

was therefore compared with that of a Freon 13 solution containing 1 vol. % of O_3F_2 alone. If the equilibrium reaction is responsible, the intensity of the former should be weaker than that of the latter by a factor of 2-3. Instead it was stronger. Thus, the decomposition

reaction characterized above appears to be responsible for the abundant $FO_2\cdot$ radical in O_3F_2 .

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Exchange Reactions of Gallium Bromide with Hydrogen Bromide and with Methyl Bromide in 1,2,4-Trichlorobenzene and in Nitrobenzene¹

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The solubilities of HBr and CH_3Br in 1,2,4-trichlorobenzene and in nitrobenzene have been determined with and without gallium bromide in solution. They all obey Henry's law over the limits tested except for the $C_6H_5NO_2-GaBr_3-HBr$ system where there is evidence for a 1:1 $GaBr_3-HBr$ complex. Values for the Henry's law constants are given. The experimental rate laws for exchange of bromine with $GaBr_3$ are $R = k[HBr]^2$ for HBr and $R = k[CH_3Br][GaBr_3]^2$ for CH_3Br , seemingly independent of the complexing. Temperature coefficients have been determined. The observed exchange is much faster for HBr than for CH_3Br . Exchange is faster in 1,2,4-trichlorobenzene than in nitrobenzene, the difference between solvents being much greater for CH_3Br than for HBr.

Introduction

Gallium bromide catalyzes the alkylation of aromatic compounds by alkyl bromides, the kinetics of the reaction being dependent on the solvent. In pure benzene or toluene the rate is proportional to the square of the gallium bromide concentration and independent of the alkyl bromide^{2,3} concentration, whereas in 1,2,4-trichlorobenzene the reactions are first order with respect to each reactant: the aromatic, the alkyl bromide, and the catalyst.⁴

To investigate the interaction of an alkyl bromide with gallium bromide in the absence of an aromatic reactant, we have determined the kinetics of the exchange of bromine between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene and in nitrobenzene. For comparison, and because HBr is a product of alkylations catalyzed by gallium bromide, we have studied the exchange reactions between gallium bromide and HBr in the same solvents. Gallium bromide forms homogeneous solutions, making it possible to determine quantitatively the dependence of exchange

rates on its concentration, in contrast to the exchange studies which have been made with a number of other metal halide catalysts.⁵ In order to know the concentrations of CH_3Br and HBr in the exchange experiments and whether they are appreciably complexed with gallium bromide, we have determined their Henry's law solubility constants in 1,2,4-trichlorobenzene and in nitrobenzene in the absence and presence of gallium bromide.

Experimental

Materials. Gallium bromide, prepared by the direct combination of metallic gallium with bromine,⁶ was sealed in small ampoules with fragile tips after several resublimations *in vacuo*. Nitrobenzene (Baker Chemical Co., purified) and 1,2,4-trichlorobenzene (Eastman Organic Chemicals, practical) were fractionated in a Todd column and stored over Drierite until used. Hydrogen bromide (Matheson Co.) and methyl bromide (Matheson Co.) were introduced from the cylinders into the vacuum line through a phosphorus pentoxide column.

Procedures for the Exchange Studies. The gallium bromide for each exchange run was sublimed into the reaction vessel in the vacuum system by heating after breaking the tip of an ampoule with a magnetic hammer. Dry Ice was used to aid in condensing the sublimate at the desired place. Following the sublimation, the tube containing the gallium bromide ampoule was sealed off from the vacuum system, and the weight of gallium bromide which had been introduced to the reaction vessel was determined by the difference in weight of the ampoule and its fragments before and after the transfer. The solvent was distilled through a phosphorus pentoxide column onto the gallium bromide. Figure 1 shows the reaction system as it appeared after sealing off the tubes used for introduction of gallium bromide and solvent. A known quantity of $HBr(Br^{82})$ or $CH_3Br(Br^{82})$ was frozen into the system GFB from the calibrated bulb E. With the aid of the

(1) (a) This work was supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-32; (b) presented at the XVIIth International Congress of Pure and Applied Chemistry, Munich, Germany, 1959.

