

고진공 상태에서 아닐린과 *o*-클로로 아닐린 용액중 브롬화갈륨과 브롬화에탄과의 착물형성에 관한 연구

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The Study on Complex of Gallium Bromide with Ethyl Bromide in Aniline and in *o*-Chloroaniline under High Vacuum

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요 약. 아닐린 및 *o*-클로로아닐린 용액내에서 브롬화에탄의 용해도를 5, 15° 및 25°C에서 브롬화갈륨이 존재할 때와 존재하지 않을 때의 두 경우에 대하여 각각 측정하여 보았다. 브롬화갈륨이 존재하지 않을 때에 *o*-클로로아닐린에서 브롬화에탄의 용해도가 아닐린에서 보다 크다. 이것은 브롬화에탄과 *o*-클로로아닐린의 상호작용이 아닐린보다 더 강하다는 것을 나타낸다. 그리고 브롬화갈륨이 존재할 경우에는 용액내에서 브롬화에탄과 브롬화갈륨이 불안정한 착물이 생성된다. 이 착물을 여러 경우로 가정하여 계산하여 본 결과 1:1 착물일 때, 불안정 상수 *K*값이 비교적 일정한 값을 나타내었다. 그러므로 1:1 착물 $C_2H_5Br \cdot GaBr_3$ 가 형성됨을 알았으며, 이 착물은 용액내에서 다음 평형식에 의해서 이루어진다고 본다. $C_2H_5Br \cdot GaBr_3 \rightleftharpoons C_2H_5Br + 1/2Ga_2Br_6$. 브롬화갈륨과 브롬화에탄의 착물의 불안정도를 이와 대응하는 브롬화에탄과 비교하여 보았다. 또한 이 착물의 해리에 대한 엔탈피, 자유에너지 및 엔트로피 변화도 산출하였다.

ABSTRACT. The solubilities of ethyl bromide in aniline and *o*-chloroaniline have been measured at 5, 15° and 25°C in the presence and the absence of gallium bromide. When gallium bromide does not exist in the system, the solubility of ethyl bromide in *o*-chloroaniline is greater than in aniline, indicating a stronger interaction of ethyl bromide with *o*-chloroaniline than that with aniline. It could be thought that ethyl bromide forms unstable complex with gallium bromide in the presence of gallium bromide in the system. This complex has been assumed in various ways and evaluated, that instability constant (*K* value) is relatively constancy under the assumption of 1:1 complex, $C_2H_5Br \cdot GaBr_3$. Therefore, the complex forms the following equilibrium in the solution: $C_2H_5Br \cdot GaBr_3 \rightleftharpoons C_2H_5Br + 1/2Ga_2Br_6$. The instability of the complex of ethyl bromide with gallium bromide is compared with similar complexes of gallium bromide with methyl bromide. The changes of enthalpy, free energy and entropy for the dissociation of the complex are also calculated.

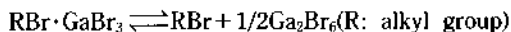
INTRODUCTION

It has been reported that gallium bromide was an effective, but mild catalyst¹ which avoid undesirable side reaction, such as isomerization and disproportion, characteristic of aluminium bromide and gallium chloride catalysis^{2,3}. In order to inves-

tigate more precisely its reaction mechanism, kinetic studies have been carried out by Brown *et al.*⁴⁻⁶.

In addition has been reported that the systematic studies of the interaction between gallium iodide and alkyl iodide in nitrobenzene and *m*-xy-

lene⁷⁻⁹ are made and also a relation of the interaction between gallium bromide and alkyl bromide in nitrobenzene and 1,2,4-trichlorobenzene¹⁰⁻¹⁵ at 19°C is expressed following equation:



In this study an attempt has been made to closely examine the latter interaction of gallium bromide and alkyl bromide measuring the solubilities of gallium bromide in aniline and *o*-chloroaniline at 5, 15° and 25°C in the presence and absence of gallium bromide. The instability constant *K* of the complex $RBr \cdot GaBr_3$ is evaluated from the results of the attempt and compared with the previously obtained one¹⁶. The change of enthalpy, free energy and entropy are calculated by using of the relation between *K* and temperature. The stability of the complex is compared with that of methyl bromide.

