

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

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The rate of the bromine-exchange reaction between gallium bromide and *n*-propyl bromide in 1,2,4-trichlorobenzene and in nitrobenzene was measured at 19, 25 and 40 °C, using *n*-propyl 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*-propyl bromide. The third-order rate constant determined at 19 °C is  $2.9 \times 10^{-2} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$  in 1,2,4-trichlorobenzene and  $4.5 \times 10^{-3} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ , in nitrobenzene. The activation energy, the enthalpy of activation and the entropy of activation for the exchange reaction were also determined. Reaction mechanism for the bromine exchange of *n*-propyl bromide seemed to be similar to those observed in earlier studies with other alkyl bromides.

### Introduction

In the previous papers of this series, we reported experimental results on the kinetic studies of the bromine exchange reactions of gallium bromide with methyl, ethyl, *i*-propyl and *n*-butyl in 1,2,4-trichlorobenzene and in nitrobenzene solution<sup>1-4</sup>. The results indicated that the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides.

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

We 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 rate of the exchange reactions.<sup>2</sup>

As the results of previous studies it was concluded that ethyl bromide exchanged bromine with gallium bromide more rapidly than methyl bromide, and *n*-butyl bromide did more slowly than ethyl bromide. The relative rates of the exchange reactions of these three alkyl bromides did not seem to indicate clear correlation with the chain lengths of the alkyl bromides examined. It appeared of interest to extend the exchange studies to the system of gallium bromide with *n*-propyl bromide in order to compare the reaction of *n*-propyl bromide with those of methyl, ethyl, and *n*-butyl bromides. In the hope of making closer comparison, the present study on the bromine exchange between gallium bromide and *n*-propyl bromide in 1,2,4-trichlorobenzene and in nitrobenzene solution was undertaken.

### Experimental Part

**Apparatus and Materials.** The apparatus used in the present study was essentially the same as that used previously.<sup>1,2</sup> The methods of preparation and/or purification of gallium bromide and solvents were described in previous papers of this series.<sup>1-4</sup>

**Preparation of *n*-Propyl Bromide (<sup>82</sup>Br).** A small quantity

of solid potassium bromide (Reagent grade, Merck, Germany) was irradiated with neutrons to induce the (*n*,  $\gamma$ ) reaction of bromine.

The irradiated potassium bromide was mixed with an appropriate amount of inactive potassium bromide. The mixture was then used to synthesize *n*-propyl bromide labelled with <sup>82</sup>Br by the reaction of potassium bromide with *n*-propyl alcohol in the presence of concentrated sulfuric acid<sup>5</sup>. After *n*-propyl 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*-propyl bromide (<sup>82</sup>Br) 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<sup>1,2</sup>.

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 and 40 °C, within  $\pm 0.05$  °C. Vapors were circulated over the surface of the magnetically stirred solution, with the aid of a small heating coil, as described previously<sup>1,2</sup>.

A known quantity of labelled *n*-propyl 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*-propyl 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*-propyl 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*-propyl bromide in solution was determined by the usual Guggenheim method<sup>1,2</sup>.

TABLE 1: Solubility of *n*-Propyl Bromide in 1,2,4-Trichlorobenzene and in Nitrobenzene in the Presence and Absence of Gallium Bromide

Solvent	Temp. (°C)	CaBr <sub>3</sub> mole·l <sup>-1</sup>	Henry's law const. (mm) <sup>a</sup>
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	19	0	176
		0	175
		0.218	163
		0.234	162
		0.298	163
		0	246
	25	0	246
		0	246
		0.231	228
		0.266	230
		0	435
		0	434
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	19	0.201	415
		0.237	416
		0	166
		0	165
		0.204	156
		0.284	154
	25	0.324	154
		0	237
		0	237
		0.215	223
		0.315	221
		0	427
40	0	427	
	0	406	
	0.201	406	
	0.228	406	
	0	406	
	0.228	406	

<sup>a</sup>Henry's law constant is the equilibrium pressure of the gas divided by its mole fraction in the solution

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

where *a* denotes the molar concentration of gallium bromide and *b* that of *n*-propyl bromide in solution.

The term (*A<sub>t</sub>* - *A<sub>t+ν</sub>*) 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 Determinations.* In order to calculate the rates of the exchange reactions, the solubility of *n*-propyl 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<sup>2,6</sup>.

