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Bromine–Exchange Reaction of Antimony Tribromide with Benzyl Bromide in Nitrobenzene and in 1,2,4-Trichlorobenzene*

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The rate of the bromine–exchange reaction of antimony tribromide with benzyl bromide in nitrobenzene or 1,2,4–trichlorobenzene has been measured, using Br–82 labelled antimony tribromide. The result of the study indicates that the exchange reaction is first order with respect to benzyl bromide, and either second or first order with respect to antimony tribromide depending on its concentrations. The second–order kinetics with respect to antimony tribromide have been observed at relatively high (SbBr₃) concentrations, and the first–order kinetics at lower [SbBr₃] concentrations. Reaction mechanisms are proposed for the exchange reaction.
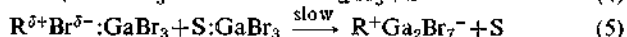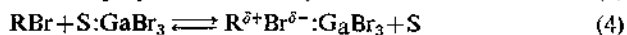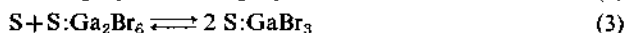
Introduction

In the previous papers of this series, we reported the results of the kinetic studies on the bromine–exchange reactions between gallium bromide and organic bromides in solution.[1-6] The organic bromides used for the kinetic studies were methyl, ethyl, *n*–propyl, *i*–propyl, *n*–butyl and *i*–butyl bromides. Nitrobenzene and 1,2,4–trichlorobenzene were used as solvents.

The results of these studies indicated that all the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides examined.

$$\text{Rate} = k_3 [GaBr_3]^2 [RBr] \tag{1}$$

Reaction mechanism for the exchange reactions was also proposed in the previous papers.

$$S + Ga_2Br_6 \rightleftharpoons S:Ga_2Br_6 \tag{2}$$
$$S + S:Ga_2Br_6 \rightleftharpoons 2\,S:GaBr_3 \tag{3}$$
$$RBr + S:GaBr_3 \rightleftharpoons R^{\delta+}Br^{\delta-}:GaBr_3 + S \tag{4}$$
$$R^{\delta+}Br^{\delta-}:GaBr_3 + S:GaBr_3 \xrightarrow{\text{slow}} R^+Ga_2Br_7^- + S \tag{5}$$
$$S + R^+Ga_2Br_7^- \rightleftharpoons RBr + S:Ga_2Br_6 \tag{6}$$

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. Thus, step (5) was considered to be the rate–determining step of the exchange reactions. This mechanism would lead to the following kinetic expression:

$$\text{Rate} = k [S:GaBr_3]^2 [RBr]$$

Furthermore, it was concluded from the experimental data that the relative rates of alkyl bromides for the bromine-exchange reaction with gallium bromide increased in the following orders:

Methyl<ethyl<n-propyl
n-Butyl<ethyl<n-propyl
n-Propyl<i-propyl
n-Butyl<i-butyl
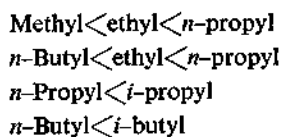
In view of fairly intensive studies on gallium bromide-organic bromide systems, it appeared of interest to extend the studies to the corresponding systems with antimony tribromide. It was observed, however, that antimony tribromide exchanged bromine atoms with organic bromides much more slowly than gallium bromide.[7] It was planned to study the bromine exchange reaction between antimony tribromide and benzyl bromide, because benzyl bromide was thought to be generally more reactive than methyl, ethyl or propyl bromide. Thus, the present study was undertaken on the bromine–exchange reaction between antimony tribromide and benzyl bromide in nitrobenzene or 1,2,4–trichlorobenzene.