EXPERIMENT

Material. The gallium bromide was prepared by the direct combination of metallic gallium with bromine in high vacuum line¹⁷ ($10^{-5} \sim 10^{-6}$ torr). The sample of aniline (Reagent grade, Merck, Germany) and *o*-chloroaniline (Reagent grade, Merck,

Germany) were used without further purification. The sample of ethyl bromide (Reagent grade, Merck, Germany) was purified under high vacuum.

Apparatus and Measurement of Solubility. The equipment used in this experiment is similar to that described previously^{6,10,11}. The solubility measurements of ethyl bromide in aniline and *o*-chloroaniline in the presence and absence of gallium bromide are based on those propounded by Corbett *et al*¹⁸.

RESULT AND DISCUSSION

Solubility of ethyl bromide in aniline and *o*-chloroaniline. The solubilities of ethyl bromide in aniline and *o*-chloroaniline are measured at 5, 15° and 25°C, respectively. In this case, adding ethyl bromide to the solvent and measuring pressures of the system, the relation between mole fraction and partial pressure of ethyl bromide in the solution are plotted to Henry's law constant. These results are shown in Fig. 1 and 2 and summarized in Table 1 and 2:

These experimental data shown in these figures are correspond to Henry's law and the ratio ($K_{obs.}/K_{id.}$) of the experimental data $K_{obs.}$ for ethyl bromide in both solvent and calculated data $K_{id.}$ in

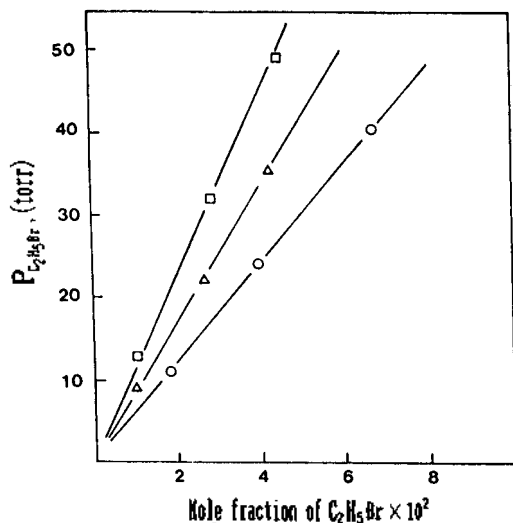


Fig. 1. Solubilities of ethyl bromide in aniline at various temperatures. (—○—: 5°C, —△—: 15°C, —□—: 25°C).

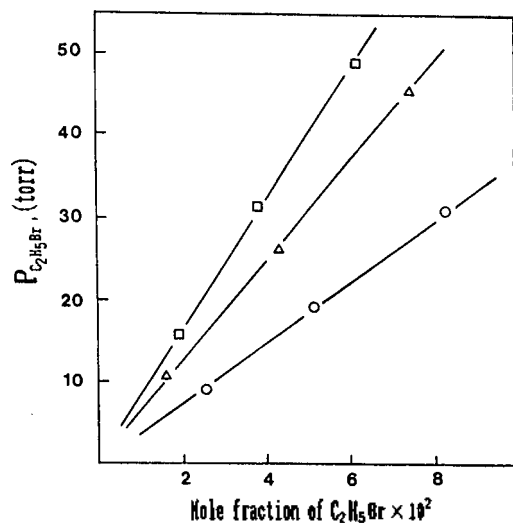


Fig. 2. Solubilities of ethyl bromide in *o*-chloroaniline at various temperatures. (—○—: 5°C, —△—: 15°C, —□—: 25°C).