(2) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245 (1956).

(3) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

(4) S. U. Choi and H. C. Brown, *ibid.*, **85**, 2596 (1963).

(5) (a) C. H. Wallace and J. E. Willard, *ibid.*, **72**, 5275 (1950); (b) W. T. Carnall, M. Blau, and J. E. Willard, *ibid.*, **74**, 5762 (1952); (c) M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951); **75**, 3330 (1953).

(6) W. C. Johnson and J. B. Parsons, *J. Phys. Chem.*, **34**, 1210 (1930).

warming coil G it was then circulated continuously over the surface of the magnetically stirred solution and through an annular vessel F surrounding a thin-walled Geiger tube. The temperature of the reaction vessel was maintained by a surrounding bath.

From the observed counting rates as a function of time the rate of exchange of bromine was determined by the usual relationship⁷ modified to utilize the Guggenheim method⁸ to eliminate the error of repeated use of a measured value of the exchange at infinite time. The relationship used was

$$R = -2.3 \left(\frac{3ab}{3a + b} \right) \frac{\log(A_{t+\tau} - A_t)}{t}$$

where a denotes the molar concentration of gallium bromide and b that of hydrogen bromide or methyl bromide in solution. The term $(A_{t+\tau} - A_t)$ represents the change in counting rate during a constant time interval τ starting at different times t after the start of reaction. Counting rates used were ordinarily in the range of 1000–10,000/min.

The experiments on the very slow exchange of methyl bromide with gallium bromide in nitrobenzene were carried out using a separate sample in a sealed ampoule to determine each data point. On opening the ampoules an aqueous-organic extraction was done and the two phases were counted separately. The exchange rates were calculated by the standard equation.⁷

Procedures for the Solubility Determinations. The apparatus used to determine the solubilities of hydrogen bromide and methyl bromide in the solutions of gallium bromide in 1,2,4-trichlorobenzene and in nitrobenzene was similar to that of Figure 1 but employed a second mercury manometer which allowed the pressure in the reaction vessel system GFB to be measured independently of the storage system E.

A known quantity of hydrogen bromide or methyl bromide was transferred from the calibrated volume E to the reaction vessel B, which contained the solution of gallium bromide of known volume and concentration. The liquid phase in the vessel was magnetically stirred until pressure equilibrium was indicated by the manometer. Then the pressure and temperature of the gas volume of the system were measured. This procedure was repeated after each of successive additions of hydrogen bromide or methyl bromide to the reaction vessel. The solubilities of the bromides were determined at several temperatures from a knowledge of the pressures, volumes, and temperatures of the gas volumes of the system and the volume of the liquid phase.

Results

Solubility Determinations. The solubilities of hydrogen bromide and methyl bromide in 1,2,4-trichlorobenzene and in nitrobenzene with and without gallium bromide dissolved, determined at several different temperatures, are summarized in Table I. Both gaseous solutes gave clear, colorless solutions in both solvents in the absence of gallium bromide. In the absence of hydrogen bromide or methyl bromide, both solvents showed a light yellow color when gallium bromide was

(7) See, for example, R. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

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

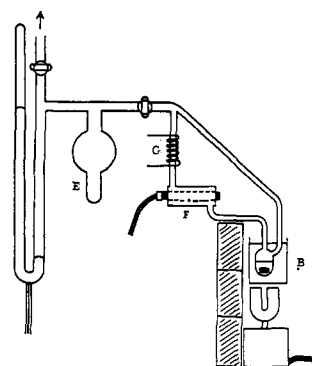


Figure 1. Apparatus for determining the rate of exchange of dissolved gallium bromide with hydrogen bromide and with methyl bromide.

dissolved. This light yellow turned toward amber-red or brown when hydrogen bromide or methyl bromide was added.