Experimental Part

Materials. Nitrobenzene (Extra Pure Grade, Junsei-Kagaku, Japan) and 1,2,4–trichlorobenzene (Extra Pure Grade, Tokyo–Kasei, Japan) were dried with anhydrous magnesium sulfate and fractionated in a 100 cm Todd column packed with glass helices. The middle fraction of the distillate was stored over anhydrous magnesium sulfate until its use. Benzyl bromide was synthesized by the reaction of toluene with bromine and purified by fractionation.[8]

Preparation of Antimony Tribromide Labelled with Br–82. A small quantity (about 30 mg) of solid ammonium bromide was irradiated with neutron (the neutron flux, 10^{13} neutrons/cm^2/sec) for about 24 hours in the nuclear reactor, TRIGA-III, of the Korea Advanced Energy Research Institute, in order to prepare radioactive ammonium bromide, labelled with Br–82. The irradiated solid was mixed with a larger amount (about 1 g) of inactive ammonium bromide. The mixture was dissolved in distilled water (about 30 ml), and carbon tetrachloride (about 20 ml) was added. Then, a small quantity (about 1 ml) of conc. sulfuric acid was added, and $KMnO_4$ solution was dropped into the mixture while stirring. The carbon tetrachloride layer, colored with bromine, was separated and dried with anhydrous magnesium sulfate.

The carbon tetrachloride solution was placed in a 50 ml flask, and metallic antimony powder (about 1 g) was added. The mixture was refluxed for about 30 minutes until the red–brownish solution turned colorless. The crystal of antimony tribromide formed, upon cooling, in the carbon tetrachloride solution was filtered, dried under vacuum, and stored in a desiccator.

Experimental Procedures for Kinetic Study of the Exchange Reaction. A weighed quantity of radioactive antimony tribromide, labelled with Br–82, was dissolved in nitrobenzene or 1,2,4–trichlorobenzene, and diluted to an appropriate volume by adding solvent. Thus, a solution of radioactive

antimony tribromide of known concentration was prepared (Solution A). A solution of benzyl bromide of known concentration was also prepared similarly (Solution B).

Known amounts of solvent were placed in several Erlenmeyer flasks, and appropriate quantities of Solutions A and B were mixed into the solvent. The flasks were kept in an air–bath of constant temperature.

After the flasks were shaked for certain length of time, an alliquot of the reaction mixture (5 ml) was pipetted out from a reaction flask. About 3 ml of 2 M–hydrochloride acid was added and shaked vigorously for about a minute. The aqueous layer was centrifuged out. Hydrochloric acid was added, shaked and centrifuged again. This procedure was repeated about 3 times. A known volume of the organic layer was pipetted out (2 ml), and its radioactivity was counted with a scaler and a NaI scintillation detector (Nuclear Chicago, Model No. 8778, Serial No. 30). The radioactivity thus counted was taken as the activity at time zero, A_0.

After an elapse of time t, the above–mentioned procedure was repeated to count the radioactivity, A_t. From the measured counting rates as a function of time, the rate of the bromine–exchange reaction, R, was determined by the following equation[9]:

$$R = -2.303\left(\frac{3ab}{3a+b}\right)\frac{d}{dt}\log\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) \qquad (7)$$

In this equation a denotes the molar concentration of antimony tribromide, b that of benzyl bromide, and A_∞ the counting rate at the completion of the exchange reaction.

In order to obtain the values of $(A_\infty - A_t)/(A_\infty - A_0)$ in equation(7), the value of A_∞ should be known. The value of A_∞ was calculated by the equation,

$$A_\infty = \frac{b}{3a+b} \times A_{total} \qquad (8)$$

where A_{total} denotes the total radioactivity present in both organic and aqueous layers. The values of log $\{(A_\infty - A_t)/(A_\infty - A_0)\}$ were plotted against t. The slope of the plots was calculated by the least square method. Then the rate of the exchange reaction, R, was calculated by the equation (7).

The values of A_0, A_t and A_∞ mentioned above were corrected for the decay of radioactive bromine during the course of the experimental procedure.

The above–mentioned procedures for the kinetic study were repeated using different reaction mixtures in the other Erlenmeyer flasks.

