

Substitution of approximate values, $k \cong 0.8$ hartrees,¹² $\Delta\epsilon \cong 0.06$ hartrees,¹³ $s \cong 0.089$ (for *trans* overlap)¹² and $s \cong 0.072$

(for *cis* overlap),¹² into $\frac{2x}{\Delta\epsilon} = 2\left(\frac{ks}{\Delta\epsilon}\right)^2$ indicates that

$1 < \frac{2x}{\Delta\epsilon}$ and $\epsilon_{av} - \epsilon_0$ is always negative. However $\frac{2x}{\Delta\epsilon}$ is

approximately 2.82 for *trans* while it is 1.84 for *cis* reducing the magnitude of $\epsilon_{av} - \epsilon_0$ for the *cis* to approximately 2/3 of that for the *trans*.

The average, ϵ_{av} , is always lower than the basis level ϵ_0 in eq. (18), irrespective of whether the N is odd or even. Moreover according to eq. (18), through-space dominated (destabilizing) interaction is not possible. This absurdity is of course a result of the approximation that $x \cong y$.

Photoelectron spectroscopic data^{1e} included in Table 3 are in full accord with our predictions: (i) the nitrogen atoms in 1,6-diazabicyclo [4.4.4] tetradecane must be inwardly pyramidalized increasing the direct overlap so that the interaction is through-space dominated and is destabilizing, $\epsilon_{av} > \epsilon_0$, (ii) interactions in the other two diazabicyclo compounds are through-bonds dominated and are stabilizing, $\epsilon_{av} < \epsilon_0$, (iii) energy splitting, ΔE , for $N = \text{odd}$ (DA BCO) is larger than that for $N = \text{even}$ [1,5-diazabicyclo (3.3.3) undecane] even allowing for the increase in N by 1.

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Kinetic Study on Bromine-Exchange Reaction of Antimony Tribromide with *t*-Butyl Bromide in Nitrobenzene and in 1,2,4-Trichlorobenzene*

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The kinetic study on the bromine-exchange reaction of antimony tribromide with *t*-butyl bromide in nitrobenzene or 1,2,4-trichlorobenzene has been carried out, using Br-82 labelled antimony tribromide. The results show that the exchange reaction is first order with respect to *t*-butyl bromide and 1.5th order with respect to antimony tribromide. It is assumed that the 1.5th order indicates the coexistence of first- and second-order kinetics. Reaction mechanisms for the exchange reaction are proposed.

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Introduction

We have recently investigated the kinetic study on the bromine-exchange reaction between antimony tribromide and benzyl bromide in nitrobenzene or 1,2,4-trichlorobenzene, using Br-82 labelled antimony tribromide.¹ The result of the study indicated that the rate of the exchange reaction was first order with respect to benzyl bromide, and was either second or first order with respect to antimony tribromide depending on its concentrations.

$$\text{Rate} = k_3 [\text{C}_6\text{H}_5\text{CH}_2\text{Br}] [\text{SbBr}_3]^2$$

(at higher $[\text{SbBr}_3]$ concentrations) (1)

$$\text{Rate} = k_2 [\text{C}_6\text{H}_5\text{CH}_2\text{Br}] [\text{SbBr}_3]$$

(at lower $[\text{SbBr}_3]$ concentrations) (2)

These two rate expressions were interpreted by two different reaction mechanisms.

On the other hand, as the results of similar studies on the systems of gallium bromide with alkyl bromides, we reported that the bromine-exchange reactions of gallium bromide with alkyl bromides followed simpler kinetics, *i.e.*, first order with respect to the organic bromides and second order with respect to gallium bromide.²⁻⁷

$$\text{Rate} = k_3 [\text{RBr}] [\text{GaBr}_3]^2 \quad (3)$$

These two systems with different metal bromides and different organic bromides indicated fairly large difference in reaction kinetics of the bromine-exchange reactions. It appeared of interest to try to clarify whether the difference in kinetics was ascribed to the properties of different metal bromides or those of organic bromides. It was hoped to extend the exchange studies to the system of antimony tribromide with simpler alkyl bromides such as methyl and ethyl bromides. It has been observed that antimony tribromide exchanges bromine atoms with alkyl bromides much more slowly than gallium bromide.⁸ Thus, t -butyl bromide was chosen as alkyl bromide in this experiment because t -butyl bromide was thought to be generally more reactive than methyl and ethyl bromides. The present study was undertaken on the system of antimony tribromide with t -butyl bromide in nitrobenzene or 1,2,4-trichlorobenzene.