Table I. Solubilities of Hydrogen Bromide and of Methyl Bromide in 1,2,4-Trichlorobenzene and in Nitrobenzene with and without Dissolved Gallium Bromide

Solute gas	Solvent	[GaBr ₃], moles/l.	Temp., °C.	Henry's law const., ^a mm. × 10 ⁻³		
HBr	C ₆ H ₃ Cl ₃	0	19	18.2		
		0	25	23.6		
		0	40	29.2		
		0.114	19	16.2		
		0.134	19	16.0		
		0.168	19	16.0		
		0.247	19	16.6		
		0.191	40	26.0		
		HBr	C ₆ H ₅ NO ₂	0	5.5	4.98
				0	19	7.13
0	25			8.53		
0.112	5.5			... ^b		
0.341	19			... ^b		
0.397	19			... ^b		
CH ₃ Br	C ₆ H ₃ Cl ₃			0	19	1.96
		0	25	2.46		
		0	40	4.00		
		0.121	19	1.76		
		0.134	19	1.78		
		0.168	19	1.73		
		0.155	25	2.18		
		0.286	40	3.50		
		CH ₃ Br	C ₆ H ₅ NO ₂	0	5.5	1.15
				0	19	1.79
0	25			2.17		
0.293	5.5			1.08		
0.235	19			1.72		

^a Henry's law constant = equilibrium pressure of the gas (mm.) divided by its mole fraction in the solution. ^b Did not obey Henry's law.

All the systems, except HBr–GaBr₃–C₆H₅NO₂, gave linear relationships between the equilibrium pressure of hydrogen bromide or methyl bromide and the mole fraction of the bromide in solution at the temperature studied.

The Henry's law constants in the gallium bromide solutions were some 10% smaller than the corresponding values obtained in the pure solvents at each temperature, indicating an interaction between the gallium bro-

amide and hydrogen bromide or methyl bromide.

The system of $\text{HBr-GaBr}_3\text{-C}_6\text{H}_5\text{NO}_2$ did not obey Henry's law. Upon adding successive increments of hydrogen bromide to the solution of gallium bromide in nitrobenzene, the pressure of hydrogen bromide above the solution increased only slowly until the mole ratio of HBr/GaBr_3 approached 1.0, after which a rapid increase in pressure was observed as shown in Figure 2. This indicates that an addition compound of the composition $(\text{C}_6\text{H}_5\text{NO}_2)_n\text{GaBr}_3\text{HBr}$ is formed in solution.

Exchange Determinations. Data on the rate of the bromine exchange reaction between gallium bromide and hydrogen bromide in 1,2,4-trichlorobenzene at 19 and 40° and on the exchange in nitrobenzene at 19 and 5.5° are given in Tables II and III.

Table II. Rates of Exchange of Bromine between Hydrogen Bromide and Gallium Bromide in 1,2,4-Trichlorobenzene

Temp., °C.	[GaBr ₃], mole/l.	[HBr], mole/l. ^a	Rate, moles l. ⁻¹ sec. ⁻¹ × 10 ⁶	R/[HBr] ² , l. mole ⁻¹ sec. ⁻¹ × 10 ²
19	0.191	0.12	100	6.9
	0.191	0.058	25	7.4
	0.191	0.035	10	8.2
	0.191	0.024	5.2	9.0
	0.0908	0.032	8.5	8.3
	0.0908	0.021	3.5	7.9
	0.0550	0.023	4.1	7.8
	0.141	0.049	19	7.9 ^b
	0.141	0.048	19	8.2 ^c
	0.0572	0.065	38	9.0 ^d
	0.0572	0.065	5.1	8.2 ^d
	0.0465	0.044	15	7.7 ^d
	0.0465	0.034	9.6	8.3 ^d
	0.0177	0.041	14	8.3 ^d
0.0177	0.026	6.3	9.3 ^d	
		Average	8.2	
40	0.191	0.032	13	13
	0.0908	0.019	5.6	16
	0.0550	0.030	14	16
			Average	15

^a These values for HBr concentration and those for HBr and CH_3Br in subsequent tables are for the formal concentration in solution, exclusive of that in the gas phase. ^b With faster stirring of the solution. ^c With slower stirring of the solution. ^d With larger reaction vessel.