Results

Bromine–Exchange Reaction of Antimony Tribromide with Benzyl Bromide in Nitrobenzene. The rates of bromine exchange between antimony tribromide and benzyl bromide in nitrobenzene were measured with various concentrations of both antimony tribromide and benzyl bromide. In each run of the experiments, good linearity was observed between log $\{(A_\infty - A_t)/A_\infty - A_0)\}$ and t. An example of the linear plots of log $\{(A_\infty - A_t)/(A_\infty - A_0)\}$ versus time is shown in Figure 1. From the slope of the straight line and the values

of molar concentrations of antimonay tribromide and benzyl bromide, the rate of the bromine exchange was calculated by equation (7). The experimental results are summarized in Tables 1 and 2. Table 1 shows the data obtained at given [SbBr₃] concentrations, and Table 2 the data at given {C₆H₅CH₂Br} concentrations.

In order to determine the kinetic order of the reaction with respect to each reactants, the rate of the exchange-reaction, R, was expressed by the equation,

$$R = k[SbBr_3]^m [C_6H_5CH_2Br]^n.$$

The values of log R obtained at given [SbBr₃] concentration (Table 1) were plotted against log {C₆H₅CH₂Br}. The plots (Figure 2) indicated fairly good linearity between log R and log [C₆H₅CH₂Br]. Since the slope of the straight line in Figure 2 was approximately equal to 1, it was concluded that $n=1$.
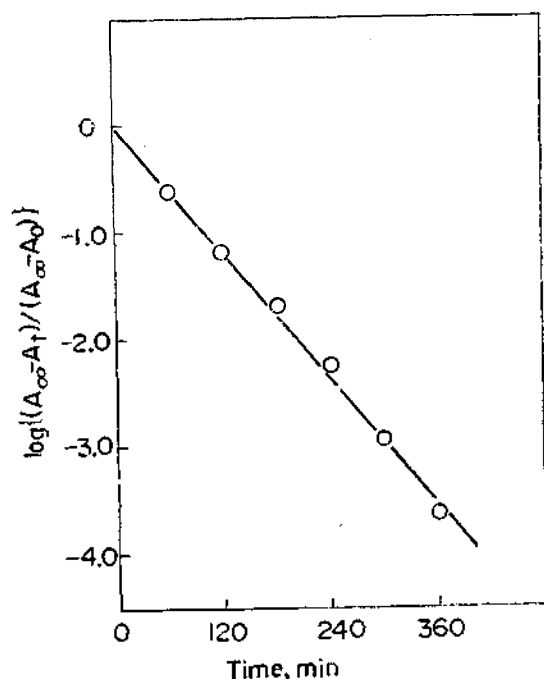

Figure 1. Plots of log $\{(A_\infty - A_t)/(A_\infty - A_0)\}$ versus time for the system of antimony tribromide (0.0833 M) with benzyl bromide (0.101 M) in nitrobenzene at 29 °C.

TABLE 1: Rates of Bromine Exchange between Antimony Tribromide and Benzyl Bromide at Given [SbBr₃] Concentration in Nitrobenzene at 29 °C

[SbBr₃] mole·l^{-1}	{C₆H₅CH₂Br} mole·l^{-1}	Rate×10⁹ mole·$l^{-1}sec^{-1}$
0.0833	0.0405	6.79
0.0833	0.0607	7.58
0.0833	0.0810	9.64
0.0833	0.101	12.1
0.0850	0.0307	4.49
0.0850	0.0767	10.8
0.0850	0.153	16.2
0.0876	0.0956	11.3
0.0876	0.134	15.9
0.0876	0.169	20.9
0.0876	0.210	32.9

TABLE 2: Rates of Bromine Exchange between Antimony Tribromide and Benzyl Bromide at Given (C₆H₅CH₂Br) Concentrations in Nitrobenzene

