

1, 2, 4-트리클로로벤젠용액 및 니트로벤젠용액 내에서의 브롬화갈륨과 브롬화*n*-부틸의 브롬 교환반응

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Kinetics of the Bromine-Exchange Reaction of Gallium Bromide with *n*-Butyl Bromide in 1, 2, 4-Trichlorobenzene and in Nitrobenzene

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요 약. 방사성 브롬으로 표시한 브롬화 *n*-부틸을 사용하여 1, 2, 4-트리클로로벤젠용액 및 니트로벤젠용액 내에서 브롬화갈륨과 *n*-브롬화부틸 사이에 일어나는 브롬교환 반응의 속도를 19, 25 및 40°C에서 측정하였다. 본 실험의 결과는 이 브롬 교환반응이 브롬화갈륨에 관하여 2차반응이고 *n*-브롬화부틸에 관하여 1차 반응임을 보여준다. 19°C에서의 반응속도상수 값이 1, 2, 4-트리클로로벤젠용액에서 $1.15 \times 10^{-4} l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ 이고, 니트로벤젠용액에서 $4.21 \times 10^{-4} l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ 임을 알았다. 그리고 반응속도상수와 온도와의 관계로부터 이 교환반응에 대한 활성화 에너지, 활성화 엔탈피 및 활성화 엔트로피 값을 계산하였다.

ABSTRACT. The rate of the bromine-exchange reaction between gallium bromide and *n*-butyl bromide in 1, 2, 4-trichlorobenzene and in nitrobenzene was measured at 19, 25 and 40°C., using *n*-butyl 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 *n*-butyl bromide. The third-order rate constant determined at 19°C. is $1.15 \times 10^{-4} l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ in 1, 2, 4-trichlorobenzene and $4.21 \times 10^{-4} l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ in nitrobenzene. 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

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experimental results on the kinetic studies of the bromine exchange reactions of gallium bromide with methyl, ethyl and isopropyl bromides in 1, 2, 4-trichlorobenzene and in nitrobenzene

solution.¹⁻³ The results indicated that the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides.

$$\text{Rate} = k_3[\text{GaBr}_3]^2[\text{RBr}]$$

The third-order rate constants obtained for the three alkyl bromides at 19°C in nitrobenzene were 2.4×10^{-5} , 1.9×10^{-3} and $3.2 \times 10^{-2} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$, and those for the first two alkyl bromides in 1,2,4-trichlorobenzene were 0.82×10^{-2} and $2.8 \times 10^{-2} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$. 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 methyl, ethyl and isopropyl bromides followed similar reaction mechanism in the bromine-exchange reactions with gallium bromide in the two solvents. Methyl, ethyl bromide was observed, however, to exchange bromine with gallium bromide much more slowly than isopropyl bromide. In view of a large difference in rate constant for the three alkyl bromides, it appeared important to extend the exchange studies to the system of gallium bromide with *n*-butyl bromide in order to compare the reaction of *n*-butyl bromide with those of methyl, ethyl and isopropyl bromides. Thus, in the hope of making closer comparison, the present study on the bromine exchange between gallium bromide and *n*-butyl bromide in 1,2,4-trichlorobenzene and in nitrobenzene solution was undertaken.

EXPERIMENTAL

Apparatus. The apparatus used in the present study was essentially the same as that used previously.¹⁻³ All experiments were carried out

in a high vacuum system. The general vacuum line techniques were similar to those described by Sanderson.⁴

Materials. Gallium bromide was prepared by the direct combination of metallic gallium with bromine in a vacuum line.^{1,2,5} It was resublimed several times in vacuo and was collected in small ampoules with fragile tips.^{1,2} Nitrobenzene (reagent grade, Merck, Germany) and 1,2,4-trichlorobenzene (special grade, Wako, Japan) were dried with Drierite, fractionated in a 100 cm. Todd column packed with glass helices and stored over Drierite.