Table 1. Solubilities of ethyl bromide in aniline in the presence and absence of gallium bromide

Temp.(°C)	GaBr ₃ (mole·l ⁻¹)	Henry's law const. ^a (torr)
5	0	574
	0	573
		Av. 574
	0.144	554
	0.203	555
15	0	810
	0	812
		Av. 811
	0.302	791
	0.408	789
25	0	1099
	0	1100
		Av. 1099
	0.183	1070
	0.318	1070
	Av. 1070	

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

the ideal solution at 5°C. K_{id} value is equal to vapor pressure in that temperature. Table 3 exhibits Henry's law constant of alkyl bromide and its ratios for each solvent. The less a ratio of K_{obs}/K_{id} is, the more soluble ethyl bromide is in the solvent. Then, the interaction of ethyl bromide with *o*-chloroaniline is stronger than with aniline. If it is assume that the interaction is electron donor-acceptor interaction, acid-base reaction, between alkyl bromide and solvent, *o*-chloroaniline is stronger base than aniline. Also, it is noticed that the Table 3 shown a stronger interaction of methyl bromide than ethyl bromide in *o*-chloroaniline and aniline.

Solubility of ethyl bromide in aniline with gallium bromide. Adding gradually ethyl bromide to aniline with gallium bromide, the solution appears light brown color. Table 1 reveals that Henry's law constant have value with increasing temperatures from 5°C to 25°C, and this indicates that the solubilities of ethyl bromide are lower with rising temperatures. The typical result obtained

Table 2. Solubilities of ethyl bromide in *o*-chloroaniline in the presence and absence of gallium bromide

Temp.(°C)	GaBr ₃ (mole·l ⁻¹)	Henry's law const. ^a (torr)
5	0	365
	0	368
		Av. 367
	0.178	332
	0.246	332
15	0	603
	0	605
		Av. 604
	0.162	579
	0.284	581
25	0	780
	0	780
		Av. 780
	0.215	761
	0.228	761
	Av. 761	

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

Table 3. Henry's law constants for the alkyl iodide over nitrobenzene and *m*-xylene

Solvent	CH ₃ Br ^a		C ₂ H ₅ Br ^a	
	K_{obs} (torr)	K_{obs}/K_{id}	K_{obs} (torr)	K_{obs}/K_{id}
C ₆ H ₅ NH ₂	1321	1.69	555	2.64
C ₆ H ₄ NH ₂ Cl	1125	1.44	332	1.58

^areference 16, ^bthe present study.

ned at 5, 15° and 25°C are shown in Fig. 3.

It is found that the solubilities measured with gallium bromide are greater than those without it (Fig. 4). This is because of formation of complex of gallium bromide in the solution.

If ethyl bromide is considered to be similar to the previous paper¹⁶, it is expected that one to one molecular complex, C₂H₅Br·GaBr₃ is formed and dissociated according to the following equation:



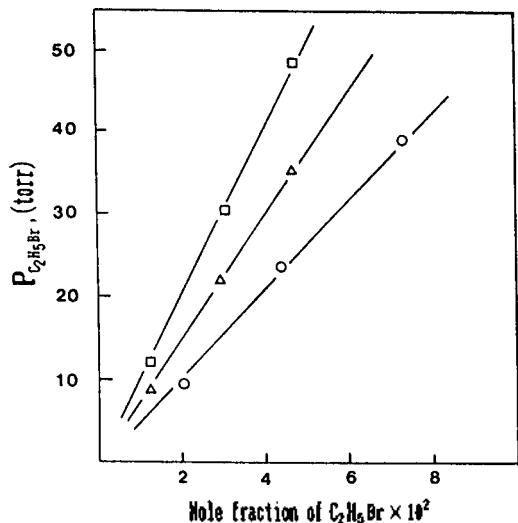


Fig. 3. Solubilities of ethyl bromide in aniline in the presence of gallium bromide at various temperatures. (—○—: 5°C, —△—: 15°C, —□—: 25°C).