Temp. °C	[SbBr₃] mole·l^{-1}	[C₆H₅CH₂Br] mole·l^{-1}	Rate×10⁹ mole·$l^{-1}sec^{-1}$	$\dfrac{Rate}{[C_6H_5CH_2Br]} \times 10^8$ sec^{-1}
23	0.0414	0.128	5.00	3.91
	0.0829	0.128	11.0*	8.59
	0.124	0.128	22.5*	17.6
	0.166	0.128	34.5*	27.0
29	0.0544	0.122	11.5	9.43
	0.0816	0.122	18.9*	15.5
	0.109	0.122	25.2*	20.7
	0.136	0.122	48.9*	40.1
36	0.0167	0.128	5.56	4.34
	0.0416	0.128	12.8	10.0
	0.0833	0.128	32.9*	25.7
	0.125	0.128	64.0*	50.0
	0.167	0.128	115*	89.8

*Data used for the estimation of the third-order rate constant, k_3.
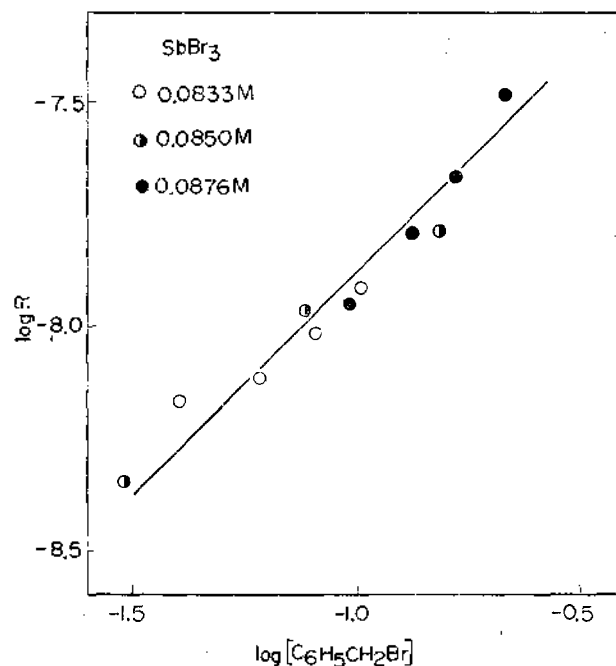
Figure 2. The effect of [C₆H₅CH₂Br] concentration on the rate of bromine exchange between antimony tribromide and benzyl bromide in nitrobenzene at 29 °C.

$$R = k[SbBr_3]^m [C_6H_5CH_2Br]$$

$$R/[C_6H_5CH_2Br] = k[SbBr_3]^m$$

The values of log{$R/$[C₆H₅CH₂Br]} at given [C₆H₅CH₂Br] concentration (Table 2) were plotted against log [SbBr₃]. The plots (Figure 3) did not show a simple, linear relation between log {$R/$[C₆H₅CH₂Br]} and log[SbBr₃]. It would be concluded, however, that the slopes of each lines seemed to indicate that $m=2$ at relatively higher [SbBr₃]concentrations, and in the region of lower [SbBr₃] concentrations the m value seemed to be much smaller than 2, probably being close to 1. Hence, it seemed reasonable to conclude that the rate of the exchange reaction could be expressed by the following two different equations:

$$R = k_3[SbBr_3]^2[C_6H_5CH_2Br] \qquad (9)$$

(at higher [SbBr$_3$] concentrations)

$$R = k_2[SbBr_3][C_6H_5CH_2Br] \qquad (10)$$

(at lower [SbBr$_3$] concentrations)

Bromine-Exchange Reaction of Antimony Tribromide with Benzyl Bomide in 1,2,4-Trichlorobenzene. The rates of bromine exchange between antimony tribromide and benzyl bromide in 1,2,4-trichlorobenzene were also measured with various concentrations of the reactants. The results are summarized in Tables 3 and 4.

The values of log R obtained at given [SbBr$_3$] concentration (Table 3) were plotted against log [C$_6$H$_5$CH$_2$Br]. Again the plots (Figure 4) indicated fairly good linearity between log R and log[C$_6$H$_5$CH$_2$Br], with the slope of approximately 1. Then, the values of log {R/[C$_6$H$_5$CH$_2$Br]} at given [C$_6$H$_5$CH$_2$-Br] concentration (Table 4) were plotted against log[SbBr$_3$]. The shape of the plots was similar to that observed in nitrobenzene solution. It seemed reasonable, therefore, to conclude that the rate of the exchange reaction in 1,2,4-trichlorobenzene could also be expressed by equations (9) and (10).