Table III. Rates of Exchange of Bromine between Hydrogen Bromide and Gallium Bromide in Nitrobenzene

Temp., °C.	[GaBr ₃], mole/l.	[HBr], mole/l.	Rate, moles l. ⁻¹ sec. ⁻¹ × 10 ⁴	R/[HBr] ² , l. mole ⁻¹ sec. ⁻¹ × 10 ²
19	0.157	0.40	16	1.0
	0.157	0.32	12	1.2
	0.157	0.25	6.8	1.1
	0.109	0.37	17	1.2
	0.109	0.25	7.3	1.2
	0.109	0.23	6.5	1.2
	0.0422	0.16	3.1	1.2
			Average	1.2
5.5	0.238	0.48	14	0.61
	0.112	0.42	11	0.62
	0.112	0.41	11	0.65
		Average	0.63	

Data on the rate of exchange between gallium bromide and methyl bromide in 1,2,4-trichlorobenzene at 19, 25, and 40° and in nitrobenzene at 19 and 5.5° are given in Tables IV and V. The values in the last column of each table are considered in the Discussion section.

Table IV. Rates of Exchange of Bromine between Methyl Bromide and Gallium Bromide in 1,2,4-Trichlorobenzene

Temp., °C.	[GaBr ₃], mole/l.	[CH ₃ Br], mole/l.	Rate, moles l. ⁻¹ sec. ⁻¹ × 10 ⁵	R/[GaBr ₃] ² [CH ₃ Br], l. ² mole ⁻² sec. ⁻¹ × 10 ²
19	0.244	0.77	37	0.81
	0.207	0.75	26	0.81
	0.207	0.20	6.7	0.78
	0.156	0.77	15	0.80
	0.156	0.52	11	0.87
	0.156	0.20	3.9	0.82
	0.093	0.59	4.4	0.86
		Average		0.82
25	0.286	0.34	40	1.4
	0.155	0.48	16	1.4
		Average		1.4
40	0.286	0.24	77	3.9
	0.155	0.61	54	3.7
	0.0930	0.39	14	4.2
			Average	3.9

Table V. Rates of Exchange of Bromine between Methyl Bromide and Gallium Bromide in Nitrobenzene

Temp., °C.	[GaBr ₃], mole/l.	[CH ₃ Br], mole/l.	Rate, moles l. ⁻¹ sec. ⁻¹ × 10 ⁷	R/[GaBr ₃] ² [CH ₃ Br], l. ² mole ⁻² sec. ⁻¹ × 10 ⁵
19	0.388	0.37	10	1.8
	0.266	0.55	11	2.8
	0.213	0.82	10	2.7
	0.211	0.35	3.6	2.3
			Average	2.4
5.5	0.293	0.36	2.1	0.68
	0.263	0.53	1.9	0.55
	0.223	0.20	0.50	0.50
	0.116	0.36	0.24	0.50
			Average	0.56

Discussion

Inspection of Tables II through IV shows that the rate of the HBr exchange is independent of the gallium bromide concentration but dependent upon the formal HBr concentration in both solvents, while the rate of the CH_3Br exchange is influenced by both the gallium bromide and CH_3Br concentrations.

