Kinetics of the Bromine-exchange Reaction of Antimony(III) Bromide with Organic Bromide in the Organic Solvents.

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⟨Abstract⟩

The rate of the bromine-exchange reaction between antimony(III) bromide and isopropyl bromide in nitrobenzene and in 1,2,4-trichlorobenzene has been determined, utilizing antimony(III) bromide labeled with radioactive bromine. The results indicate that the exchange reaction between antimony(III) bromide and isopropyl bromide is 1.4th order with respect to antimony(III) bromide and zero order with respect to isopropyl bromide in each of the two solvents. The reaction rate constants of these reaction determined at 22° are $3.3 \times 10^{-4}(l/\text{mole})^{0.4}\text{sec}^{-1}$ in nitrobenzene and $4.1 \times 10^{-4}(l/\text{mole})^{0.4}\text{sec}^{-1}$ in 1,2,4-trichlorobenzene.

The activation energy, the enthalphy of activation, and the entropy of activation for the exchange reaction have been determined. It has also been observed that antimony(III) bromide exchanges bromine slower with isopropyl bromide than tert-butyl bromide and benzyl bromide. A reaction mechanism for the bromine exchange is proposed.

유기용매에서의 삼브롬화 안티몬과 유기브롬화물사이의 브롬교환 반응의 반응속도론적 연구

배 영 일·안 정 수

공 업 화 학 과

⟨요 약⟩

삼브롬화안티몬과 브롬화이소프로필 사이의 브롬 교환반응의 반응속도를 니트로벤젠과 1,2,4-트리클로로 벤젠용매에서 측정하였다.

삼브롬화안티몬과 브롬화이소프로필 사이의 브롬 교환반응의 반응차수는 니트로벤젠 용매 및 1,2,4-트리클로로벤젠용매에서 모두 삼브롬화안티몬에 대해서는 1.4차이었으며 브롬화이소프로필에 대해서는 0차이었다. 이반응의 반응속도상수는 니트로벤젠 용매를 사용하였을 경우 22°C에서 $3.3 \times 10^{-4}(l/\text{mole})^{0.4}\text{sec}^{-1}$이었으며 1,2,4-트리클로로벤젠 용매를 사용하였을 경우 22°C에서 $4.1 \times 10^{-4}(l/\text{mole})^{0.4}\text{sec}^{-1}$이었다.

또 활성화에너지, 한성화엔트로피, 한성화엔탈피, 깁음율과 같은 열역학적 함수를 구하였으며 삼브롬화 안티몬과 유기브롬화물 사이의 브롬 교환반응의 반응메카니즘도 제시하였다.

I. Introduction

Kinetic studies of the bromine-exchange reaction of gallium bromide with some alkyl bromide in nitrobenzene and in 1,2,4-trichlorobenzene solutions were carried out previously.[1,2,3,4] The results indicated that the exchange reaction was second order with respect to gallium bromide and first order with respect

to alkyl bromide in both solvents utilized. The third order rate constants of the reaction between gallium bromide and methyl bromide obtained at 19° in two solvents were 2.4×10^{-5} $(l/mole)^2sec.^{-1}$ and $0.82 \times 10^{-2}(l/mole)^2sec^{-1}$, respectively. And the constant of the reaction between gallium bromide and ethyl bromide determined at 19° is $1.9 \times 10^{-3}(l/mole)^2sec.^{-1}$ in nitrobenzene and $2.8 \times 10^{-2}(l/mole)^2sec.^{-1}$ in 1, 2, 4-trichlorobenzene.

A similiar study was carried out by Sixma, Hendriks, and Holtzapffel on the system of aluminium bromide with ethyl bromide in carbon disulfide[5]. They reported that the bromine-exchange reaction between aluminium bromide and ethyl bromide was also second order with respect to aluminium bromide and first order with respect to ethyl bromide. The third order rate constant obtained at 0.1° was $8.5 \times 10^{-2}(l/mole)^2sec.^{-1}$.