Experimental Part

Materials. The solvents used in the present study were purified by the method described in the previous paper.¹

Radioactive antimony tribromide labelled with Br-82 was prepared by the method reported previously,¹ using radioactive ammonium bromide produced in the nuclear reactor, TRIGA-III, the Korea Advanced Energy Research Institute.

A small quantity of red phosphorus was added to carbon tetrachloride, to which liquid bromine was added slowly while stirring. Phosphorus tribromide formed by the reaction of red phosphorus with bromine was distilled from the reaction mixture. Then, t -butyl alcohol was added to phos-

phorus tribromide drop by drop. Thus, t -butyl bromide was synthesized, and it was purified by fractionation.

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.¹ The rate of the exchange reaction was calculated by the following equation⁹:

$$\text{Rate} = -2.303 \left(\frac{3ab}{3a+b} \right) \frac{d}{dt} \log \left(\frac{A_\infty - A_t}{A_\infty - A_0} \right) \quad (4)$$

In this equation a denotes the molar concentration of antimony tribromide, b that of t -butyl 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 reactions, respectively.

The values of A_∞ were obtained by the following equation:

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

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 (4).

Results

Bromine-Exchange Reaction of Antimony Tribromide with t -Butyl Bromide in Nitrobenzene. The rates of bromine exchange between antimony tribromide and t -butyl bromide in nitrobenzene were measured with various concentrations of both antimony tribromide and t -butyl 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 molar concentrations of antimony tribromide and t -butyl bromide, the exchange rate was calculated by equation (4). The results are summarized in Tables 1 and 2. Table 1 shows the data obtained at given $[\text{SbBr}_3]$ concentration, and Table 2 the data at given $[t\text{-C}_4\text{H}_9\text{Br}]$ concentration.

The rate of the exchange reaction was expressed by the

TABLE 1: Rates of Exchange of Bromine between Antimony Tribromide and t -Butyl Bromide at Given $[\text{SbBr}_3]$ Concentration in Nitrobenzene.

Temp. °C	$[\text{SbBr}_3] \times 10^2$ mole · l ⁻¹	$[t\text{-C}_4\text{H}_9\text{Br}] \times 10^2$ mole · l ⁻¹	Rate × 10 ⁷ mole · l ⁻¹ · sec ⁻¹
32	1.51	0.267	1.55*
32	1.51	0.534	2.30*
32	1.51	1.07	5.90*
32	1.51	2.14	8.74*
32	1.51	3.92	14.6*
26	0.587	0.261	0.0780*
26	0.587	0.521	0.262*

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

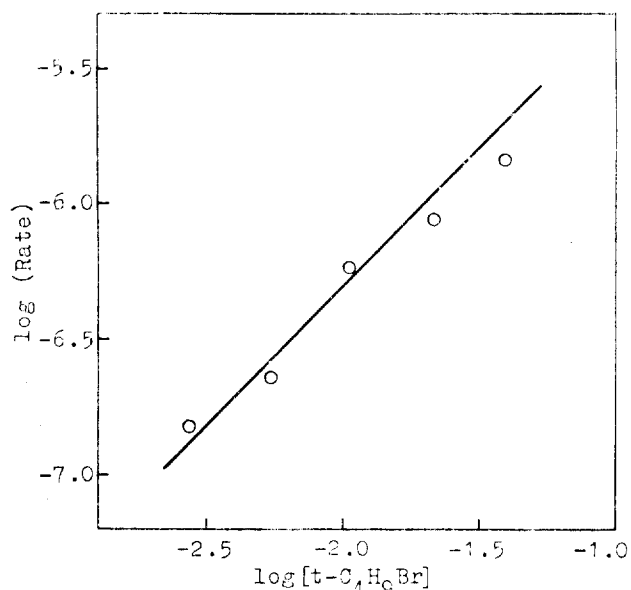


Figure 1. The effect of $[t\text{-C}_4\text{H}_9\text{Br}]$ concentration on the rate of exchange of bromine between antimony tribromide and t -butyl bromide in nitrobenzene at 32°C ($0.0151M\text{-SbBr}_3$).