Activation Parameters of the Exchange Reaction. In order to calculate various activation parameters of the exchange reaction, it was required to obtain the values of the rate constant at different temperatures. Unfortunately, the exact values of the rate constant could not be calculated because of the complexity of the kinetic order with respect to antimony tribromide. But, the approximate values of the third-order rate constant k_3 were estimated under the assumption

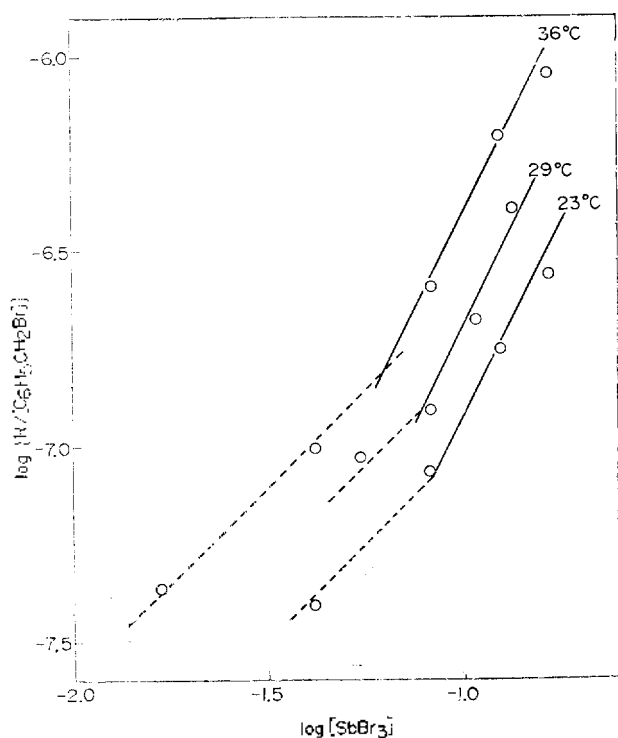**Figure 3.** The effect of [SbBr$_3$] concentration on the rate of bromine exchange between antimony tribromide and benzyl bromide in nitrobenzene at 23° (0.128 M C$_6$H$_5$CH$_2$Br), 29° (0.122 M C$_6$H$_5$CH$_2$Br) and 36° (0.128 M C$_6$H$_5$CH$_2$Br).

TABLE 3: Rates of Bromine Exchange between Antimony Tribromide and Benzyl Bromide at Given [SbBr$_3$] Concentrations in 1,2,4-Trichlorobenzene at 29 °C

[SbBr$_3$] mole·l^{-1}	[C$_6$H$_5$CH$_2$Br] mole·l^{-1}	Rate×10^9 mole·l^{-1}sec^{-1}
0.0631	0.169	22.3
0.0631	0.253	31.5
0.0631	0.338	32.0
0.0631	0.422	57.4

TABLE 4: Rates of Bromine Exchange between Antimony Tribromide and Benzyl Bromide at Given [C$_6$H$_5$CH$_2$Br] Concentrations in 1,2,4-Trichlorobenzene

