Kinetics of the Bromine-Exchange Reaction of Gallium Bromide with Isopropyl Bromide in Nitrobenzene[*]

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니트로벤젠 용액내에서의 브롬화갈륨과 브롬화이소프로필의 브롬 교환 반응

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요　약

방사성 브롬으로 표시한 브롬화이소프로필을 사용하여 니트로벤젠 용액내에서 브롬화갈륨과 브롬화이소프로필 사이에 일어나는 브롬교환반응의 속도를 19°, 25° 및 40°C에서 측정하였다. 본 실험의 결과는 이 브롬교환반응이 브롬화갈륨에 관하여 2차 반응이고 브롬화이소프로필에 관하여 1차 반응임을 보여 준다. 19°C 에서의 반응속도 상수 값이 $k_3 = 3.2 \times 10^{-2} l^2 \cdot mole^{-2} sec^{-1}$. 임을 알았다. 그리고 반응속도상수와 온도와의 관계로부터 이 교환반응에 대한 활성화에너지, 활성화엔탈피 및 활성화엔트로피 값을 계산하였다.

ABSTRACT

The rate of the bromine-exchange reaction between gallium bromide and isopropyl bromide in nitrobenzene was measured at 19°, 25° and 40°C., using isopropyl bromide labelled with Br-82. The results indicated that the exchange reaction was second order with respect to gallium bromide and first order with respect to isopropyl bromide. The third-order rate constant determined at 19°C. was $3.2 \times 10^{-2} \ l^2 \cdot mole^{-2} sec^{-1}$. The activation energy, the enthalpy of activation and the entropy of activation for the exchange reaction were also determined.

INTRODUCTION

In previous papers of this series, we reported experimental results on the kinetic studies of the bromine exchange reactions of gallium bromide with methyl or ethyl bromide in nitrobenzene and 1, 2, 4-trichloro-benzene solution. [1,2] The results indicated that the exchange reactions were second order with respect to

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

$$Rate = k_3 [GaBr_3]^2 [RBr].$$

The third-order rate constants obtained for the two alkyl bromides at 19°C in nitrobenzene solution were 2.4×10^{-5} and 1.9×10^{-3} 1^2. mole^{-2}sec.$^{-1}$, respectively. We also presented a reaction mechanism for the exchange reactions, which assumed the breaking of the carbon-bromine bond in the alkyl bromide molecules to play an important role for determining the stability of the transition state of the exchange reactions. [2]

Thus, it appeared that both methyl and ethyl bromides followed similar reaction mechanism in the bromine-exchange reactions with gallium bromide in nitrobenzene solution. Methyl bromide was observed, however, to exchange bromine with gallium bromide much more slowly than ethyl bromide. In view of a large difference in rate constant for the two alkyl bromides, it appeared important to extend the exchange-studies to the system of gallium bromide with isopropyl bromide in order to compare the reaction of isopropyl bromide with those of methyl and ethyl bromides. Thus, in the hope of making closer comparison, the present study on the bromine exchange between gallium bromide and isopropyl bromide in nitrobenzene solution was undertaken.

EXPERIMENTAL PART

Apparatus.

The apparatus used in the present study was essentially the same as that used previously. [1,2] All experiments were carried out in a high vacuum system. The general vacuum-line techniques were similar to those described by Sanderson. [3]

Materials.

Gallium bromide was prepared by the direct combination of metallic gallium with bromine in a vacuum line. [1,2,4] It was resublimed several times in vacuo and was collected in small ampoules with fragile tips. [1,2] Nitrobenzene (Reagent grade, Merck, Germany) was dried with Drierite, fractionated in a

100-cm. Todd column packed with glass helices, and stored over Drierite.

Preparation of Isopropyl Bromide (^{82}Br).

A small quantity of solid potassium bromide(Reagent grade, Merck, Germany) was irradiated with neutrons to induce the (n, γ) reaction of bromine.* The irradiated potassium bromide was mixed with an appropriate amount of inactive potassium bromide. The mixture was then used to synthesize isopropyl bromide labelled with^{82}Br by the reaction of potassium bromide with isopropyl alcohol in the presence of concentrated sulfuric acid. [5] After isopropyl bromide was distilled from the reaction mixture, it was dried with calcium chloride. It was then introduced into and fractionated inside the vacuum line. The isopropyl bromide(^{82}Br) thus obtained was stored in the vacuum line.

Procedures for Kinetic Study of the Exchange Reactions.

Experimental procedures used in the present study were described in the previous papers. [1,2] These involved preparation of the solution of gallium bromide in nitrobenzene in the vacuum line system, introduction of the appropriate amount of isopropyl bromide labelled with bromine-82, and measurement of the radioactivity of given fraction of vapor phase present above the solution at constant time intervals. A G-M tube (Nuclear Radiation Detector, Model 108) and a scaler (Nuclear Chicago, Model 8770) were used for counting of the radioactivity. From the measured counting rates as a function of time, the rate of exchange, R, of bromine between gallium bromide and isopropyl bromide in solution was determined by the usual Guggenheim method. [1,2]

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

where a denotes the molar concentration of gallium bromide and b denotes that of isopropyl bromide in solution. The term $A_t - A_{t+\tau}$ represents the change in counting rate during a constant time interval, τ, starting at different time, t, after the reaction has started. The molar concentration of isopropyl bromide in solution, b, was measured from a knowledge of the Henry's law constant for isopropyl bromide over the solution of gallium bromide in nitrobenzene. [1,2]

RESULTS

Solubility Determinations.