Assuming that the formal concentrations of HBr and GaBr_3 (or Ga_2Br_6) in solution are equal to or proportional to the concentrations of the actual exchanging species, the values of m and n in the rate expression, $R = k[\text{GaBr}_3]^m[\text{HBr}]^n$, may be determined. If $\log R$ is plotted against $\log [\text{HBr}]$ for the data of Tables II and III, all points fall on a straight line for each solvent (Figure 3) including determinations over a tenfold range of GaBr_3 concentration in 1,2,4-trichlorobenzene. For each solvent the slope of the line is 2. This implies that the exchange reaction at the concentrations

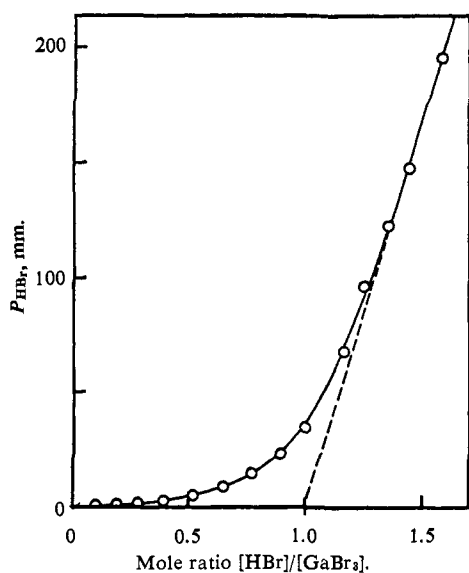


Figure 2. Solubility of hydrogen bromide in nitrobenzene containing 0.397 *M* gallium bromide at 19°.

tested is zero order with respect to gallium bromide and second order with respect to the formal HBr concentration. The last column of each table shows the apparent second-order rate constant obtained from the relation $R = k[\text{HBr}]^2$. The temperature dependence in terms of the apparent activation energy derived from these values is 5 kcal. mole⁻¹ in 1,2,4-trichlorobenzene and 8 kcal. mole⁻¹ in nitrobenzene.

The plots of $\log R$ vs. $[\text{CH}_3\text{Br}]$ for two different concentrations of GaBr₃ in 1,2,4-trichlorobenzene in Figure 4 each have a slope of 1, while the plot of $\log (R/[\text{CH}_3\text{Br}])$ vs. $\log [\text{GaBr}_3]$ in Figure 5 has a slope of 2, indicating the rate equation $R = k[\text{GaBr}_3]^2[\text{CH}_3\text{Br}]$. The data of Table V for nitrobenzene as solvent for the CH₃Br exchange indicate the same rate expression but much smaller rate constants. The apparent activation energies are 14 kcal. mole⁻¹ in 1,2,4-trichlorobenzene and 18 kcal. mole⁻¹ in nitrobenzene.

An assumption that the formal concentrations of HBr and GaBr₃ are equal to the actual concentrations of these species is clearly incorrect in nitrobenzene solutions in which the 1:1 complex is formed (Figure 2). Yet the data of Table III fit the second-order dependence on total [HBr] well, and better than other relationships we have tried including different types of dependence on the estimated concentration of the HBr not complexed with GaBr₃. If the second-order dependence in this case has physical significance, it indicates that the formation of the GaBr₃-HBr complex, which accounts for the lowering of the HBr vapor pressure illustrated in Figure 2, is not involved as a rate-determining step in the exchange, but that the HBr in the complex is as available for participation in such rate-determining steps as that which is not complexed.

Aside from the HBr-GaBr₃-C₆H₅NO₂ system, the systems studied obeyed Henry's law, and the Henry's law constants for the solubilities were only slightly different in the presence of GaBr₃ than in the pure solvents, indicating relatively little complexing with GaBr₃ though color changes showed that some must occur. The ratios of the observed Henry's law con-

