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

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The rate of the bromine-exchange reaction between gallium bromide and *i*-butyl bromide in 1,2,4-trichlorobenzene or nitrobenzene was measured at 19, 25 and 40 °C., using *i*-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 *i*-butyl bromide. The third-order rate constant determined at 19°C was $3.28\times10^{-2}\ l^2\cdot\text{mole}^{-2}\cdot\text{sec}^{-1}$ in 1,2,4-trichlorobenzene and $9.25\times10^{-3}\ l^2\cdot\text{mole}^{-2}\cdot\text{sec}^{-1}$ in nitrobenzene. The activation energy, the enthalpy of activation and the entropy of activation for the exchange reaction were also determined.

Introduction

Previously we published the results of the kinetic studies, on the bromine exchange reactions of gallium bromide with methyl, ethyl, *n*-propyl, *i*-propyl and n-butyl in 1,2,4-trichlorobenzene or nitrobenzene[1-5]. The results indicated that the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides examined.

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

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[2].

The third-order rate constants obtained at 19°C for the systems of gallium bromide with *n*-propyl and *i*-propyl bromides in nitrobenzene were 4.5×10^{-3} and $3.2\times10^{-2}\ l^2\cdot\text{mole}^{-2}\text{sec}^{-1}$., respectively[3,5]. Thus, fairly large difference was observed between the two isomeric propyl bromides regarding the rates of bromine-exchange with gallium bromide. It seemed of interest to compare *n*-butyl bromide with *i*-butyl bromide as to the rates of bromine-exchange with gallium bromide. Since the system of *n*-butyl bromide with gallium bromide in 1,2,4-trichlorobenzene or nitrobenzene was already examined[4], it was decided to extend the studies to the corresponding system of *i*-butyl bromide.

Experimental Part

Apparatus and Materials. The apparatus used in the present study was essentially the same as that used previously[1,2]. The methods of preparation and/or purification of gallium bromide and solvents were described in previous papers of this series[1-5].

Preparation of i-Butyl Bromide (^{82}Br). A samll 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, and used to synthesize *i*-butyl bromide (^{82}Br) by the method described in the previous paper[6,7].

Procedures for Kinetic Study of the Exchange Reactions. The procedures for the kinetic study and the method of calculation of the exchange rates were described previously[1,2].

A solution of gallium bromide in 1,2,4-trichlorobenzene or nitrobenzene of known concentration was prepared inside the vacuum line. A known quantity of labelled *i*-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 *i*–butyl bromide vapor above the reaction–mixture solution was measured at constant time intervals with the scintillation counter (well type scintillation detector–Nuclear Chicago, Model 967 and scaler–Nuclear Chicago, Model 8703). From the measured counting rates as a function of time, the rate of exchange of bromine between gallium bromide and *i*–butyl bromide in solution was determined by the usual Guggenheim method[1,2];

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

where a denotes the molar concentration of gallium bromide and b that of *i*–butyl bromide in solution.

Procedures for the Solubility Determinations. In order to calculate the rates of the exchange reactions, the solubility of *i*–butyl bromide in the solution of gallium bromide in both 1,2,4–trichlorobenzene or nitrobenzene was measured. The apparatus and procedures were similar to those described previously[2,5].

Results

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

TABLE 1: Solubilities of *i*–Butyl Bromide in Nitrobenzene and 1,2,4–Trichlorobenzene in the Presence and Absence of Gallium Bromide

Solvent	Temp. (°C)	$[GaBr_3]$ mole·l^{-1}	Henry's law Const. (mm)[a]
$C_6H_5NO_2$	19	0	131
		0	131
		0.179	119
		0.221	119
		0.312	118
	25	0	172
		0	171
		0.106	150
		0.142	150
	40	0	270
		0	270
		0.179	245
		0.233	245
$C_6H_3Cl_3$	19	0	139
		0	139
		0.157	118
		0.202	117
		0.273	117
	25	0	210
		0	210
		0.182	173
		0.237	173
	40	0	306
		0	306
		0.184	265
		0.375	265

[a]; Henry'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 *i*–butyl bromide over gallium bromide solution are smaller than those observed in the pure solvent at each temperature. This indicates that *i*–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 *i*–butyl bromide in solution, as was considered in the previous studies[2,5,8].

Bromine–Exchange Reaction of Gallium Bromide with i–Butyl Bromide in Nitrobenzene. The rate of bromine exchange between gallium bromide and *i*–butyl bromide in nitrobenzene was 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 the slope of each straight line and molar concentrations of gallium bromide and *i*–butyl bromide, the rate of the bromine exchange, R, was calculated by equation (1). The results are summarized in Table 2. The rate of the bromine exchange between gallium bromide and alkyl bromides may generally be expressed by

$$R = k[GaBr_3]^m[RBr]^n \qquad (2)$$

Previously, we observed that $m=2$ and $n=1$ for the exchange reactions of gallium bromide with methyl bromide, ethyl bromide, *n*–propyl bromide, *i*–propyl bromide and *n*–butyl bromide in nitrobenzene[1~5]. Thus, it was assumed that $m=2$ and $n=1$ in this case with *i*–butyl bromide also.