Preparation of *n*-Butyl Bromide (⁸²Br). 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 an appropriate amount of inactive potassium bromide. The mixture was then used to synthesize *n*-butyl bromide labelled with ⁸²Br by the reaction of potassium bromide with *n*-butyl alcohol in the presence of concentrated sulfuric acid.⁶ After *n*-butyl 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 *n*-butyl bromide (⁸²Br) thus obtained was stored in the vacuum line.

Procedures for Kinetic Study of the Exchange Reactions. The experimental procedures used in the present study and the method of calculation of the exchange rates were similar to those described previously.^{1,2}

Gallium bromide was introduced into the reaction vessel of the vacuum line. The weight of gallium bromide introduced was determined by weighing the ampoule and its fragments

*The irradiation was carried out in the nuclear reactor, TRIGA-II, of the Korea Atomic Energy Research Institute, Seoul, Korea. This assistance is gratefully acknowledged.

before and after the transfer. A known quantity of solvent, 1, 2, 4-trichlorobenzene or nitrobenzene, was then introduced into reaction vessel from a side tube of the reaction vessel. Thus, a solution of gallium bromide in 1, 2, 4-trichlorobenzene or nitrobenzene of known concentration was prepared inside the vacuum line.

The reaction vessel was maintained at the desired temperatures, 19, 25, 40 °C, by a water bath whose temperature was constant within ± 0.05 °C. Vapors were circulated over the surface of the magnetically stirred solution, with the aid of a small heating coil, as described previously.^{1,2}

A known quantity of labeled *n*-butyl bromide vapor was introduced to the reaction vessel by expanding the vapor from the storage system. This was taken as time zero. Radioactivity of the *n*-butyl bromide vapor near the scintillation detector (Well type Scintillation detector-Nuclear Chicago, Model 967 and Scaler-Nuclear Chicago, Model, 8703) was measured at constant time intervals.

The measured activity was proportional to the activity of *n*-butyl bromide in solution. Hence, from the measured counting rates as a function of time, the rate of exchange of bromine between gallium bromide and *n*-butyl bromide in solution was determined by the usual Guggenheim method^{1,2}

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

where *a* denotes the molar concentration of gallium bromide and *b* denotes that of *n*-butyl bromide in solution respectively. The term $(A_t - A_{t+\nu})$ represents the change in counting rate during a constant time interval ν starting at different time *t* from the beginning of the reaction. Counting rates were ordinarily in the range of 50,000 to 550,000 counts per minute.

Procedures for the Solubility Determina-

tions. In order to calculate the rates of the exchange reactions, the solubility of *n*-butyl bromide in the solution of gallium bromide in both 1, 2, 4-trichlorobenzene and nitrobenzene was measured. The apparatus and procedures were similar to those described previously.^{2,7}

RESULTS

Solubility Determinations. The solubility of *n*-butyl bromide in 1, 2, 4-trichlorobenzene and nitrobenzene were determined at several temperatures in the presence and absence of gallium bromide. The results are summarized in Table 1.

Table 1. Solubility of *n*-butyl bromide in 1, 2, 4-trichlorobenzene and in nitrobenzene in the presence and absence of gallium bromide.

Solvent	Temp. (°C)	GaBr ₃ , mole·l ⁻¹	Henry's law const. (mm) ^a	
C ₆ H ₃ Cl ₃	19	0	77.4	
		0.116	68.7	
		0.218	68.8	
		0.219	68.5	
		0.239	67.6	
		0.236	68.7	
	25	0	113	
		0.299	98.2	
		0.312	98.9	
		40	0	189
			0.274	173
			0.186	173
C ₆ H ₅ NO ₂	19	0	70.7	
		0.198	65.7	
		0.278	65.1	
		0.342	64.8	
		0.365	65.3	
		25	0	103
	0.055		91.4	
	0.082		91.8	
	40		0	181
			0.158	170
			0.174	170

^aHenry's law constant is the equilibrium pressure of the gas divided by its mole fraction in the solution.