## Results

*Solubility Determinations.* The solubility of *n*-propyl 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 shows that the Henry's law constants for *n*-propyl bromide over gallium bromide solution are smaller than those observed in the pure solvent at each temperature. This indicates that *n*-propyl bromide dissolves better in the gallium

TABLE 2: Rates of Bromine Exchange between Gallium Bromide and *n*-Propyl Bromide in Nitrobenzene

Temp. (°C)	[GaBr <sub>3</sub> ] mole·l <sup>-1</sup>	[ <i>n</i> -C <sub>3</sub> H <sub>7</sub> Br] mole·l <sup>-1</sup>	Rate × 10 <sup>5</sup> mole·l <sup>-1</sup> sec <sup>-1</sup>	<i>k<sub>3</sub></i> × 10 <sup>3</sup> l·mole <sup>-2</sup> sec <sup>-1</sup>	
19	0.178	0.315	4.44	4.45	
	0.178	0.634	9.05	4.51	
	0.166	0.268	3.27	4.43	
	0.166	0.670	8.26	4.48	
	0.166	1.204	14.9	4.50	
	0.343	0.363	19.1	4.47	
	0.343	0.698	37.2	4.53	
	0.343	1.178	61.9	4.47	
	0.343	1.351	71.2	4.48	
	0.263	0.260	8.06	4.48	
				av. 4.48	
	25	0.196	0.218	4.86	5.80
		0.196	0.302	6.74	5.81
		0.196	0.614	13.8	5.83
		0.231	0.233	7.24	5.82
0.231		0.415	12.9	5.84	
0.231		0.584	18.3	5.87	
0.314		0.168	9.64	5.82	
0.314		0.282	16.2	5.83	
				av. 5.83	
40		0.353	0.211	32.7	12.5
		0.353	0.356	55.3	12.5
		0.353	0.618	96.6	12.6
		0.226	0.212	14.6	13.5
		0.226	0.305	21.0	13.5
		0.226	0.383	26.4	13.5
	0.284	0.236	24.0	12.6	
	0.284	0.404	41.3	12.7	
				av. 12.9	

bromide solution than in the pure solvent. This may be attributed to some interaction between gallium bromide and *n*-propyl bromide in solution, as was considered in the previous studies<sup>2,6,7</sup>.

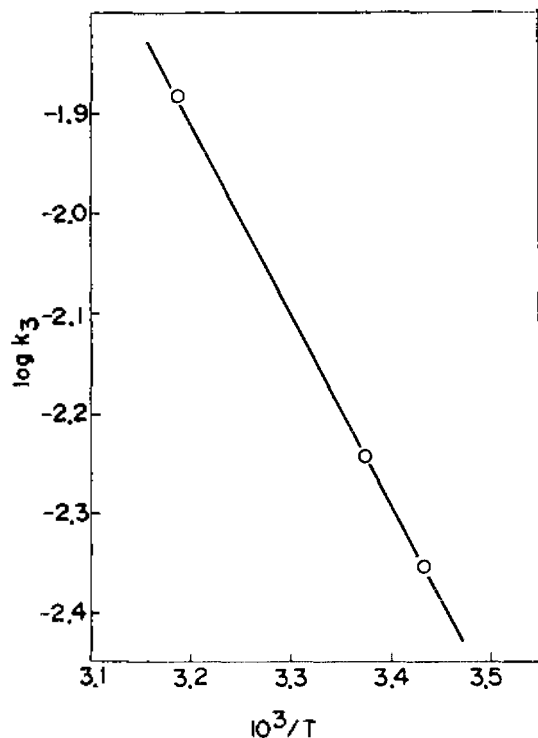
*Bromine-Exchange Reaction of Gallium Bromide with *n*-Propyl Bromide in Nitrobenzene.* The rates of bromine exchange between gallium bromide and *n*-propyl bromide in nitrobenzene were measured at 19, 25 and 40 °C. In each run good linearity was observed between long (*A<sub>t</sub>* - *A<sub>t+ν</sub>*) and time, *t*. From the slope of each straight line and molar concentrations of gallium bromide and *n*-propyl 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 generally be expressed by

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

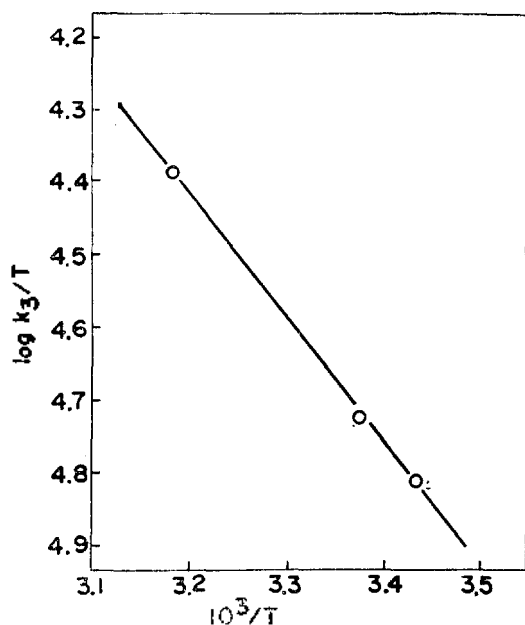
Previously, we observed that *m*=2 and *n*=1 for the exchange reactions of gallium bromide with methyl bromide, ethyl bromide, *i*-propyl bromide and *n*-butyl bromide in nitrobenzene<sup>1-4</sup>. Thus, it was assumed that *m*=2 and *n*=1 in this case with *n*-propyl bromide also.