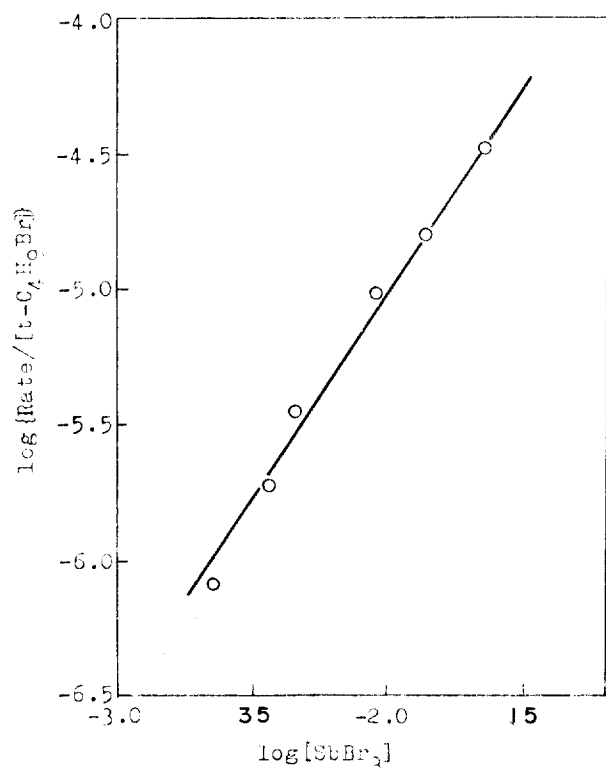


Figure 2. The effect of $[\text{SbBr}_3]$ concentration on the rate of exchange of bromine between antimony tribromide and t -butyl bromide in nitrobenzene at 23°C ($0.0178 M t\text{-C}_4\text{H}_9\text{Br}$)

following equation:

$$\text{Rate} = k[\text{SbBr}_3]^m [t\text{-C}_4\text{H}_9\text{Br}]^n$$

In order to estimate the value of n , the $\log(\text{Rate})$ values obtained at given $[\text{SbBr}_3]$ concentration (Table 1) were plotted against $\log [t\text{-C}_4\text{H}_9\text{Br}]$. The plots showed fairly good linearity between $\log(\text{Rate})$ and $\log [t\text{-C}_4\text{H}_9\text{Br}]$, as shown in Figure 1. Since the slope of the straight line was approximately equal to 1, it was concluded that $n=1$.

$$\text{Rate} = k[\text{SbBr}_3]^m [t\text{-C}_4\text{H}_9\text{Br}]$$

TABLE 2: Rates of Exchange of Bromine between Antimony Tribromide and t -Butyl Bromide at Given $[t\text{-C}_4\text{H}_9\text{Br}]$ Concentration in Nitrobenzene at 23°C

$[\text{SbBr}_3] \times 10^2$ mole·l ⁻¹	$[t\text{-C}_4\text{H}_9\text{Br}] \times 10^2$ mole·l ⁻¹	Rate $\times 10^7$ mole·l ⁻¹ ·sec ⁻¹	$\frac{\text{Rate}}{[t\text{-C}_4\text{H}_9\text{Br}]} \times 10^5$ sec ⁻¹
0.225	1.78	0.147	0.0826
0.338	1.78	0.342	0.192
0.450	1.78	0.633	0.356
0.901	1.78	1.70*	0.955
1.35	1.78	2.87*	1.61
2.25	1.78	5.97*	3.35

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

TABLE 3: Rates of Exchange of Bromine between Antimony Tribromide and t -Butyl Bromide at Given $[\text{SbBr}_3]$ Concentration in 1,2,4-Trichlorobenzene

Temp. °C	$[\text{SbBr}_3] \times 10^2$ mole·l ⁻¹	$[t\text{-C}_4\text{H}_9\text{Br}] \times 10^2$ mole·l ⁻¹	Rate $\times 10^9$ mole·l ⁻¹ ·sec ⁻¹
23	1.72	0.267	2.99*
23	1.72	0.534	6.48*
23	1.72	1.07	11.7*
23	1.72	2.14	21.5*
23	1.72	3.92	34.6*
36	1.52	0.403	6.61*
36	1.52	0.805	12.6*
36	1.52	3.23	53.8*

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

TABLE 4: Rates of Exchange of Bromine between Antimony Tribromide and t -Butyl Bromide at Given $[t\text{-C}_4\text{H}_9\text{Br}]$ Concentration in 1,2,4-Trichlorobenzene at 32°C