Thus the some groups of authers carried out exchange studies using different metal bromides and different alkyl bromides, and they observed same third-order kinetics for the exchange reactions.

In order to make a comparison, it appeared important to extend to exchange studies to the system of antimony(III) bromide with some alkyl or aryl bromides. Thus the present study on the bromine exchange between antimony(III) bromide and isopropyl bromide in nitrobenzene and 1, 2, 4-trichlorobenzene solutions was undertaken.

II. Experimental Section

1. Materials.

Nitrobenzene (Reagent grade, Wako. Japan) and 1, 2, 4-trichlorobenzene (Reagent grade, Eastman Organic co.,) were dried with Drierite, were fractionated in a 100cm Todd column packed with glass helices, and were stored over Drierite.[2]

2. Preparation of Antimony(III) Bromide (Br⁸²).

Antimony(III) bromide was prepared by the direct combination of metallic antimony with radioactive bromine in the carbon tetrachloride solution. Radioactive bromine was obtained as follows. A small quantity of solid ammonium bromide was irradiated with neutrons to induce (n, γ) reaction of bromine. The irradiated ammonium bromide was mixed with an apropriate amount of inactive ammonium bromide. The mixture was then oxidized to bromine using potassium permanganate as oxdizing agent. [6]

3. Preparation of Isopropyl Bromide.

Isopropyl bromide was prepared by the reaction of isopropyl alcohol with phosphorous tribromide and purified by fractional distillation.

4. Precedures used in the Study of the Exchange Reaction.

A known quantity of labeled antimony(III) bromide and organic bromide were introduced to the volumetric flast and added solvent. The solution was introduced into the reaction vesel. This was taken to be time zero. The reaction material was quenched by water at constant time intervals.

Radicactivity of isopropyl bromide in the organic solvent was measured by scintillation detector. Hence from the measured counting rates as a function of time, the rate of exchange, R, of bromine between antimony bromide and isopropyl bromide in solution was determined by the usual Guggenheim method. [7,8]

$$R = -2.303\left(\frac{3ab}{3a+b}\right)\frac{d}{dt}\log(A_{t+\nu} - A_t) \quad (1)$$

where a denotes the molar concentration of antimony(III) bromide and b denotes that of organic bromide in solution. The term $A_{t+\nu} - A_t$ represents the change in counting rate during a constant time interval, ν, starting at a different time, t, after the reaction started.

Counting rates were ordinarily in the rangs of 10,000—150,000 counts per minute.

Ⅲ. Results

1. Bromine Exchange between Antimony (Ⅲ) Bromide and Isopropyl Bromide in Nitrobenzene.

The rates of bromine exchange between antimony(Ⅲ) bromide and isopropyl bromide in nitrobenzene were measured at 18, 22 and 34°. The results are summarized in Table Ⅰ. In each run good linearity was obtained observed between $\log (A_{t+\nu} - A_t)$ and time. A typical result is shown in Figure 1. From slopes of

Table Ⅰ : Rates of Exchange of Bromine between Antimony(Ⅲ) Bromide and Isopropyl Bromide in Nitrobenzene

Reaction. temp. °C	[SbBr₃] 10^3M	[C₃H₇Br] M	Rate×10^7 (mole/l) sec⁻¹	$10^4 k$ (l/mole)$^{0.4}$ sec.⁻¹
18	0.448	1.94	0.0574	2.8
	1.34	1.94	0.228	2.4
	2.24	1.94	0.490	2.5
	3.13	1.94	0.722	2.3
	4.03	1.94	1.02	2.3
	4.03	2.72	1.20	2.7
	4.03	1.16	1.08	2.4
				av. 2.5
22	6.16	1.94	2.57	3.2
	8.63	1.94	4.26	3.3
	11.1	1.94	6.42	3.5
	6.16	2.72	2.65	3.3
	6.16	3.49	2.73	3.4
	6.16	1.16	2.41	3.0
	6.16	0.39	2.57	3.2
				av. 3.3
34	6.44	1.77	4.71	5.5
	9.01	1.77	7.40	5.4
	11.6	1.77	11.1	5.7
	6.44	1.06	4.62	5.4
	6.44	2.48	4.54	5.3
				av. 5.5

these lines and molar concentration of antimony(Ⅲ) bromide and isopropyl bromide, the rate of the bromine exchange, R, was calculated with the aid of equation 1. The observed values of R are listed in the fourth column of Table Ⅰ.