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

The values of  $R/[\text{GaBr}_3]^2[n\text{-C}_3\text{H}_7\text{Br}]$ , 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*-propyl bromide as well as in the cases with methyl, ethyl and *n*-butyl 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.



**Figure 1.** Temperature dependence of  $\log k_3$  of the bromine exchange reaction between gallium bromide and *n*-propyl bromide in nitrobenzene.



**Figure 2.** Temperature dependence of  $\log k_3/T$  of the bromine exchange reaction between gallium bromide and *n*-propyl bromide in nitrobenzene.

**TABLE 3: Rates of Bromine Exchange between Gallium Bromide and *n*-Propyl Bromide in 1,2,4-Trichlorobenzene**

Temp. (°C)	$[\text{GaBr}_3]$ mole·l <sup>-1</sup>	$[n\text{-C}_3\text{H}_7\text{Br}]$ mole·l <sup>-1</sup>	Rate × 10 <sup>4</sup> mole·l <sup>-1</sup> sec <sup>-1</sup>	$k_3 \times 10^2$ l <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup>	
19	0.155	0.199	1.41	2.93	
	0.155	0.317	2.17	2.84	
	0.141	0.217	1.25	2.89	
	0.224	0.181	2.65	2.93	
	0.224	0.254	3.73	2.93	
	0.224	0.362	5.33	2.94	
	0.225	0.169	2.55	2.96	
	0.225	0.217	3.31	2.99	
	0.156	0.153	1.07	2.86	
	0.156	0.247	1.73	2.87	
	0.156	0.385	2.73	2.90	
	0.235	0.165	2.59	2.85	
			av.	2.91	
25	0.183	0.221	2.78	3.77	
	0.183	0.292	3.69	3.79	
	0.183	0.362	4.59	3.80	
	0.161	0.164	1.59	3.74	
	0.161	0.284	2.79	3.77	
	0.161	0.328	3.23	3.80	
	0.158	0.176	1.66	3.76	
	0.158	0.326	3.10	3.78	
				av.	3.78
	40	0.144	0.318	4.25	6.44
0.144	0.463	6.23	6.48		
0.144	0.521	7.04	6.50		
0.127	0.168	1.75	6.42		
0.127	0.346	3.61	6.45		
0.127	0.482	5.05	6.48		
0.162	0.241	4.26	6.73		
0.162	0.307	5.45	6.75		
			av.	6.53	

In order to obtain the enthalpy of activation,  $\Delta H^\ddagger$  and the entropy of activation,  $\Delta S^\ddagger$ , the  $\log(k_3/T)$  values were plotted against the reciprocal of the absolute temperature. These plots indicated good linearity (Figures 1 and 2). From slopes and intercepts of the straight lines, the activation parameters were evaluated. The results obtained are as follows:

$$E_a = 9.3 \text{ kcal/mole}, \quad \log A = 4.7,$$

$$\Delta H^\ddagger = 8.7 \text{ kcal/mole}, \quad \Delta S^\ddagger = -40 \text{ e.u.}$$

*Bromine Exchange Reaction of Gallium Bromide with *n*-Propyl Bromide in 1,2,4-Trichlorobenzene.* The rates of bromine exchange between gallium bromide and *n*-propyl bromide in 1,2,4-trichlorobenzene were also measured at 19, 25 and 40 °C. The results are summarized in Table 3.

The values of  $R/[\text{GaBr}_3]^2[n\text{-C}_3\text{H}_7\text{Br}]$ , listed in the last column of Table 3, indicated fairly good constancy at each temperature examined. Therefore, it can be concluded that the assumption of the third-order kinetics is correct in this solvent system also.

$$R = k_3[\text{GaBr}_3]^2[n\text{-C}_3\text{H}_7\text{Br}]$$

The activation parameters for the exchange reaction in 1,2,4-trichlorobenzene solution were also estimated from the

TABLE 4: Summary of Data Obtained for the Reactions of Bromine Exchange between Gallium Bromide and Alkyl Bromides