$[\text{SbBr}_3] \times 10^2$ mole·l ⁻¹	$[t\text{-C}_4\text{H}_9\text{Br}] \times 10^2$ mole·l ⁻¹	Rate $\times 10^9$ mole·l ⁻¹ ·sec ⁻¹	$\frac{\text{Rate}}{[t\text{-C}_4\text{H}_9\text{Br}]} \times 10^7$ sec ⁻¹
0.415	1.61	3.20	1.99
0.832	1.61	8.07*	5.01
1.66	1.61	22.0*	13.7
3.33	1.61	64.4*	40.0

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

$$\therefore \text{Rate}/[t\text{-C}_4\text{H}_9\text{Br}] = k[\text{SbBr}_3]^m$$

In order to estimate the value of m , the values of $\log \{\text{Rate}/[t\text{-C}_4\text{H}_9\text{Br}]\}$ at given $[t\text{-C}_4\text{H}_9\text{Br}]$ concentration (Table 2) were plotted against $\log [\text{SbBr}_3]$. The plots (Figure 2) indicated good linearity with the slope of approximately 1.5. Hence, it was concluded that the rate of the exchange reaction could be expressed by the following reaction kinetics:

$$\text{Rate} = k[\text{SbBr}_3]^{1.5} [t\text{-C}_4\text{H}_9\text{Br}] \quad (5)$$

Bromine-Exchange Reaction of Antimony Tribromide with t-Butyl Bromide in 1,2,4-Trichlorobenzene. The rates of exchange of bromine between antimony tribromide and t -butyl 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 $\log(\text{Rate})$ obtained at given $[\text{SbBr}_3]$ concentration (Table 3) were plotted against $\log [t\text{-C}_4\text{H}_9\text{Br}]$. The plots, as shown in Figure 3, indicated fairly good linearity

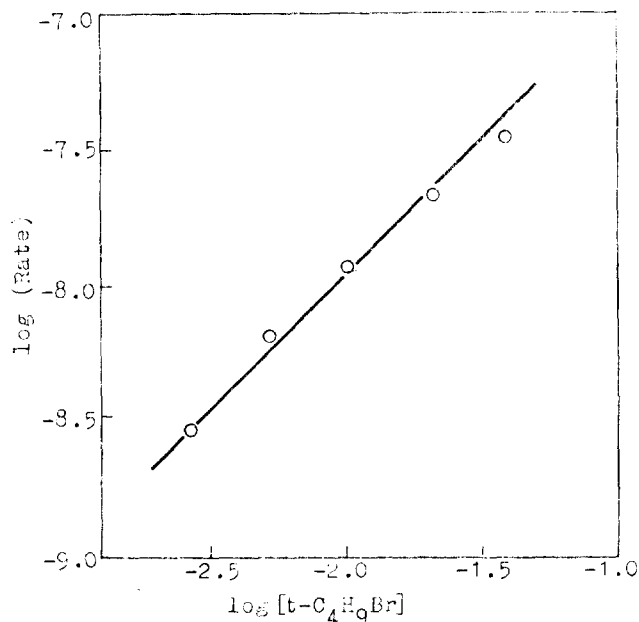


Figure 3. The effect of $[t\text{-C}_4\text{H}_9\text{Br}]$ concentration on the rate of exchange of bromine between antimony tribromide and t -butyl bromide in 1,2,4-trichlorobenzene at 23°C (0.0172 M SbBr_3).

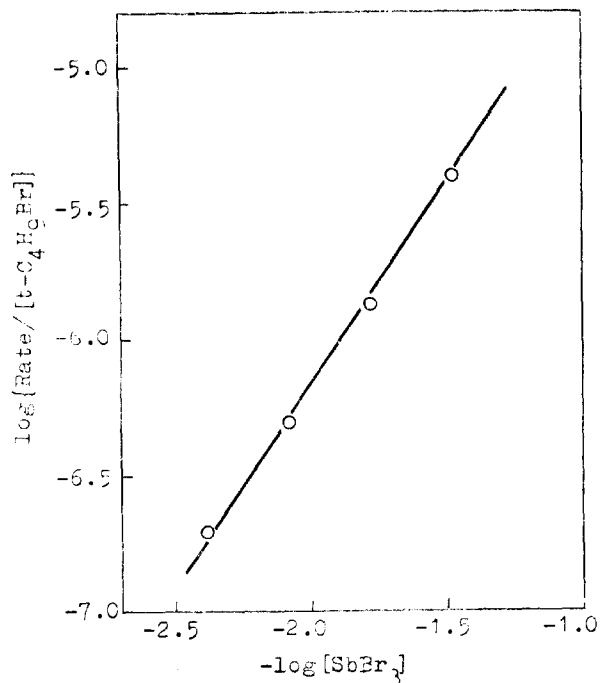


Figure 4. The effect of $[\text{SbBr}_3]$ concentration on the rate of exchange of bromine between antimony tribromide and t -butyl bromide in 1,2,4-trichlorobenzene at 32°C (0.0161 M $t\text{-C}_4\text{H}_9\text{Br}$).