The exchange reaction rate may also be expressed as

$$R = k [C_3H_7Br]^m [SbBr_3]^n$$

When the values of $\log R$ obtained at given SbBr₃ concentration were plotted against log [C₃H₇Br], good linearity was observed. Since the slope of each line (Fig. 2) was approximately equal to 0, it was concluded that $m=0$. Hence

$$R = k [C_3H_7Br]^0 [SbBr_3]^n$$

When the values of R were plotted against log [SbBr₃] at given [C₃H₇Br], good linearity was again observed. Since the slope of the line (Fig. 3) was approximately equal to 1.4, $n=1.4$ and the following equation was obtained

$$R = k [SbBr]^{1.4} \qquad (2)$$

It is concluded, therefore, that the bromine exchange in nitrobenzene is 1.4th order with respect to antimony(Ⅲ) bromide, and zero order with respect to isopropyl bromide.

The rate constant, k was evaluated by dividing the observed rate of exchange by [SbBr₃]$^{1.4}$. The values of k are listed in the
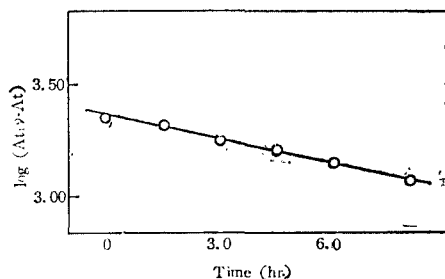

Fig. 1 Plots of $\log (A_{t+\nu} - A_t)$ vs. time for the system of antimony(Ⅲ) bromide (6.44×10⁻³M) with isopropyl bromide (1.77M) in nitrobenzene at 34°C.
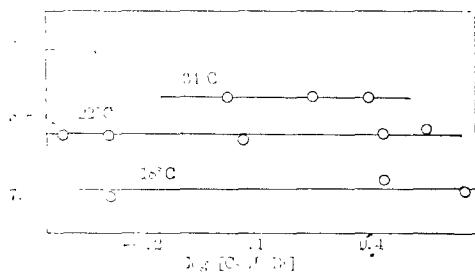
Fig. 2 The effect of concentration of isopropyl bromide on the rate of bromine exchange between isopropyl bromide and antimony(Ⅲ) bromide in nitrobenzene at 18, 22 and 31°C.
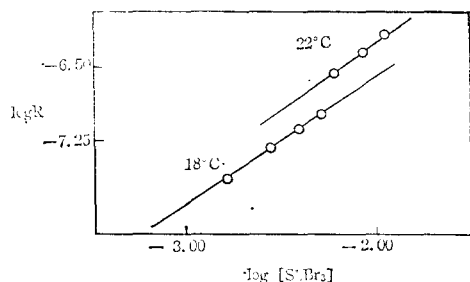

Fig. 3 The effect of concentration of antimony(Ⅲ) bromide on the rate of bromine exchange between isopropyl bromide and antimony(Ⅲ) bromide in nitrobenzene at 18 and 22°C
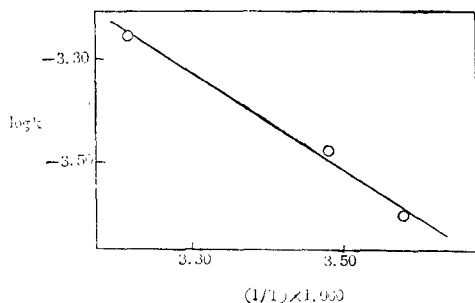