Table 1 shows that the Henry's law constants for *n*-butyl bromide over gallium bromide solution are smaller than those observed in the pure solvent at each temperature. This indicates that *n*-butyl bromide dissolves better in the gallium bromide solution than in the pure solvent. This may be attributed to some interaction between gallium bromide and *n*-butyl bromide in solution, as was considered in the previous studies.^{2,7}

Bromine-Exchange Reaction of Gallium Bromide with *n*-Butyl Bromide in Nitrobenzene. The rates of bromine exchange between gallium bromide and *n*-butyl bromide in nitrobenzene were measured at 19, 25 and 40°C. In each run good linearity was observed between $\log(A_t - A_{t+\infty})$ and time, *t*. From slope of each straight line and molar concentrations of gallium bromide and *n*-butyl bromide, the rate of the bromine exchange, *R*, was calculated by equation(1). The experimental results are summarized in Table 2.

The rate of the bromine exchange between gallium bromide and alkyl bromides may

Table 2. Rates of bromine exchange between gallium bromide and *n*-butyl bromide in nitrobenzene.

Temp. (°C)	GaBr ₃ , mole·l ⁻¹	<i>n</i> -C ₄ H ₉ Br, mole·l ⁻¹	$R \times 10^3$, mole·l ⁻¹ ·sec ⁻¹	$k \times 10^4$, l ² ·mole ⁻² ·sec ⁻¹
19	0.298	0.457	1.05	4.30
	0.305	0.682	1.58	4.14
	0.305	0.981	2.31	4.21
	0.305	1.54	3.66	4.26
	0.392	0.772	2.96	4.16
			Av : 4.21	
25	0.302	1.46	4.57	5.74
	0.761	0.635	12.8	5.80
			Av : 5.77	
40	0.262	0.803	3.05	9.22
	0.510	0.441	6.47	9.40
	0.357	1.32	10.4	9.37
			Av : 9.33	

generally be expressed by

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

Previously, we observed that $m=2$ and $n=1$ for the exchange reactions of gallium bromide with methyl, ethyl, and isopropyl bromides in nitrobenzene.¹⁻³ Thus, it was also assumed that $m=2$ and $n=1$ in this case with *n*-butyl bromide.

$$R = k_3 [\text{GaBr}_3]^2 [n\text{-C}_4\text{H}_9\text{Br}] \quad (3)$$

The values of $R/[\text{GaBr}_3]^2 [n\text{-C}_4\text{H}_9\text{Br}]$, listed in the last column of Table 2, 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 *n*-butyl bromide as well as in the cases with methyl, ethyl and isopropyl 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 acti-

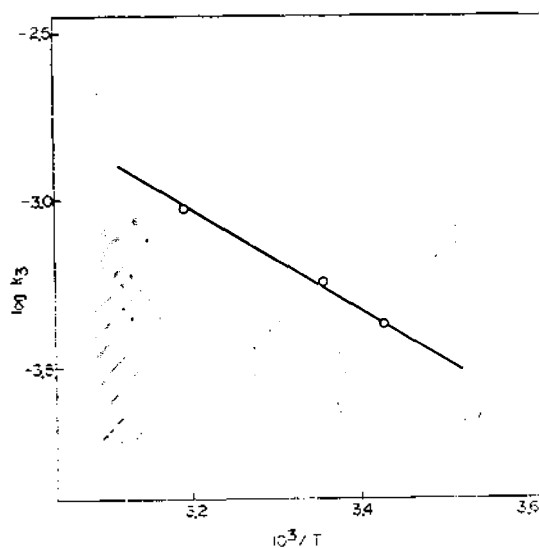


Fig. 1. Temperature dependence of $\log k_3$ of the bromine exchange reaction in nitrobenzene.