between $\log (\text{Rate})$ and $\log [t\text{-C}_4\text{H}_9\text{Br}]$, with the slope of approximately 1. Then, the values of $\log \{\text{Rate}/[t\text{-C}_4\text{H}_9\text{Br}]\}$ at given $[t\text{-C}_4\text{H}_9\text{Br}]$ concentration (Table 4) were plotted against $\log [\text{SbBr}_3]$. Again, the plots (Figure 4) showed a straight line with the slope of approximately 1.5. It seems reasonable, therefore, to conclude that the rate of the exchange reaction in 1,2,4-trichlorobenzene could also be expressed by equation (5).

It was hoped to obtain the values of various activation parameters of the exchange reaction. In order to do so, it was required to calculate the rate constants at different temperatures. The present study indicated an unusual kinetic order, 1.5th order, with respect to antimony tribromide. The values of 2.5th-order rate constant ($k_{2.5}$) could be formally obtained from the data of the present study. But it was tried to calculate third-order rate constant (k_3) by dividing the observed exchange rate by $[\text{SbBr}_3]^2[t\text{-C}_4\text{H}_9\text{Br}]$, assuming that the data obtained at comparatively higher $[\text{SbBr}_3]$ concentrations, shown by asterisks in Table 1-4, might fit the following equation:

$$\text{Rate} = k_3[\text{SbBr}_3]^2[t\text{-C}_4\text{H}_9\text{Br}]$$

The average values of k_3 thus obtained at different temperatures are listed in Table 5.

From the temperature dependence of the rate constant k_3 , the activation parameters of the exchange reaction, such as activation energy E_a , frequency factor A , enthalpy of activation ΔH^\ddagger , and entropy of activation ΔS^\ddagger , were calculated using the following equations:

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

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

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

Discussion

As a result of the present investigation it is concluded that the bromine-exchange reaction of antimony tribromide with t -butyl bromide in nitrobenzene or 1,2,4-trichlorobenzene exhibits first-order kinetics with respect to t -butyl bromide and 1.5th order with respect to antimony tribromide.

The 1.5th order may be interpreted as the mixture of both first-order and second-order kinetics. Thus, it is proposed that the bromine-exchange reaction between antimony tribromide and t -butyl bromide may proceed through two different reaction mechanisms which lead to the first-order and second-order rate expressions with respect to antimony tribromide.

Previously, we have observed in the similar study on the antimony tribromide-benzyl bromide system that the bromine-exchange reaction follows either second-order or first-order kinetics with respect to antimony tribromide depending on its concentration.¹

$$\begin{aligned} \text{Rate} &= k_3[\text{SbBr}_3]^2[\text{RBr}] \\ &\text{(at higher } [\text{SbBr}_3] \text{ concentration)} \\ \text{Rate} &= k_2[\text{SbBr}_3][\text{RBr}] \end{aligned} \quad (6)$$

TABLE 5: Third-Order Rate Constants of the Bromine-Exchange Reaction between Antimony Tribromide and t -Butyl Bromide.

Nitrobenzene		1,2,4-Trichlorobenzene	
Temp. $^\circ\text{C}$	$k_3 \times 10^2$ $1^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$	Temp. $^\circ\text{C}$	$k_3 \times 10^3$ $1^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$
23	9.1	23	3.6
26	12	32	5.3
32	21	36	7.0

TABLE 6: Summary of Data Obtained for the Bromine-Exchange Reactions between Metal Bromides and Organic Bromides