The solubility of isopropyl bromide in nitrobenzene was determined in the presence and absence of gallium bromide. The results are summarized in Table I.

TABLE 1. Solubility of Isopropyl Bromide in Nitrobenzene in the Presence and Absence ofGallium Bromide.

Temp., °C.	GaBr$_3$, mole l^{-1}.	Henry's law const.,* 10^{3}mm
19	0	0.28
	0	0.29
	0	0.27
	0.305	0.26
	0.170	0.27
25	0	0.37
	0	0.36
	0.195	0.35
40	0	0.65
	0	0.64
	0.203	0.62

* Henry's law constant is the equilibrium pressure of the gas (in mm.)divided by its mole fraction in the solution.

Table I shows that the Henry's law constants for isopropyl bromide over gallium bromide solution are smaller than those observed in the pure solvent at each temperature. This indicates that isopropyl bromide dissolves better in the gallium bromide solution than in the pure solvent. This may be attributed to some interaction between gallium bromide and isopropyl bromide in solution, as was considered in the previous studies. [2,6]

Bromine-Exchange Reaction of Gallium Bromide with Isopropyl Bromide.

The rates of bromine exchange between gallium bromide and isopropyl bromide in nitrobenzene were measured at 19°, 25° and 40°C. In each run good linearity was observed between log $(A_t - A_{t+\nu})$ and time, t. From slope of each straight line and molar concentrations of gallium bromide and isopropyl bromide, the rate of the bromine exchange, R, was calculated by equation (1). The experimental results are summarized in Table II.

The rate of the bromine exchange between gallium

TABLE II. Rates of Bromine Exchange between Gallium Bromide and Isopropyl Bromide in Nitrobenzene.

Temp., °C	GaBr$_3$, mole/l.	i-C$_3$H$_7$Br, mole/l.	R, 10^{-4} mole l^{-1}. sec^{-1}.	k_3 10^{-2}l^2. mole^{-2} sec^{-1}.
19	0.26	0.48	11	3.4
	0.13	0.65	3.5	3.2
	0.13	0.87	4.8	3.3
	0.13	1.13	6.5	3.4
	0.12	0.83	3.3	2.8
				av. 3.2
25	0.18	0.61	10	5.1
	0.13	0.35	2.6	4.4
				av. 4.8
40	0.20	0.28	12	11
	0.15	0.30	6.9	10
				av. 11

bromide and alkyl bromides may generally be expressed by

$$R = k[\text{GaBr}_3]^m[\text{RBr}]^n \quad \cdots\cdots(2).$$

Previously, we observed that $m=2$ and $n=1$ for the exchange reactions of gallium bromide with methyl bromide and ethyl bromide in nitrobenzene. [1,2]Thus, it was assumed that $m=2$ and $n=1$ in this case with isopropyl bromide also.

$$R = k_3[\text{GaBr}_3]^2[i\text{-}\text{C}_3\text{H}_7\text{Br}] \quad \cdots\cdots(3).$$

The values of $R/[\text{GaBr}_3]^2$ $[i\text{-}\text{C}_3\text{H}_7\text{Br}]$, listed in the last column of Table II, indicated fairly good constancy at each temperature examined. Therefore, it can be concluded that the assumption of the third-order kinetics (equation 3) is correct in this exchange reaction with isopropyl bromide as well as in the cases with methyl and ethyl bromides.

In order to obtain the values of activation energy, E_a, and logarithm of the frequency factor, log A, of the bromine-exchange reaction, the log k_3 values were plotted against the reciprocal of the absolute temperature. In order to obtain more activation parameters, the enthalpy of activation, $\triangle H^*$, and the entropy of activation, $\triangle S^*$, the log (k_3/T) values were protted against the reciprocal of the absolute temperature.

$$k_3 = A \exp(-E_a/RT) \quad \cdots\cdots(4),$$
$$k_3 = (kT/h) \exp(\triangle S^*/R - \triangle H^*/RT) \quad \cdots\cdots(5),$$

$$\log\left(\frac{k_3}{T}\right)=10.32+\frac{\triangle S^*}{2.3R}-\frac{\triangle H^*}{2.3R}\cdot\frac{1}{T}\cdots(5),$$

These plots indicated good linearity (Figs. 1 and 2). From slopes and intercepts of the straight lines, the activation parameters were evaluated. The results obtained are as follows:

$E_a=11$kcal./mole

$\log A=6.5$

$\triangle H^*=10$kcal./mole

$\triangle S^*=-31$ e. u.
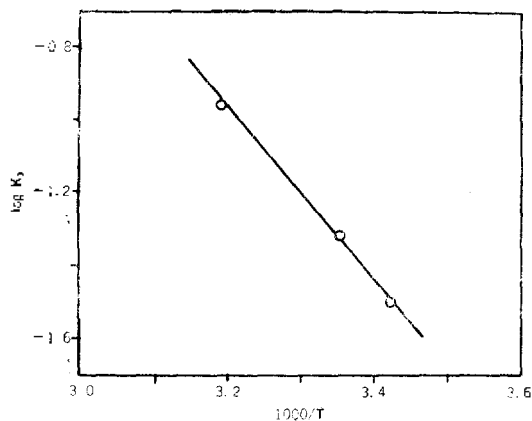
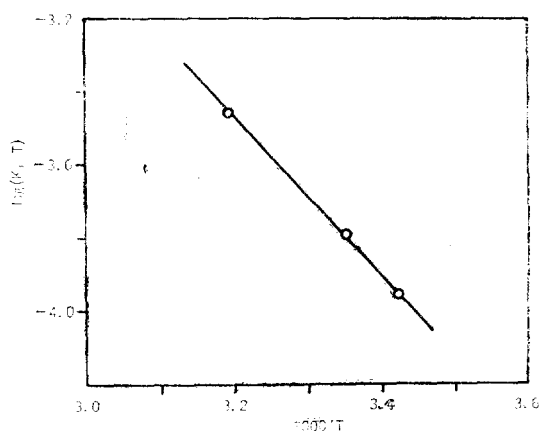Fig. 1. Plots of log k_3 versus 1/T for the exchange reaction.

Fig. 2. Plots of log (k_3/T) versus 1/T for the exchange reaction.

DISCUSSION

Reaction Mechanism of the Bromine-Exchange Reaction.

As the result of the present investigation, it is concluded that the bromine-exchange reaction of gallium bromide with isopropyl bromide is second order with respect to gallium bromide and first order with respect to isopropyl bromide. The results of the present study are now compared with those of the previous studies on the systems of methyl bromide-gallium bromide[1] and ethyl bromide-gallium bromide[2] (Table Ⅲ). It can be seen in Table Ⅲ that the three exchange reactions are all third-order reactions, second order with respect to gallium bromide and first order with respect to alkyl bromides. It is also seen that the rate of bromine exchange increases in the order,
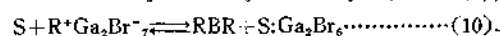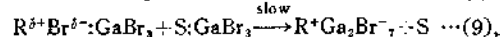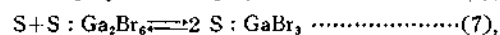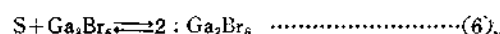
$$CH_3Br<C_2H_5Br<i-C_3H_7Br.$$

Therefore, it appears that the three exchange reactions proceed through a similar reaction mechanism, and that the transition states of the reactions are attained more readily in the order written above.

TABLE Ⅲ. Data for the Bromine-Exchange Reactions between Gallium Bromide and Alkyl Bromides in Nitrobenzene.

Alkyl bromide	Kinetics (order)	k_3(at 19°C.), l^2.mole^{-2}sec^{-1}.	E_a, kcal. mole^{-1}
CH$_3$Br*	3rd	2.4×10^{-5}	18
C$_2$H$_5$Br**	3rd	1.9×10^{-3}	13
i-C$_3$H$_7$Br***	3rd	3.2×10^{-2}	11

*Ref. 1. **Ref. 2. ***The present study.

In the previous paper, [2] we postulated a reaction mechanism for the bromine-exchange reaction of gallium bromide with methyl or ethyl bromide.

$$S+Ga_2Br_6\rightleftharpoons2\ :\ Ga_2Br_6\ \cdots\cdots\cdots\cdots\cdots\cdots(6),$$
$$S+S\ :\ Ga_2Br_6\rightleftharpoons2\ S\ :\ GaBr_3\ \cdots\cdots\cdots\cdots(7),$$
$$RBr+S:GaBr_3\rightleftharpoons R^{\delta+}Br^{\delta-}:GaBr_3+S\cdots\cdots\cdots(8),$$
$$R^{\delta+}Br^{\delta-}:GaBr_3+S:GaBr_3\xrightarrow{slow}R^+Ga_2Br_7^-:S\ \cdots(9),$$
$$S+R^+Ga_2Br_7^-\rightleftharpoons RBr+S:Ga_2Br_6\cdots\cdots\cdots\cdots(10).$$

If this mechanism is assumed again for the exchange reaction with isopropyl bromide, the breaking of carbon-bromine bond (R-Br) in the polarized alkyl

bromide-gallium bromide addition compound, $R^{\delta+}Br^{\delta-}$: $CaBr_3$, may play an important role in determining the stability of the transition state of the exchange reaction. Since isopropyl group may tolerate positive charge more readily than ethyl group which in turn does more readily than methyl group, it must be said that alkyl bromides exchange bromine atoms with gallium bromide faster in the order written above.

Furthermore, if step (9) is the rate-determining step of the exchange reaction, this reaction mechanism leads to the kietic expression,

$$\text{rate} = k [S:GaBr_3]^2 [i-C_3H_7Br] \quad \cdots\cdots\cdots\cdots(11).$$

This agrees with the experimental observations.

Acknowledgment.

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