TABLE 2: Rates of Bromine Exchange between Gallium Bromide and *i*–Butyl Bromide in Nitrobenzene.

Temp. (°C)	$[GaBr_3]$ mole·l^{-1}	$[i\text{–}C_4H_9Br]$ mole·l^{-1}	Rate×10^4 mole·l^{-} sec^{-1}	$k_3 \times 10^3$ l^2·mole^{-2}sec^{-1}
19	0.288	0.141	1.06	9.08
	0.288	0.353	2.49	8.52
	0.288	0.524	3.96	9.14
	0.248	0.282	1.69	9.73
	0.248	0.401	2.42	9.77
	0.354	0.386	4.37	9.02
	0.354	0.669	7.64	9.11
	0.354	0.804	9.68	9.61
			av.	9.25
25	0.308	0.397	4.08	10.8
	0.308	0.504	5.28	11.0
	0.308	0.858	9.27	11.4
	0.151	0.350	0.83	10.9
	0.151	0.424	1.10	11.4
	0.151	0.665	1.73	11.5
	0.214	0.260	1.30	10.8
	0.214	0.467	2.37	11.0
			av.	11.1
40	0.160	0.276	1.30	18.4
	0.160	0.380.	1.82	18.7
	0.160	0.507	2.49	19.2
	0.167	0.488	2.52	18.6
	0.167	0.604	3.08	18.3
	0.167	0.744	3.76	18.1
	0.261	0.230	2.83	18.0
	0.261	0.381	4.85	18.6
			av.	18.5

$$R=k_3[\mathrm{GaBr_3}]^2[i\text{-}\mathrm{C_4H_9Br}] \qquad (3)$$

The values of $R/[\mathrm{GaBr_3}]^2\ [i\text{-}\mathrm{C_4H_9Br}]$, 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 *i*-butyl bromide as well as the other alkyl 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 the enthalpy of activation $\Delta H^{\neq}$, and the entropy of activation, $\Delta S^{\neq}$, 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;

$$E_a=6.2\ \text{kcal/mole}, \qquad \log A=2.5,$$
$$\Delta H^{\neq}=5.5\ \text{kcal/mole}. \qquad \Delta S^{\neq}=-49\ \text{e.u.}$$

Bromine Exchange Reaction of Gallium Bromide with i-Butyl Bromide in 1,2,4-*Trichlorobenzene.* The rate of bromine exchange between gallium bromide and *i*-butyl bromide in 1, 2, 4-trichlorobenzene was also measured at 19 , 25 and 40 °C. The results are summarized in Table 3.

The values of $R/[\mathrm{GaBr_3}]^2\ [i\text{-}\mathrm{C_4H_9Br}]$, 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.

$$R=k_3[\mathrm{GaBr_3}]^2\ [i\text{-}\mathrm{C_4H_9Br}]$$

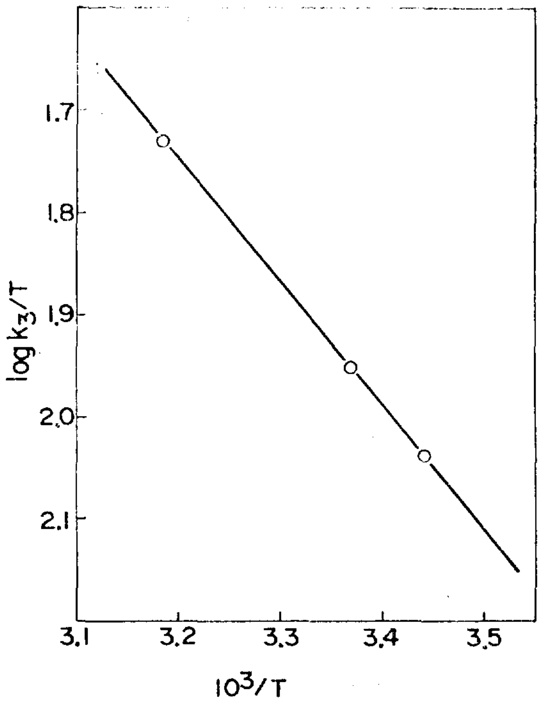

Figure 1. Temperature dependence of log k_3 of the bromine exchange reaction between gallium bromide and *i*-butyl bromide in nitrobenzene.

