzene

Temp. °C	$[SbBr_3] \times 10^2$ mole·l^{-1}	$[C_6H_5CH(CH_3)Br] \times 10^2$ mole·l^{-1}	Rate × 10^6 mole·l^{-1}sec^{-1}	$\frac{\text{Rate}}{[C_6H_5CH(CH_3)Br]} \times 10^5$ sec^{-1}
26	3.49	1.40	1.67	—
26	3.49	2.79	3.22	—
26	3.49	4.19	5.18	—
26	3.49	6.98	9.38	—
28	0.0498	6.98	0.0243	0.0348
28	0.0997	6.98	0.0483	0.0692
28	0.199	6.98	0.122	0.160
28	0.399	6.98	0.242	0.347
28	0.598	6.98	0.444	0.636
28	0.885	6.98	0.712	1.02
28	0.997	6.98	0.905	1.30
28	1.77	6.98	2.67	3.83
28	3.54	6.98	11.0	15.8
28	5.31	6.98	23.8	34.1
28	8.85	6.98	63.0	90.3

Results

Bromine-Exchange Reaction of Antimony Tribromide with α-Phenylethyl Bromide in Nitrobenzene. The rates of bromine exchange between antimony tribromide and α-phenylethyl bromide in nitrobenzene were measured with various concentrations of both antimony tribromide and α-phenylethyl bromide. In each run of the experiments, good linearity was observed between $\log\{(A_\infty - A_t)/(A_\infty - A_0)\}$ and t. From the slope of the plots and the molar concentrations of antimony tribromide and α-phenylethyl bromide, the exchange rate was calculated by equation(1). The results are summarized in Table 1.

The rate of the exchange reaction was expressed by the following equation:

$$\text{Rate} = k[SbBr_3]^m[C_6H_5CH(CH_3)Br]^n$$

In order to estimate the value of n, the log (Rate) values obtained at given $SbBr_3$ concentration (Table 1) were plotted against log $[C_6H_5CH(CH_3)Br]$. The plots showed fairly good linearity between log (Rate) and log $[C_6H_5CH(CH_3)Br]$, as shown in Figure 1. Since the slope of the straight line was approximately equal to 1, it was concluded that $n=1$.

$$\text{Rate} = k[SbBr_3]^m[C_6H_5CH(CH_3)Br]$$
$$\therefore \text{Rate}/[C_6H_5CH(CH_3)Br] = k[SbBr_3]^m$$

In order to estimate the value of m, the values of $\log\{\text{Rate}/[C_6H_5CH(CH_3)Br]$ obtained at given $C_6H_5CH(CH_3)Br$ concentration (Table 1) were plotted against log $[SbBr_3]$. The plots (Figure 2) did not show simple linear relation between $\log\{\text{Rate}/[C_6H_5CH(CH_3)Br]\}$ and log $[SbBr_3]$. It would be concluded, however, that the slope of the plots seemed to be equal to 2 at relatively high $SbBr_3$ concentrations, and be close to 1 in the region of lower $SbBr_3$ concentrations. Hence, it seemed

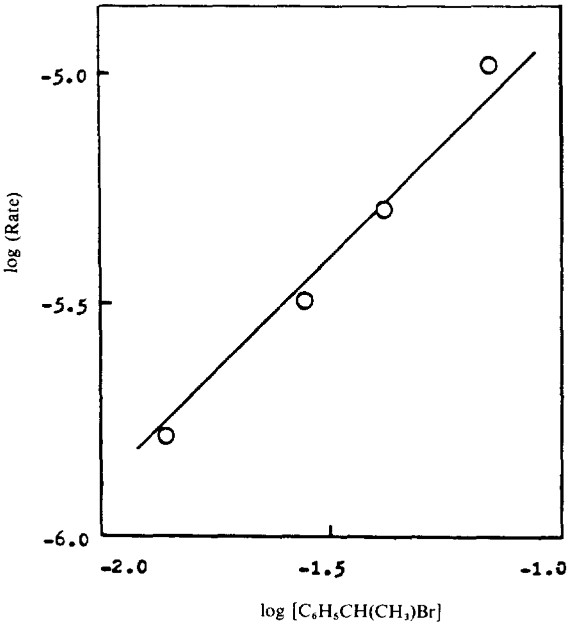


Figure 1. The effect of $C_6H_5CH(CH_3)Br]$ on the rate of bromine-exchange reaction between antimony tribromide and α-phenylethyl bromide in nitrobenzene at 26°C (0.0349 M $SbBr_3$).