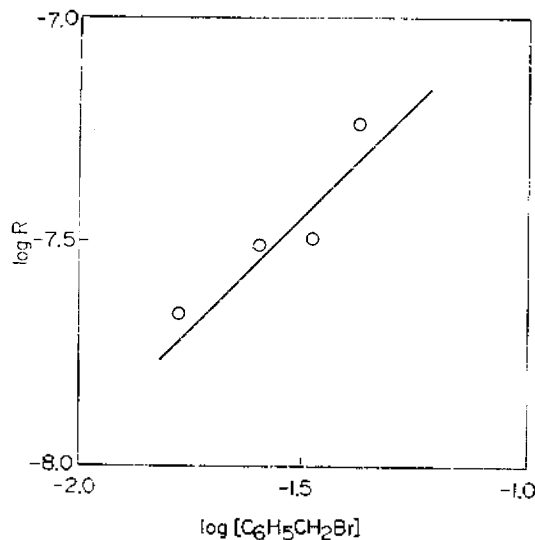| Temp. °C	[SbBr$_3$] mole·l^{-1}	[C$_6$H$_5$CH$_2$Br] mole·l^{-1}	Rate×10^9 mole·l^{-1} sec^{-1}	$\frac{Rate}{[C_6H_5CH_2Br]}$×10^8 sec^{-1}
36	0.0179	0.0779	7.97	10.2
	0.0357	0.0779	13.3	17.1
	0.0714	0.0779	32.5*	41.7
	0.125	0.0779	86.8*	111
	0.179	0.0779	161*	207
29	0.0340	0.0779	3.97*	5.10
	0.0681	0.0779	13.8*	17.7

*Data used for the estimation of the third-order rate constant, k_3.

Figure 4. The effect of [C$_6$H$_5$CH$_2$Br] concentration on the rate of bromine exchange between antimony tribromide and benzyl bromide in 1, 2, 4-trichlorobenzene at 29 °C (0.0631 M SbBr$_3$).

of rate equation (9). The exchange rates indicated by asterisks in Tables 2 and 4 were divided by [SbBr$_3$]^2[C$_6$H$_5$CH$_2$Br] to get approximate values of k_3, because these data seemed to follow the third-order kinetics (9). The average values of k_3 obtained at different temperatures are listed in Table 5.

From the temperature dependence of the rate constant, the activation parameters of the reaction, such as activation energy E_a, frequency factor A, enthalpy of activation ΔH^* and entropy of activation ΔS^*, were estimated with the aid of the following equations:
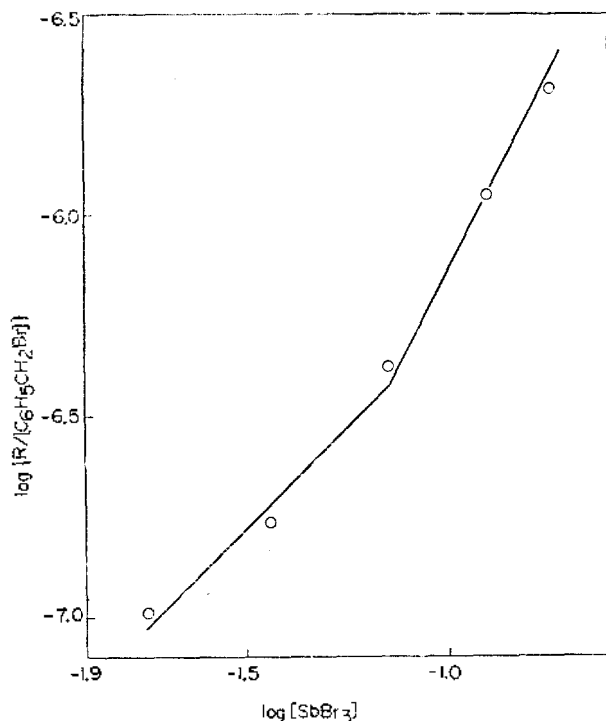
$$k_3 = A \exp(-E_a/RT)$$

Figure 5. The effect of [SbBr₃] concentration on the rate of bromine exchange between antimony tribromide and benzyl bromide in 1,2,4–trichlorobenzene at 36 °C (0.0779 M C₆H₅–CH₂Br).
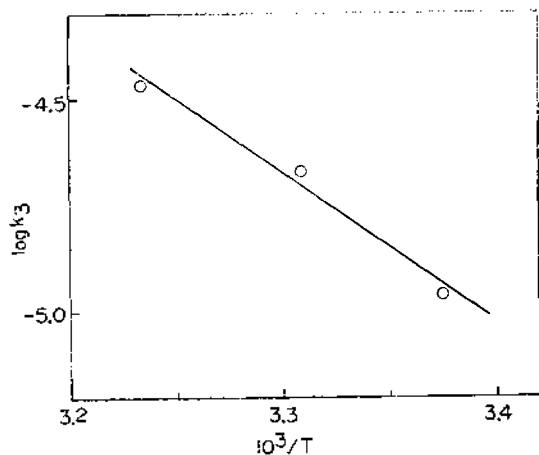

Figure 6. Temperature dependence of log k_3 in nitrobenzene.