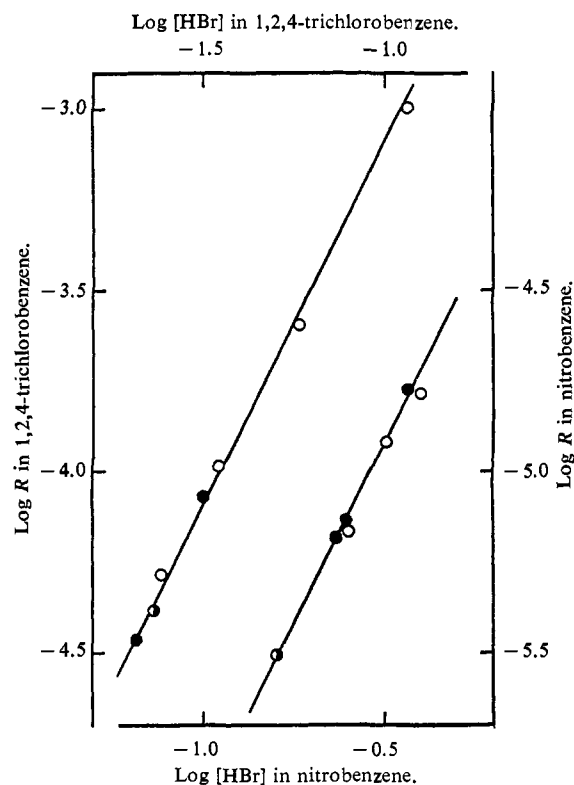


Figure 3. The effect of concentration of hydrogen bromide on the rate of bromine exchange between hydrogen bromide and gallium bromide in 1,2,4-trichlorobenzene and in nitrobenzene at 19°: Upper line for C₆H₃Cl₃: ●, 0.0908 *M* GaBr₃; ◐, 0.0550 *M* GaBr₃; ○, 0.191 *M* GaBr₃. Lower line for C₆H₅NO₂: ●, 0.109 *M* GaBr₃; ◐, 0.0422 *M* GaBr₃; ○, 0.157 *M* GaBr₃.

stants to the ideal solution constants calculated from the vapor pressures of the pure solutes and their mole fractions were 1.1 for HBr in 1,2,4-C₆H₃Cl₃, 0.42 for HBr in C₆H₅NO₂, 1.5 for CH₃Br in 1,2,4-C₆H₃Cl₃, and 1.3 for CH₃Br in C₆H₅NO₂.

The systems studied may contain GaBr₃ as the monomer or dimer in different proportions as well as various complexes of each with the solvent and with the HBr or CH₃Br. The distribution of these species is not known. The experimental rate equations indicate that two or more elementary steps must be involved in the exchange process in each case but do not make possible a decision as to their nature. Certain possibilities can, however, be evaluated.

Thus, the zero-order dependence of the hydrogen bromide exchange on gallium bromide concentration might be explained if all of the hydrogen bromide in the solutions were rapidly complexed with gallium bromide. This possibility is eliminated by the lack of evidence for such complexing in 1,2,4-trichlorobenzene (Table I) and by the fact that the hydrogen bromide concentrations in the nitrobenzene studies and in some of the trichlorobenzene measurements were substantially in excess of the gallium bromide concentration. The zero-order dependence on the gallium bromide concentration would result if the hydrogen bromide must form a complex with the solvent by a slow step prior to rapid exchange with gallium bromide. There is no evidence for this other than the observed kinetics. If the dissolution equilibrium between hydrogen bromide in the gas phase and hydrogen bromide in solution were achieved only slowly compared to the rate of

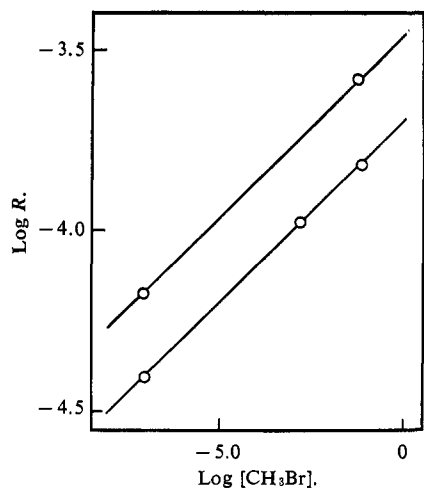


Figure 4. The effect of concentration of methyl bromide on the rate of bromine exchange reaction between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene at 19°: upper line, 0.20 *M* GaBr₃; lower line, 0.156 *M* GaBr₃.