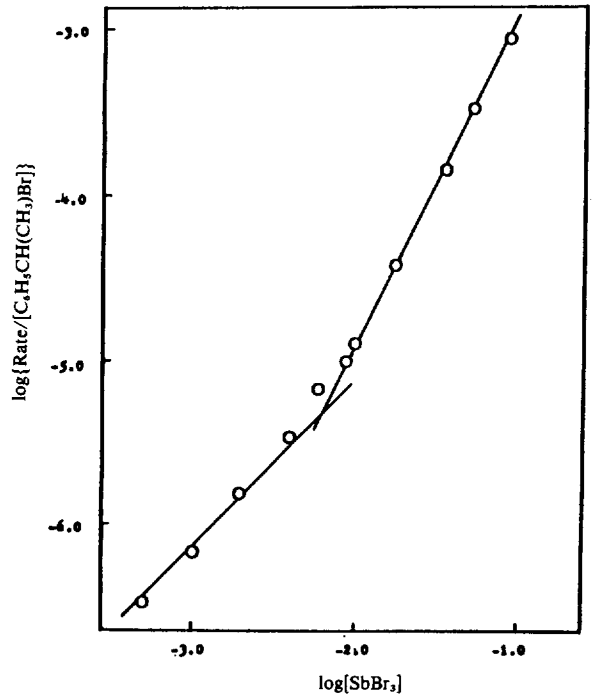


Figure 2. The effect of [SbBr$_3$] on the rate of bromine-exchange reaction between antimony tribromide and α-phenylethyl bromide in nitrobenzene at 28°C (0.0698 M $C_6H_5CH(CH_3)Br$).

TABLE 2: Third-Order Rate Constants of the Bromine-Exchange Reaction between Antimony Tribromide and α-Phenylethyl Bromide in Nitrobenzene

Temp. °C	[SbBr$_3$] × 10^2 mole·l^{-1}	[$C_6H_5CH(CH_3)Br$] × 10^2 mole·l^{-1}	Rate × 10^6 mole·l^{-1}sec^{-1}	k_3 l^2·mole^{-2}sec^{-1}	Av.
26*	3.49	1.40	1.67	0.0979	
26*	3.49	2.79	3.22	0.0948	
26*	3.49	4.19	5.18	0.101	
26*	3.49	6.98	9.38	0.110	0.10
28*	1.77	6.98	2.67	0.122	
28*	3.54	6.98	11.0	0.126	
28*	5.31	6.98	23.8	0.121	
28*	8.85	6.98	63.0	0.115	0.12
34.5	1.11	6.98	2.37	0.276	
34.5	1.66	6.98	4.88	0.254	
34.5	2.77	6.98	12.7	0.237	
34.5	4.43	6.98	30.0	0.219	
34.5	6.64	6.98	68.5	0.223	0.24

*Included in Table 1.

reasonable to conclude that the rate of the exchange reaction could be expressed by the following two equations:

$$\text{Rate} = k_3[\text{SbBr}_3]^2[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}] \qquad (2)$$

(at higher SbBr$_3$ concentrations; 10^{-2} M or greater)

$$\text{Rate} = k_2[\text{SbBr}_3][\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}] \qquad (3)$$

(at lower SbBr$_3$ concentrations; less than 10^{-2} M)

Activation Parameters of the Bromine-Exchange Reaction. In order to calculate the values of various activation parameters of the exchange reaction, it was required to obtain the values of the rate constant at different temperatures. Unfortunately, it was difficult to calculate the exact values of the rate constant because of complexity of the kinetic order 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 [SbBr$_3$]^2 [$C_6H_5CH(CH_3)Br$], assuming the rate equation (2) being correct and using the experimental data obstained at relatively high concentration of SbBr$_3$. The average values of k_3 thus obtained at different temperatures are shown in Table 2.

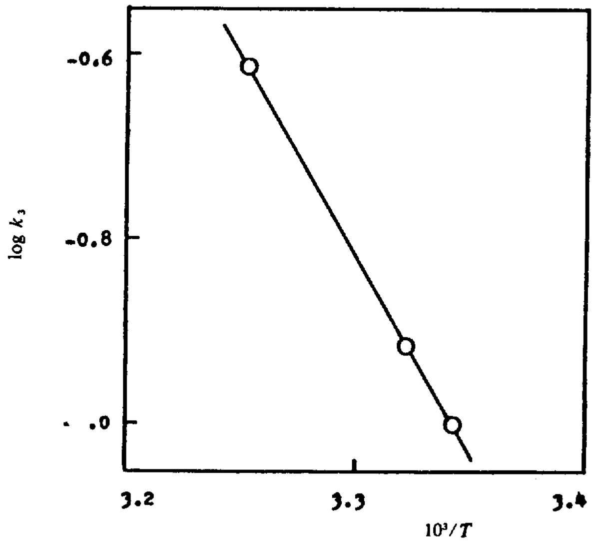


Figure 3. Temperature dependence of log k_3 of the bromineexchange reaction of antimony tribromide with α-phenylethyl bromide in nitrobenzene.

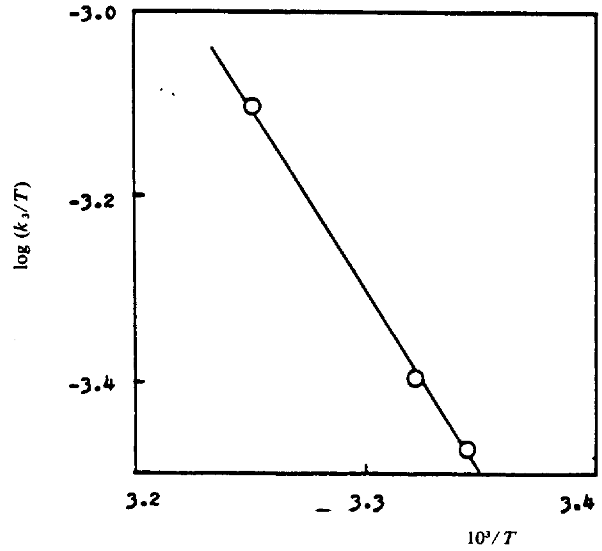


Figure 4. Temperature dependence of log (k_3/T) of the bromine-exchange reaction of antimony tribromide with α-phenylethyl bromide in nitrobenzene.