Solvent	Alkyl bromide	Kinetics (order)	$K_3(\text{at } 19^\circ\text{C})$ $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$	$E_a$ , $\text{kcal} \cdot \text{mole}^{-1}$	$\log A$	$\Delta H^\ddagger$ , $\text{Kcal} \cdot \text{mole}^{-1}$	$\Delta S^\ddagger$ , e.u.
$\text{C}_6\text{H}_5\text{Cl}_3$	$\text{CH}_3\text{Br}^a$	3rd	$0.82 \times 10^{-2}$	14	7.9	13	-24
	$\text{C}_2\text{H}_5\text{Br}^b$	3rd	$2.8 \times 10^{-2}$	8.2	4.6	7.6	-40
	$n\text{-C}_3\text{H}_7\text{Br}^c$	3rd	$2.9 \times 10^{-2}$	7.0	3.7	6.4	-44
	$n\text{-C}_4\text{H}_9\text{Br}^d$	3rd	$1.2 \times 10^{-4}$	9.0	2.8	11	-40
$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_3\text{Br}^a$	3rd	$2.4 \times 10^{-5}$	18	8.4	12	-37
	$\text{C}_2\text{H}_5\text{Br}^b$	3rd	$1.9 \times 10^{-3}$	13	6.7	12	-29
	$n\text{-C}_3\text{H}_7\text{Br}^c$	3rd	$4.5 \times 10^{-3}$	9.3	4.7	8.7	-40
	$n\text{-C}_4\text{H}_9\text{Br}^d$	3rd	$4.2 \times 10^{-4}$	6.8	1.7	8.7	-44

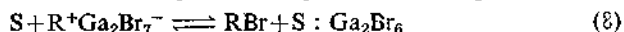
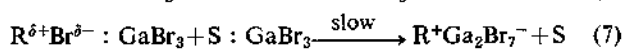
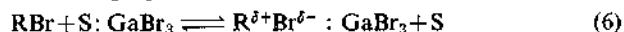
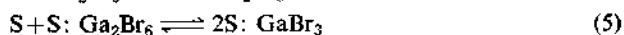
<sup>a</sup>Ref. 1, <sup>b</sup>Ref. 2, <sup>c</sup>The present study, <sup>d</sup>Ref. 4.

temperature dependence of the rate constant. From the variation of  $\log k_3$  with the reciprocal of the absolute temperature, the activation energy and logarithm of the frequency factor of the exchange reaction were estimated to be 7.0 kcal/mole and 3.7, respectively. From the variation of  $\log(k_3/T)$  with the reciprocal of the absolute temperature, the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the exchange reaction were estimated to be 6.4 kcal/mole and -44 e.u., respectively.

## Discussion

*Reaction Mechanism of the Bromine-Exchange Reaction.* As the result of the present study, it is concluded that the bromine-exchange reaction of gallium bromide with *n*-propyl bromide is second order with respect to gallium bromide and first order with respect to *n*-propyl bromide. The results of the present study are now compared with those of the previous studies on the systems of methyl bromide-gallium bromide<sup>1</sup>, ethyl bromide-gallium bromide<sup>2</sup> and *n*-butyl bromide-gallium bromide<sup>4</sup> (Table 4). It can be seen in Table 4 that all the exchange reactions are third-order reactions, second order with respect to gallium bromide and first order with respect to alkyl bromides. Therefore, it appears that these exchange reactions proceed through a similar reaction mechanism.

In the previous paper<sup>2</sup>, we postulated a reaction mechanism for the bromine-exchange reactions of gallium bromide with methyl and ethyl bromides.



If this mechanism is assumed again for the exchange reaction of *n*-propyl bromide, the step (7) may be the rate-determining step of the reaction. Thus, this mechanism leads to the following kinetic expression:

$$\text{Rate} = k[\text{S} : \text{GaBr}_3]^2 [n\text{-C}_3\text{H}_7\text{Br}]$$

This agrees with the experimental observations.

It can be seen from Table 4 that the third-order rate constants obtained with various alkyl bromides increase in the following order:



This order of increasing rates might be explained by considering that the alkyl group with longer chain forms more stable carbonium ion, and hence, leads to faster breaking of the C-Br bond in the polarized alkyl bromide-gallium bromide addition compound in step (7). On this basis, it is expected that the rate of the exchange reaction of *n*-butyl bromide should be greater than *n*-propyl bromide. This is opposite to the experimental observation. The reason for the exceptionally lower rate of *n*-butyl bromide is not clear. It is speculated, however, that the bulky group such as *n*-butyl group may hinder the polarized alkyl bromide-gallium bromide addition compound from being attacked by the species of  $\text{S} : \text{GaBr}_3$  in step (7).

It is also seen from Table 4 that there might exist solvent effects on the rates of the exchange reactions.

The rates are generally greater in 1,2,4-trichlorobenzene than in nitrobenzene, although rather reverse effect has been observed in the case on *n*-butyl bromide. The reason for the slower reaction in nitrobenzene is not clear. But, it is speculated that nitrobenzene interacts with gallium bromide to form more stable complex,  $\text{S} : \text{GaBr}_3$ , which may be more resistant against the attack by the alkyl bromide-gallium bromide addition compound in step (7).

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