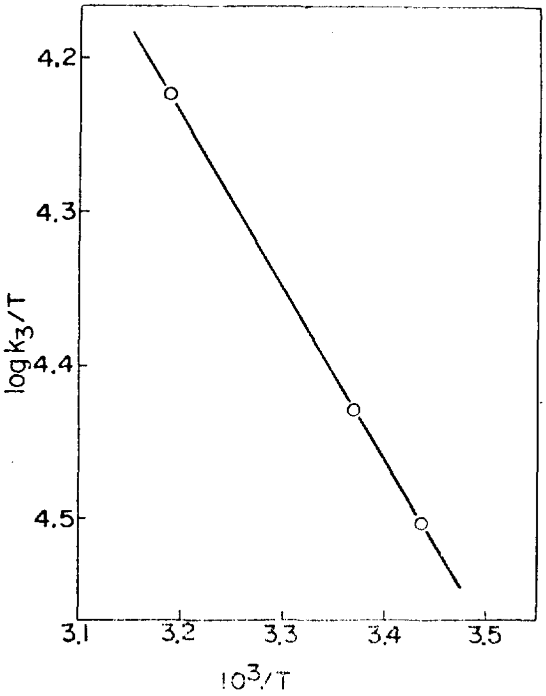

Figure 2. Temperature dependence of log k_3/T of the bromine exchange reaction between gallium bromide and *i*-butyl bromide in nitrobenzene.

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

Temp. (°C)	$[\mathrm{GaBr_3}]$ mole·l^{-1}	$[i\text{-}\mathrm{C_4H_9Br}]$ mole·l^{-1}	Rate$\times10^4$ mole·l^{-1}·sec^{-1}	$k_3\times10^2$ l^2·mole^{-2}·sec^{-1}
19	0.246	0.432	8.24	3.16
	0.246	0.579	11.2	3.22
	0.246	0.632	12.5	3.27
	0.220	0.237	3.63	3.17
	0.220	0.357	5.51	3.19
	0.176	0.388	3.94	3.26
	0.163	0.309	2.72	3.32
	0.163	0.414	3.72	3.40
	0.163	0.443	4.13	3.53
			av.	3.28
25	0.210	0.299	5.43	4.12
	0.210	0.426	7.82	4.16
	0.210	0.609	11.4	4.25
	0.219	0.325	6.29	4.05
	0.219	0.534	10.5	4.11
	0.219	0.602	12.0	4.16
	0.304	0.285	10.8	4.11
	0.304	0.513	20.3	4.28
			av.	4.16
40	0.207	0.220	6.73	7.15
	0.207	0.326	10.1	7.23
	0.207	0.504	15.7	7.29
	0.169	0.193	4.21	7.60
	0.169	0.304	6.63	7.61
	0.169	0.510	11.2	7.68
	0.264	0.244	12.3	7.24
	0.264	0.453	22.6	7.16
			av.	7.37

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

Solvent	Alkyl bromide	Kinetics (order)	k_3(at19°C) $l^2\cdot$mole$^{-2}\cdot$sec^{-1}	E_a, kcal·mole^{-1}	log A	$\Delta H^{\ddagger}$, kcal·mole^{-1}	$\Delta S^{\ddagger}$, e.u.
$C_6H_5NO_2$	n-$C_3H_7Br^a$	3rd	4.5×10^{-3}	9.3	4.7	8.7	−40
	i-$C_3H_7Br^b$	3rd	3.2×10^{-2}	11	6.5	10	−31
	n-$C_4H_9Br^c$	3rd	4.2×10^{-4}	6.8	1.7	8.7	−44
	i-$C_4H_9Br^d$	3rd	9.3×10^{-3}	6.1	2.5	5.5	−49
$C_6H_3Cl_3$	n-$C_4H_9Br^c$	3rd	1.2×10^{-4}	9.0	2.8	11	−40
	i-$C_4H_9Br^d$	3rd	3.3×10^{-2}	7.0	3.8	6.4	−43

[a] Ref. 5, [b] Ref. 3, [c] Ref. 4, [d] The present study.

The activation parameters for the exchange reaction were also estimated from the 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 3.8, 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 −43 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 i-butyl bromide is second order with respect to gallium bromide and first order with respect to i-butyl bromide. The results of the present study are now compared with those of the previous studies with other allkyl bromides (Table 4)[3,5]. 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[2], we postulated reaction mechanism for the bromine-exchange reactions of gallium bromide with methyl and ethyl bromides.

$$S+Ga_2Br_6 \rightleftharpoons S:Ga_2Br_6 \quad (4)$$

$$S+S:Ga_2Br_6 \rightleftharpoons 2S:GaBr_3 \quad (5)$$

$$RBr+S:GaBr_3 \rightleftharpoons R^{\delta+}Br^{\delta-}:GaBr_3+S \quad (6)$$

$$R^{\delta+}Br^{\delta-}:GaBr_3+S:GaBr_3 \xrightarrow{\text{slow}} R^+Ga_2Br^-_7+S \quad (7)$$

$$S+R^+Ga_2Br^-_7 \rightleftharpoons RBr+S:Ga_2Br_6 \quad (8)$$

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

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

This agrees with the experimental observations.

It can also be seen from Table 4 that n-alkyl bromides exchange bromine with gallium bromide much more slowly than the corresponding i-alkyl bromide isomers. This might be explained by considering that the i-alkyl groups form more stable carbonium ions than the corresponding n-alkyl groups, and hence, the i-alkyl groups may lead to faster breaking of the C–Br bond in step (7) than the corresponding n-alkyl groups.

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