Fig. 4 Temperature dependence of log k of the bromine exchange reaction between isopropyl bromide and antimony(Ⅲ) bromide in nitrobenzene.
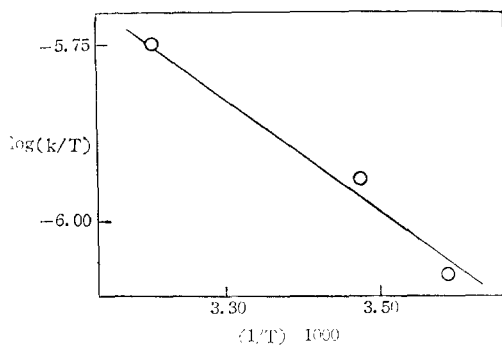

Fig. 5 Temperature dependence of log (k/T) of the bromine exchange reaction between isopropyl bromide and antimony(Ⅲ) bromide in nitrobenzene.

last column of table Ⅰ. The k values show good constancy at each temperature examined.

Good linearity was obtained by plotting the values of log k against the reciprocal of the absolute temperature T(Fig. 4). From the slope and intercept of this line, the activation energy, Ea and the logarithm of the frequency factor, log A of the bromine exchange were calculated to be 8.6 kcal/mole and 2.9 respectively.

In order to obtain other activation parameters of the exchange reaction, such as enthalphy of activation $\mathnormal{\varDelta H^*}$ and entropy of activation $\mathnormal{\varDelta S^*}$, the value of log (k/T) were plotted against the reciprocal of absolute temperature. Good linearity was again observed(Fig. 5). From the slope and intercept of the line, the values of $\mathnormal{\varDelta H^*}$ and $\mathnormal{\varDelta S^*}$ for the exchange reaction were calculated to be 8.0 kcal/mol. and -48 eu respectively.

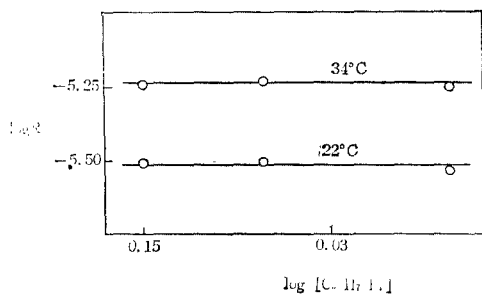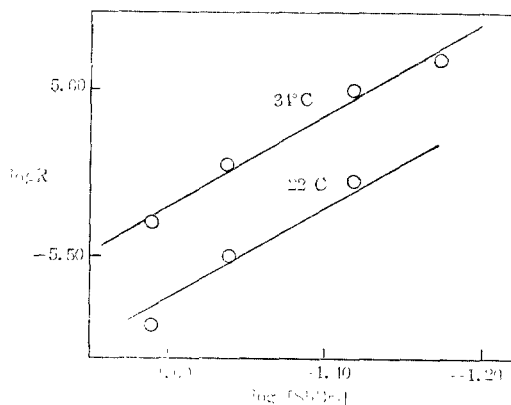## 2. Bromine Exchange between Antimony (Ⅲ) Bromide and Isopropyl Bromide in 1, 2, 4-trichlorobenzene.

The rates of bromine exchange between antimony(Ⅲ) bromide and isopropol bromide in 1, 2, 4-trichlorobenzene were also measured at 22 and 34°C. The results are summarized in Table Ⅱ.

Kinetics of the Bromine-exchange Reaction of Antimony (Ⅲ)
Bromide with Organic Bromide in the Organic Solvents.