Solvent	Metal Bromide	RBr	Kinetics (order)	k_3 $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$	E_a $\text{kcal} \cdot \text{mole}^{-1}$	$\log A$	ΔH^\ddagger $\text{kcal} \cdot \text{mole}^{-1}$	ΔS^\ddagger eu	Ref.
$\text{C}_6\text{H}_5\text{NO}_2$	GaBr ₃	<i>n</i> -C ₄ H ₉ Br	3rd	$4.2 \times 10^{-4}(19^\circ\text{C})$	6.8	1.7	8.7	-44	5
$\text{C}_6\text{H}_5\text{NO}_2$	GaBr ₃	<i>i</i> -C ₄ H ₉ Br	3rd	$9.3 \times 10^{-3}(19^\circ\text{C})$	6.1	2.5	5.5	-49	7
$\text{C}_5\text{H}_6\text{NO}_2$	SbBr ₃	C ₆ H ₅ CH ₂ Br	3rd & 2nd	$0.21 \times 10^{-4}(29^\circ\text{C})$	16	6.7	15	-30	1
$\text{C}_6\text{H}_5\text{NO}_2$	SbBr ₃	<i>t</i> -C ₄ H ₉ Br	2.5th	$9.1 \times 10^{-2}(23^\circ\text{C})$	17	11	16	-8.5	*
$\text{C}_6\text{H}_3\text{Cl}_3$	GaBr ₃	<i>n</i> -C ₄ H ₉ Br	3rd	$1.2 \times 10^{-4}(19^\circ\text{C})$	9.0	2.8	11	-40	5
$\text{C}_6\text{H}_3\text{Cl}_3$	GaBr ₃	<i>i</i> -C ₄ H ₉ Br	3rd	$3.3 \times 10^{-2}(19^\circ\text{C})$	7.0	3.8	6.4	-43	7
$\text{C}_6\text{H}_3\text{Cl}_3$	SbBr ₃	C ₆ H ₅ CH ₂ Br	3rd & 2nd	$0.41 \times 10^{-4}(29^\circ\text{C})$	15	6.7	15	-30	1
$\text{C}_6\text{H}_3\text{Cl}_3$	SbBr ₃	<i>t</i> -C ₄ H ₉ Br	2.5th	$3.6 \times 10^{-3}(23^\circ\text{C})$	9	4.4	8.3	-42	*

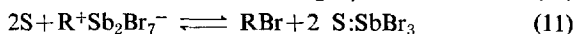
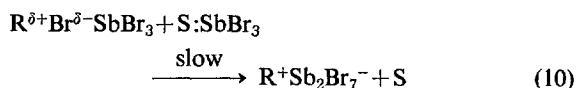
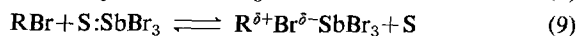
*The present study.

(at lower [SbBr₃] concentration) (7)

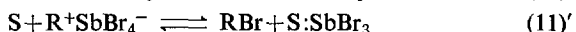
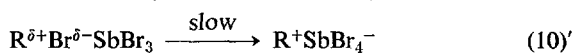
In equations (6) and (7) RBr denotes the organic bromide examined.

We have proposed the following two reaction mechanisms for these two different kinetic dependences¹ (S denotes the solvent molecules):

(a) Second-order kinetics with respect to antimony tribromide



(b) First-order kinetics with respect to antimony tribromide



In these two reaction schemes, the reactions (10) and (10)' are assumed to be the slowest steps among the other reaction steps involved. In other words, the breaking of the carbon-bromine bond in the polarized molecules of the addition compounds of antimony tribromide with the organic bromide is assumed to be the rate-determining step of the exchange reaction. These two reaction mechanisms (a) and (b) would lead to the following kinetic expressions:

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

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

In order to rationalize the result of the present study, it is assumed that the bromine-exchange reaction of antimony tribromide with *t*-butyl bromide proceed through the above-mentioned reaction mechanisms (a) and (b) simultaneously.

$$\text{Rate} = k_3[\text{SbBr}_3]^2[\textit{t}\text{-C}_4\text{H}_9\text{Br}] \quad (12)$$

$$\text{Rate} = k_2[\text{SbBr}_3][\textit{t}\text{-C}_4\text{H}_9\text{Br}] \quad (13)$$

The result of the present study is now compared with the

results of previous studies on similar systems with other metal bromides and other organic bromides^{1,5,7} (Table 6). It can be seen from Table 6 that antimony tribromide exchanges bromine atoms with *t*-butyl bromide faster than with benzyl bromide in the two solvents examined. It is speculated, therefore, that the carbon-bromine bond in the addition compound of antimony tribromide with *t*-butyl bromide can be broken more easily than the corresponding system with benzyl bromide.

It is also seen from Table 6 that the rate of the bromine-exchange reaction is not greater in nitrobenzene than in 1,2,4-trichlorobenzene in most systems examined, but is much greater in nitrobenzene than in 1,2,4-trichlorobenzene in the *t*-butyl bromide-antimony tribromide system. The scarcity of the information makes it difficult to interpret the aforementioned observations at present stage. And it seems to require further studies to draw the definite conclusion.

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