TABLE 5: Rate Contants of the Bromine–Exchange Reaction between Antimony Tribromide and Benzyl Bromide

Nitrobenzene		1,2,4–Trichlorobenzene	
Temp. °C	$k_3 \times 10^4$ l^2 mole⁻² sec⁻¹	Temp. °C	$k_3 \times 10^4$ l^2 mole⁻² sec⁻¹
23	0.11		
29	0.21	29	0.41
36	0.34	36	0.72

$$k_3 = \frac{kT}{h} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

In these equations k denotes the Boltzmann constant and h the Planck constant. The results of the estimation of the activation parameters are shown in Table 6.

TABLE 6: Activation Parameters of the Bromine–Exchange Reaction of Antimony Tribromide with Benzyl Bromide

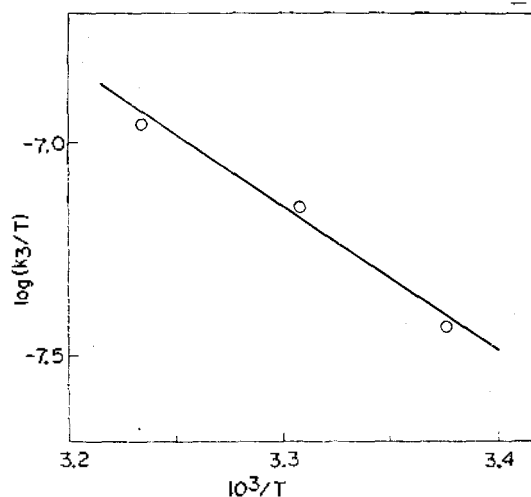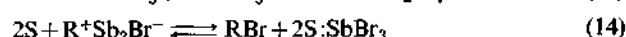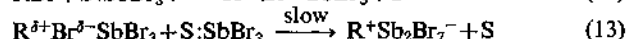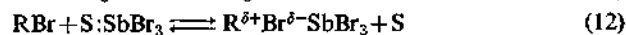|	In nitrobenzene	In 1,2,4–trichlorobenzene
E_a(kcal/mole)	16	16
log A	6.9	7.1
ΔH^* (kcal/mole)	16	15
ΔS^* (eu)	−29	−28

Figure 7. Temperature dependence of log (k_3/T) in nitrobenzene.

Discussion

As the result of the present study it is concluded that the reaction of bromine exchange between antimony tribromide and benzyl bromide in nitrobenzene or 1,2,4–trichlorobenzene solution follows the first–order kinetics with respect to benzyl bromide. The exchange reaction indicates, however, a little more complicated reaction order with respect to antimony tribromide. The reaction kinetics with respect to antimony tribromide seem to follow the second order at relatively higher [SbBr₃] concentrations and the first order at lower [SbBr₃] concentrations.
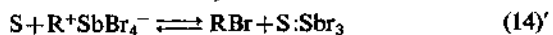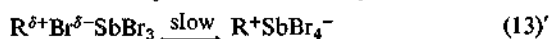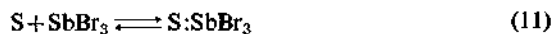
The second–order kinetics with respect to antimony tribromide, expressed by equation (9), seems to be similar to what was observed previously on the systems of gallium bromide with alkyl bromides.[1–6] Hence, this reaction kinetics might be explained by a reaction mechanism similar to the bromine exchange between gallium bromide and alkyl bromides in solution. The following reaction schemes are assumed (S denotes solvent molecules and RBr benzyl bromide):

$$S + SbBr_3 \rightleftharpoons S:SbBr_3 \tag{11}$$
$$RBr + S:SbBr_3 \rightleftharpoons R^{\delta+}Br^{\delta-}SbBr_3 + S \tag{12}$$
$$R^{\delta+}Br^{\delta-}SbBr_3 + S:SbBr_3 \xrightarrow{slow} R^+Sb_2Br_7^- + S \tag{13}$$
$$2S + R^+Sb_2Br_7^- \rightleftharpoons RBr + 2S:SbBr_3 \tag{14}$$