5

Table Ⅱ : Rates of Exchange of Bromine between Antimony(Ⅲ) Bromine and Isopropyl Bromide in 1,2,4-trichlorobenzene

Reaction temp °C	[SbBr₃] 10³M	[C₃H₇Br] M	Rate×10⁶ (mole/l) sec⁻¹	10⁴k (l/mole)⁰·¹ sec⁻¹
22	2.432	1.77	4.94	7.3
	3.040	1.77	5.16	7.7
	4.256	1.77	9.03	7.5
	5.472	1.77	13.01	7.6
	3.040	1.42	5.75	7.6
	3.040	2.48	5.64	7.5
				av. 7.6
34	2.432	1.77	2.14	3.9
	3.040	1.77	3.10	4.1
	4.256	1.77	5.18	4.3
	3.040	1.42	3.03	4.1
	3.040	2.48	2.97	4.0
				av. 4.1

Values of log R at given SbBr₃ concentration were plotted against log C₃H₇Br (Fig. 6), and values of log R were plotted against log [SbBr₃] (Fig. 7). Again, good linearity was observed. From the slopes of these lines, the following rate equation was obtained for the exchange reaction in 1,2,4-trichlorobenzene solution

$$R = k [C_3H_7Br]^0 [SbBr_3]^{1.4}$$
$$= k [SbBr_3]^{1.4}$$

Fig. 6 The effect of concentration of isopropyl bromide on the rate of bromine exchange between isopropyl bromide and antimony(Ⅲ) bromide in 1,2,4-trichlorobenzene at 22 and 34°C

Fig. 7 The effect of concentration of antimony(Ⅲ) bromide on the rate of bromine exchange between isopropyl bromide and antimony(Ⅲ) bromide in 1,2,4-trichlorobenzene at 22 and 34°C

The activation parameters for the exchange reaction in 1,2,4-trichlorobenzene solution were also estimated from the temperature dependence of the rate constant, although experimental data were taken only at two different temperatures. From the variation of log k with the reciprocal of absolute temperature, the activation energy and the logarithm of the frequency factor of the exchange reaction were estimated to be 9.5kcal/mol. and 3.7 respectively. From the variation of log (k/T) with the reciprocal of alsolute temperature, the vaues of ΔH^* and ΔS^* for the exchange reaction were estimated to be 8.8 kcal/mole and −44 eu respectively.

Ⅳ. Discussion

The results of the present study are compared with those of the earlier study on the corresponding system with tert-butyl bromide and benzyl bromie(Table Ⅲ). Similiar kinetics were observed earlier on the system of antimony(Ⅲ) bromide-tert. butyl bromide and antimony(Ⅲ) bromide-benzyl bromide. It was discussed that

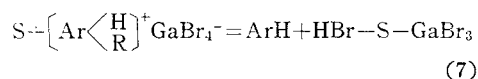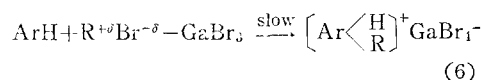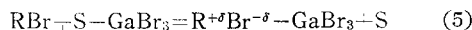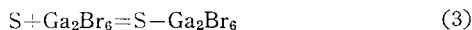**Table. Ⅲ: Summary of Data obtained for the Reactions of Bromine Exchange between Antimony(Ⅲ) bromide and Organic Bromides.**

Reactants	Solvent	Reaction Order		Rate Constant			Ea, kcal/mole	log A	ΔH^*, kcal/mole	ΔS^*, e.u.
		SbBr$_3$	RBr							
SbBr$_3$ C$_6$H$_5$CH$_2$Br	C$_6$H$_5$NO$_2$	1.7	0	1.3×10^{-2} (16°C)	1.7×10^{-2} (26°C)	2.5×10^{-2} (40°C)	4.9	1.8	4.3	−52
SbBr$_3$ C$_6$H$_5$CH$_2$Br	C$_6$H$_3$Cl$_3$	1.7	0	0.71×10^{-2} (19°C)	1.3×10^{-2} (30°C)	1.7×10^{-2} (35°C)	9.7	5.1	9.1	−37
SbBr$_3$ (CH$_3$)$_3$CBr	C$_6$H$_5$NO$_2$	1.7	1	1.1×10^{-1} (21°C)	2.0×10^{-1} (26°C)	3.0×10^{-1} (30°C)	20	14	19	2.5
SBBr$_3$ (CH$_3$)$_3$CBr	C$_6$H$_3$Cl$_3$	1.7	0	0.81×10^{-3} (21°C)	1.2×10^{-3} (26°C)	1.3×10^{-3} (30°C)	9.9	4.3	7.4	−41
SbBr$_3$ C$_3$H$_7$Br	C$_6$H$_5$NO$_2$	1.4	0	2.5×10^{-4} (18°C)	3.3×10^{-4} (22°C)	5.5×10^{-4} (34°C)	8.6	2.9	8.0	−48
SbBr$_3$ C$_3$H$_7$Br	C$_6$H$_3$Cl$_3$	1.4	0	7.6×10^{-4} (22°C)	4.1×10^{-4} (34°C)		9.5	3.7	8.8	−44