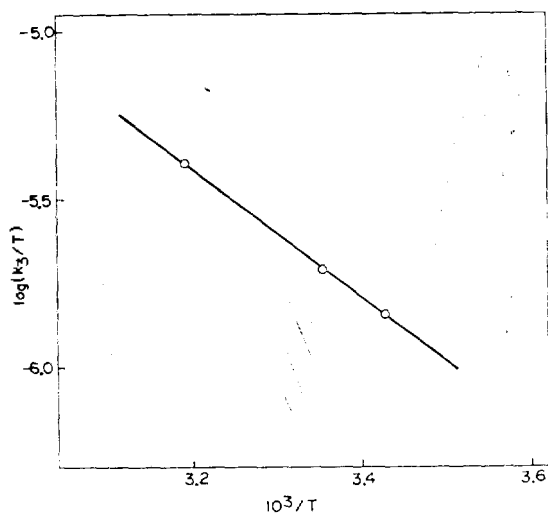


Fig. 2. Temperature dependence of (k_3/T) of the bromine exchange reaction in nitrobenzene.

vation, ΔH^\ddagger , and the entropy of activation, ΔS^\ddagger , the $\log(k_3/T)$ values were plotted against the reciprocal of the absolute temperature. 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:

$$E_a = 6.8 \text{ kcal./mole}, \quad \log A = 1.7,$$

$$\Delta H^\ddagger = 8.7 \text{ kcal./mole}, \quad \Delta S^\ddagger = -44 \text{ e. u.}$$

Bromine Exchange Reaction of Gallium Bromide with *n*-Butyl Bromide in 1,2,4-Trichlorobenzene. The rates of bromine exchange between gallium bromide and *n*-butyl bromide in 1,2,4-trichlorobenzene were also measured at 19, 25, 40°C. The results are summarized in Table 3. Previously, we observed that $m=2$ and $n=1$ for the exchange reactions of gallium bromide with methyl and ethyl bromides in 1,2,4-trichlorobenzene^{1,2}. Thus, it was also assumed that $m=2$ and $n=1$ in this case with *n*-butyl bromide.

$$R = k_3 [\text{GaBr}_3]^2 [n\text{-C}_4\text{H}_9\text{Br}]$$

The values of $R/[\text{GaBr}_3]^2 [n\text{-C}_4\text{H}_9\text{Br}]$, listed

Table 3. Rates of bromine exchange between gallium bromide and *n*-butyl bromide in 1,2,4-trichlorobenzene.

Temp. (°C)	GaBr ₃ , mole·l ⁻¹	<i>n</i> -C ₄ H ₉ Br, mole·l ⁻¹	$R \times 10^3$, mole·l ⁻¹ ·sec ⁻¹	$k \times 10^4$, l ² ·mole ⁻² ·sec ⁻¹
19	0.281	0.792	0.420	1.12
	0.209	0.927	0.240	0.986
	0.322	0.620	0.474	1.23
	0.322	0.831	0.605	1.17
	0.322	1.04	0.809	1.25
				Av : 1.15
25	0.837	1.51	10.4	1.61
	1.03	1.51	15.2	1.58
				Av : 1.61
40	0.577	1.39	9.75	3.52
	0.374	0.726	19.1	3.14
	0.861	1.29	18.9	3.31
				Av : 3.32

in the last column of Table 3, indicated fairly good constancy at each temperature examined. Therefore, it can be also concluded that the assumption of the third-order kinetics is correct in this exchange reaction with *n*-butyl bromide as well as in the cases with methyl and ethyl bromides. The activation parameters for the exchange reaction in 1,2,4-trichlorobenzene solution were also estimated from the temperature dependence of the rate constant. From the variation of $\log k_3$ with the reciprocal of absolute temperature, the activation energy and logarithm of the frequency factor of the exchange reaction were estimated to be 9.0 kcal/mole and 2.8, respectively. From the variation of $\log(k_3/T)$ with the reciprocal of absolute temperature, the values of ΔH^\ddagger and ΔS^\ddagger for the exchange reaction were estimated to be 11 kcal/mole and ~ 40 e. u., respectively.