In this reaction scheme, the breaking of the carbon–bromine bond (step 13) in the polarized molecules of the addition compund of antimony tribromide with benzyl bromide is assumed to be the slowest step among various reaction steps. This reaction mechanism would lead to the kinetic expression,

$$R=k[\text{S:SbBr}_3]^2[\text{RBr}] \qquad (15)$$

The first order kinetics with respect to antimony tribromide in the region of lower [SbBr₃] concentration could not be well explained by this reaction mechanism. Hence, a different mechanism has to be considered in this case. The following reaction schemes are assumed to occur in the region of lower [SbBr₃] concentrations:

$$\text{S}+\text{SbBr}_3 \rightleftharpoons \text{S:SbBr}_3 \qquad (11)$$

$$\text{RBr}+\text{S:SbBr}_3 \rightleftharpoons \text{R}^{\delta+}\text{Br}^{\delta-}\text{SbBr}_3+\text{S} \qquad (12)$$

$$\text{R}^{\delta+}\text{Br}^{\delta-}\text{SbBr}_3 \xrightarrow{\text{slow}} \text{R}^+\text{SbBr}_4^- \qquad (13)'$$

$$\text{S}+\text{R}^+\text{SbBr}_4^- \rightleftharpoons \text{RBr}+\text{S:Sbr}_3 \qquad (14)'$$

In this reaction scheme, the breaking of the carbon–bromine bond (step 13′) in the polarized molecules of the addition compound of antimony tribromide with benzyl bromide is also assumed to be the slowest step among other reaction steps. This mechanism would lead to the following kinetic expression:

$$R=k[\text{S:SbBr}_3][\text{RBr}] \qquad (15)'$$

In these two reaction mechanisms, the reaction steps (13) and (13)′ are considered as the rate-determining steps of the exchange reaction. The reason for reaction (13)′ to occur instead of (13) in the region of lower [SbBr₃] concentrations is not clearly known. It is hoped that further investigations should be carried out in order to solve this question.

It has also been assumed that the addition compound of antimony tribromide with benzyl bromide is formed in solution. Although direct evidence has not been obtained for the formation of the addition compound, this has been assumed by the analogy with similar systems of gallium bromide with alkyl bromides in solution.[1-6]

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Effect of Poly(vinyl alcohol) on the Thermally Induced Conformational Change of Poly(D-Glutamic acid)

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In relation to denaturation of proteins, thermally induced conformational change of poly(D–glutamic acid) was studied in the presence of poly(vinyl alcohol) at low pH, where poly (D–glutamic acid) undergoes a helix–to–β transition without any other polymer. In a dilute solution, poly(vinyl alcohol) enhanced the α–to–β_1 transition of poly(D–glutamic acid) due to intermolecular interaction between the two polymers. On the other hand, this conformational change was interrupted to a large extent in a concentrated solution, due to the interpenetration of poly(vinyl alcohol) chain into poly(D–glutamic acid) chain which prevented the intramolecular association of poly(D–glutamic acid) chain. A conformational change from β_1 to β_2 of poly(D–glutamic acid) was observed for the films obtained by casting during annealing the mixture solutions. The β_2 content in the cast film increased with increasing poly(vinyl alcohol) content in the mixture.

Interoduction

In the previous paper[1], we reported the interaction between PGA and PVA as a model for polypeptide/polysaccharide complex formed in biological systems. It was found that the interaction due to hydrogen bonding and the mutual in-