the exchange-reaction is pseudo zero order with respect to organic bromides[3]. Therefore, it is concluded that the reaction of bromine exchange between antimony(Ⅲ) bromide and isopropyl bromide is n th order ($n=1\sim2$) with respect to antimony(Ⅲ) bromide and 1st order with respect to isopropyl bromide.

Thus it seems reasonable to consider a similar reaction mechanism for the bromine exchange between Friedel-Craft catalysts and the organic bromids in solutions.
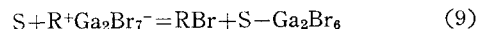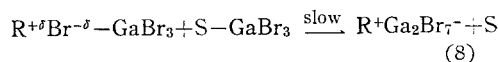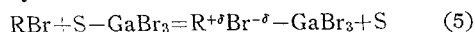
Reaction mechansim for the gallium bromide catalyzed alkylation reaction of benzene and toluene in 1,2,4-trichlorobenzene was previously postulated in the scheme (S, solvent molecules)

$$S+Ga_2Br_6=S-Ga_2Br_6 \qquad (3)$$

$$S-S-Ga_2Br_6=2S-GaBr_3 \qquad (4)$$

$$RBr+S-GaBr_3=R^{+\delta}Br^{-\delta}-GaBr_3+S \qquad (5)$$

$$ArH+R^{+\delta}Br^{-\delta}-GaBr_3 \xrightarrow{slow} \left[Ar\!\!\left\langle\begin{smallmatrix}H\\R\end{smallmatrix}\right.\right]^+GaBr_4^- \qquad (6)$$

$$S-\left[Ar\!\!\left\langle\begin{smallmatrix}H\\R\end{smallmatrix}\right.\right]^+GaBr_4^-=ArH+HBr-S-GaBr_3 \qquad (7)$$

In step 5 the formation of a polarized alkyl bromide-gallium bromide addition compound, $R^{+\delta}Br^{-\delta}-GaBr_3$, was assumed. The breaking of the carbon-bromine bond in the alkyl bromide

was assumed to contribute significantly to stability of the transition state of the alkylation reaction. Thus the relative rates of alkylation of the alkyl bromides were attributed to the varying abilities for the alkyl radicals to tolerate positive charge. In step 6, the formation of a σ complex was assumed to be the rate-determining step of the alkylation reaction.

The reaction mechanism for the bromine-exchange reactions of gallium bromide with alkyl bromides was assumed in a similar way to that described above for the Friedel-Craft alkylation reactions

$$RBr+S-GaBr_3=R^{+\delta}Br^{-\delta}-GaBr_3+S \qquad (5)$$

$$R^{+\delta}Br^{-\delta}-GaBr_3+S-GaBr_3 \xrightarrow{slow} R^+Ga_2Br_7^-+S \qquad (8)$$

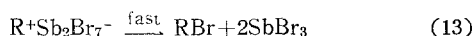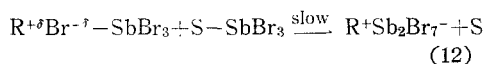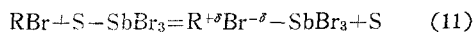$$S+R^+Ga_2Br_7^-=RBr+S-Ga_2Br_6 \qquad (9)$$