exchange of dissolved hydrogen bromide with gallium bromide, the exchange would be zero order in gallium bromide. Changes in rate of stirring or size of reaction vessel did not significantly alter the rate in the HBr-GaBr₃-C₆H₃Cl₃ system (Table II). The second-order dependence of the hydrogen bromide exchange reaction on hydrogen bromide concentration in each solvent indicates either that two molecules of hydrogen bromide are involved in the molecular complex at the time of exchange or that two intermediate steps in the exchange mechanism each require one molecule of hydrogen bromide.

The observed rates of bromine exchange between hydrogen bromide and gallium bromide are much faster than between methyl bromide and gallium bromide at similar concentrations (Tables II to V) and the rate-determining steps are different. The measurements necessary to obtain rate constants required 15 to 20 min. in the hydrogen bromide experiments, whereas the methyl bromide experiments required about 1 hr. in 1,2,4-trichlorobenzene and 1 to 3 days in nitrobenzene. The difference in rates of exchange between the two solvents was about 400-fold for methyl bromide but only 7 for hydrogen bromide.

The rate equation for the CH₃Br exchanges is consistent with the possibility that CH₃Br may not be able to exchange with monomeric GaBr₃ (which may be primarily in a solvated form) but is able to exchange with Ga₂Br₆. The concentration of the latter would be proportional to the square of the amount of gallium bromide added if most of the material is in the mono-

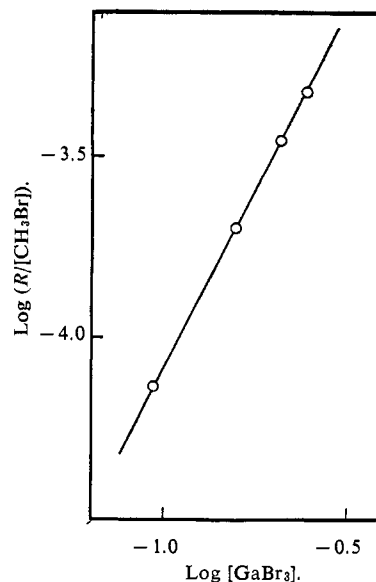


Figure 5. The effect of concentration of gallium bromide on the rate of bromine exchange reaction between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene at 19°.

meric form which is in equilibrium with some of the dimer.⁹

Kinetic data on Friedel-Crafts reactions and bromine exchange reactions involving gallium bromide now include the following: (a) for the gallium bromide catalyzed alkylation of benzene and toluene with the aromatic compound as solvent,^{2,3} $R = k[\text{gallium bromide}]^2$; (b) for the gallium bromide catalyzed alkylation of benzene and of toluene in 1,2,4-trichlorobenzene,⁴ $R = k[\text{RBr}][\text{aromatic}][\text{gallium bromide}]$; (c) for the exchange of bromine between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene or nitrobenzene, $R = k[\text{CH}_3\text{Br}][\text{gallium bromide}]^2$; (d) for the exchange of bromine between hydrogen bromide and gallium bromide in 1,2,4-trichlorobenzene or nitrobenzene, $R = k[\text{HBr}]^2$.

The available information does not appear adequate to provide a definitive correlation of these widely different rate expressions in terms of mechanisms. Further understanding of these systems should be assisted by studies of the exchange reactions in pure benzene and toluene, by determinations of the distribution of dimeric and monomeric forms of gallium bromide in the solvents used, and by studies over extended concentration ranges.

(9) Similar kinetics have been reported for the bromine exchange reaction between aluminum bromide and ethyl bromide in carbon disulfide: F. L. J. Sixma, H. Hendriks, and D. Holtzapffel, *Rec. trav. chim.*, 75, 127 (1956).