DISCUSSION

Reaction Mechanism of the Bromine-Exchange Reaction. As the result of the present,

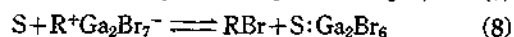
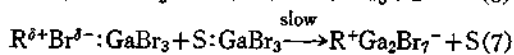
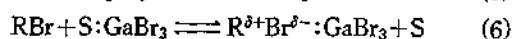
Table 4. Summary of data obtained for the reactions of bromine exchange between gallium bromide and alkyl bromides.

Solvent	Alkyl bromide	Kinetics (order)	k_3 (at 19 °C) $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$	E_a , kcal · mole ⁻¹	log A	ΔH^\ddagger , kcal · mole ⁻¹	ΔS^\ddagger , e. u.
C ₆ H ₅ Cl ₃	CH ₃ Br ^a	3 rd	0.82×10^{-2}	14	7.9	13	-24
	C ₂ H ₅ Br ^b	3 rd	2.8×10^{-2}	8.2	4.6	7.6	-40
	<i>n</i> -C ₄ H ₉ Br ^d	3 rd	1.2×10^{-4}	9.0	2.8	11	-40
C ₆ H ₅ NO ₂	CH ₃ Br ^a	3 rd	2.4×10^{-5}	18	8.4	12	-37
	C ₂ H ₅ Br ^b	3 rd	1.9×10^{-3}	13	6.7	12	-29
	<i>i</i> -C ₃ H ₇ Br ^c	3 rd	3.2×10^{-2}	11	6.5	10	-31
	<i>n</i> -C ₄ H ₉ Br ^d	3 rd	4.2×10^{-4}	6.8	1.7	8.7	-44

^aRef. 1, ^bRef. 2, ^cRef. 3, ^dThe present study.

study, it is concluded that the bromine-exchange reaction of gallium bromide with *n*-butyl bromide is second order with respect to gallium bromide and first order respect to *n*-butyl bromide. The results of the present study are now compared with those of the previous studies on the systems of methyl bromide-gallium bromide¹, ethyl bromide-gallium bromide² and isopropyl bromide-gallium bromide (Table 4). It can be seen in Table 4 that the four exchange reactions are all third-order reactions, second order with respect to gallium bromide and first order with respect to alkyl bromides. Therefore, it appears that the four exchange reactions proceed through a similar reaction mechanism.

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



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

Table 5. Data for the instability constants of the complex between gallium bromide and alkyl bromide at 19 °C.

Solvent	Alkyl bromide	K' mole ^{-1/2} · l ^{-1/2}
C ₆ H ₅ Cl ₃	CH ₃ Br ^a	1.8
	C ₂ H ₅ Br ^b	7.6
	<i>n</i> -C ₄ H ₉ Br ^c	3.2
C ₆ H ₅ NO ₂	CH ₃ Br ^a	6.5
	C ₂ H ₅ Br ^b	10.0
	<i>n</i> -C ₄ H ₉ Br ^c	4.0

^aRef. 8, ^bRef. 9, ^cRef. 7.

tion compound, R^{δ+}Br^{δ-}:GaBr₃, may play an important role in determining the stability of the transition state of the exchange reaction. If step (7) is the rate-determining step of the exchange reaction, this reaction mechanism leads to the kinetic expression,

$$\text{Rate} = k[S:GaBr_3]^2 [n-C_4H_9Br]$$

This agrees with the experimental observations.

The results of the present study indicated that the rate of bromine exchange reaction between gallium bromide and *n*-butyl bromide was much smaller than the value expected from the order (CH₃Br < C₂H₅Br < *i*-C₃H₇Br) obtained in the previous works.¹⁻³ It is speculated that the stability of the complex, RBr·GaBr₃, should also affect the stability of the transition state of the

exchange reactions. In other words, more energy may be required to break the carbon-bromine bond to form $R^+Ga_2Br_7^-$ in the more stable complex, and thus, the rate of the exchange reaction may be decreased in the case where the more stable complex is formed. Thus, it would be expected that the exchange rate observed in n -butyl bromide is smaller than that observed in ethyl bromide.

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