It was previously observed that in the presence of hydrogen bromide aromatic hydrocarbons form σ complexes more readily with dimeric molecules of aluminium and gallium bromides than with monomeric aluminium and gallium bromides. It was assumed that alkyl bromides interact more strongly with dimeric gallium bromide than with monomeric gallium bromide [9]. Thus in step 8 the formation of an ion-pair intermediate was assumed to proceed with the aid of a second molecule of gallium bromide
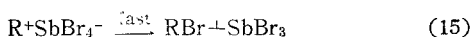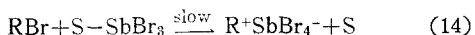
monomer associated with solvent molecules.

The reaction mechanism for the bromine-exchange reactions of antimony(Ⅲ) bromide with isopropyl bromide is now assumed in a similiar way. As the result of the present study, it can be concluded that the reation of bromine exchange between antimony(Ⅲ) bromide and isopropyl bromide has available two reaction mechanism. They are 1st order with respect to organic bromide and 1st and 2nd order with respect to antimony(Ⅲ) bromide.

If the mechanisms of the exchange-reaction is assumed as follows, it can be 2nd order with respect to antimony(Ⅲ) bromide.

$$S + SbBr_3 = S - SbBr_3 \qquad (10)$$

$$RBr + S - SbBr_3 = R^{+\delta}Br^{-\delta} - SbBr_3 + S \qquad (11)$$

$$R^{+\delta}Br^{-\delta} - SbBr_3 + S - SbBr_3 \xrightarrow{\text{slow}} R^+Sb_2Br_7^- + S \qquad (12)$$

$$R^+Sb_2Br_7^- \xrightarrow{\text{fast}} RBr + 2SbBr_3 \qquad (13)$$

If the mechanism of the exchange-reaction is assumed as follows, it can be 1st order with respect to antimony(Ⅲ) bromide.

$$S + SbBr_3 = S - SbBr_3 \qquad (10)$$

$$RBr + S - SbBr_3 \xrightarrow{\text{slow}} R^+SbBr_4^- + S \qquad (14)$$

$$R^+SbBr_4^- \xrightarrow{\text{fast}} RBr + SbBr_3 \qquad (15)$$

In this mechanism again, the breaking of the carbon-bromine bond in the alkyl bromide molecules was assumed to take an important part in determining the stability of the transition state of the exchange reaction.

Finally, it is assumed that step 12 and step 14 are the rate-determining steps of the exchange reaction. Then this proposed mechanism leads to the kinetic expression.

$$R = k[RBr][SbBr_3]^n$$

$$n = 1 \sim 2$$

If the concentration of the organic bromide is much greater than antimony(Ⅲ) bromide, the kinetic expression is

$$R = k[SbBr_3]^n$$

$$n = 1 \sim 2$$

which compares well with the expreimental observations.

Ⅴ. Acknowledgement

References

1. S. U. Choi and J. E. Willard, J. Amer. Chem. Sec., 87, 3072 (1965)

2. O. C. Kwun and S. U. Choi, J. of Phy. Chem., 72, 3148 (1968)

3. S. U. Choi and Y. I. Pae, Unpulished Results

4. S. U. Choi, Daehan Hwahak Hwoejee, 7, 65 (1963)

5. F. L. J, Sixma, H. Hendriks and D. Holtzapffel, Rec. Trav. Chim., 75, 127(1956)

6. Revzin. G. E., Shishenkova I. A., Metody Poluch Khim. Reactov Prev., 1967(16) 162—4.

7. E. A. Guggenheim, Phil. Mag., 2, 538(1926)

8. See for example, A. A. Frost and R. G. Peason "Kinetics and Mechanism", John Wiley and Sons, Inc., New York N. Y., 1953, p. 48.

9. H. C. Brown and W. J. Wallace, J. Amer. Chem. Soc., 75, 6268 (1953)