The values of log k_3 and log (k_3/T) were plotted against $1/T$ (Figures 3 and 4). From the slopes and intercepts of the linear plots, the activation parameters of the exchange reaction, such as activation energy E_a, frequency factor A, enthalpy of activation $\Delta H^{\neq}$, and entropy of activation $\Delta S^{\neq}$, were calculated, based on the following equations:

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

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

In these equations k denotes te Boltzmann constant and h the Planck constant. The results of the calculation of the activa-

TABLE 3: Activation Parameters of the Bromine-Exchange Reaction of Antimony Tribromide with α-Phenylethyl Bromide in Nitrobenzene

Item	Value
E_a (kcal·mole^{-1})	19
log A	13
$\Delta H^{\ddagger}$ (kcal·mole^{-1})	19
$\Delta S^{\ddagger}$ (eu)	-1.4

tion parameters are included in Table 3.

Discussion

As a result of the present investigation it is concluded that the bromine-exchange reaction of antimony tribromide with α-phenylethyl bromide in nitrobenzene exhibits simple first-order kinetics with respect to α-phenylethyl bromide. The exchange reaction indicates, however, complicated kinetic order with respect to antimony tribromide. The reaction kinetics with respect to antimony tribromide seem to be second order at relatively high $SbBr_3$ concentrations and first order at lower $SbBr_3$ concentrations.

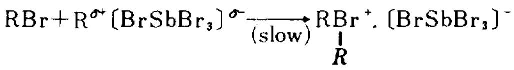
These results are similar to those observed previously on the systems of antimony tribromide with other organic bromides.[7,8] Based on the reaction mechanisms proposed previously[8], we now consider the following two reaction schemes for the bromine-exchange reaction of antimony tribromide with α-phenylethyl bromide.

(a) In the case of relatively high $SbBr_3$ concentration, it is assumed that the carbon-bromine bond in the polarized molecule of the addition compound of antimony tribromide with α-phenylethyl bromide, $R^{\delta+}[BrSbBr_3]^{\delta-}$, is broken with the aid of another molecule of antimony tribromide (solvated).

$$R^{\sigma+}[BrSbBr_3]^{\sigma-} + S:\ SbBr_3 \xrightarrow[\text{(slow)}]{} R^{+}.\ [BrSb_2Br_6]^{-} + S \quad (4)$$

This reaction step (4) is assumed to be the slowest step among various reaction steps of the exchange reaction, which will lead to the kinetic expression (2) written above.

(b) In the case of lower $SbBr_3$ conncentrations, it is assumed that the carbon-bromine bond in the polarized molecule of the addition compounds, $R^{\delta+}[BrSbBr_3]^{\delta-}$, is broken with the aid of another molecule of the organic bromide, to form bromonium ion.


(4)′

$$RBr + R^{\sigma+}[BrSbBr_3]^{\sigma-} \xrightarrow[\text{(slow)}]{} \underset{\substack{| \\ R}}{RBr}^{+}.\ [BrSbBr_3]^{-} \quad (4)'$$

This reaction step (4)′ is assumed to be the slowest step of the exchange reaction, which will explain the kinetic expression (3) written above.

TABLE 4: Summary of Data Obtained for the Bromine-Exchange Reaction between Antimony Tribromide and Organic Bromides in Nitrobenzene

Organic bromide	Kinetic order*	$k_3 \times 10^4$ l^2mole^{-2}sec^{-1}	ref.
$C_6H_5CH_2Br$	3,2	0.21 (29°C)	7
m-$CH_3C_6H_4CH_2Br$	3	0.39 (27°C)	10
o-$CH_3C_6H_4CH_2Br$	3	1.7 (27°C)	10
p-$CH_3C_6H_4CH_2Br$	3,2,1	19 (28°C)	8
$C_6H_5CH(CH_3)Br$	3,2	12×10^2 (28°C)	**

*3: Rate $= k_3[SbBr_3]^2[RBr]$, 2: Rate $= k_2[SbBr_3][RBr]$, 1: Rate $= k_1[RBr]$.
**Present study.

The result of the present study is now compared with the results of previous studies on similar systems with other organic bromides [7,8,10] (Table 4). It can be seen from Table 4 that antimony tribromide exchanges bromine atoms with α-phenylethyl bromide very much faster than with other organic bromides examined. It is speculated that the carbon-bromine bond in the polarized molecule of the addition compound of antimony tribromide with α-phenylethyl bromide can be broken much more easily than the corresponding system with other organic bromides.

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