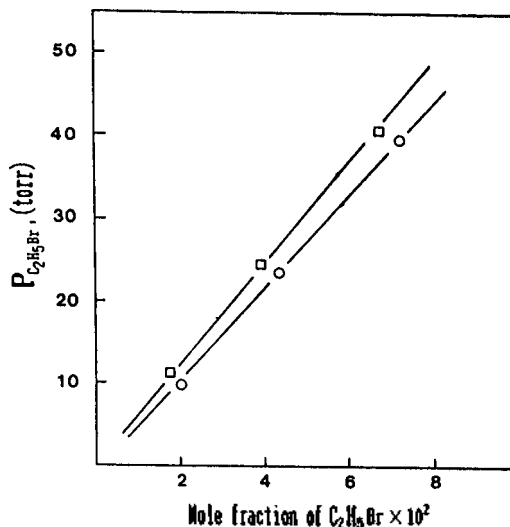


Fig. 4. Solubilities of ethyl bromide in aniline at 5°C in the presence and absence of gallium bromide. (—○—: $C_2H_5Br \cdot C_6H_5NH_2 \cdot GaBr_3$ (Ca. $0.203 \text{ mole} \cdot l^{-2}$), —□—: $C_2H_5Br \cdot C_6H_5NH_2$).

Table 4. Instability constants of $n\text{-C}_3\text{H}_7\text{I} \cdot \text{GaI}_3$ in nitrobenzene

Temp. (°C)	GaBr_3 initial (mole $\cdot l^{-1}$)	$P(\text{C}_2\text{H}_5\text{Br})$ (torr)	$[\text{C}_2\text{H}_5\text{Br}]^a$ (mole $\cdot l^{-1}$)	Mole fract. of $\text{C}_2\text{H}_5\text{Br} \times 10$	$[\text{C}_2\text{H}_5\text{Br}]^b$ free (mole $\cdot l^{-1}$)	$[1:1 \text{ complex}]$ (mole $\cdot l^{-1}) \times 10$	K (mole $^{1/2} \cdot l^{1/2}$)
5	0.144	9.5	0.19	0.17	0.18	0.12	3.99
		19.5	0.40	1.35	0.38	1.22	4.16
		32	0.66	1.58	0.62	0.25	4.09
	0.203	11	0.22	0.20	0.21	0.15	4.23
		24	0.50	0.43	0.46	0.33	4.05
		40	0.83	0.72	0.78	0.53	4.02
							Av. 4.09 ($\pm 2.2\%$)
15	0.302	9.5	0.13	0.12	0.13	0.09	5.36
		22.5	0.29	0.28	0.27	0.19	5.42
		36	0.52	0.46	0.48	0.32	5.47
	0.408	9	0.13	0.14	0.12	0.10	5.48
		21.5	0.31	0.27	0.28	0.23	5.48
		32	0.46	0.41	0.43	0.33	5.57
							Av. 5.46 ($\pm 1.3\%$)
25	0.183	13	0.14	0.12	0.13	0.06	6.65
		31.5	0.33	0.29	0.32	0.13	6.95
		49	0.51	0.46	0.49	0.20	7.02
	0.318	12	0.12	0.11	0.11	0.07	6.49
		30	0.31	0.28	0.29	0.17	6.73
		47.5	0.49	0.44	0.46	0.26	6.87
							Av. 6.78 ($\pm 2.9\%$)

^aTotal mole of liquid and gas phase in reaction vessel, ^bTotal mole of liquid and gas phase, not complexed.

where K is given by

$$K = \frac{[\text{C}_2\text{H}_5\text{Br free}] [1/2 (\text{GaBr}_3 \text{ initial} - 1:1 \text{ complex})]^{1/2}}{[1:1 \text{ complex}]} \quad (2)$$

The instability constant K of the complex is calculated by equation (2). Its calculated results are listed in Table 4.

From this data, it can be thought that they are constant to those of the one to one complex shown by Brown *et al.*^{20,21}, to the complex of gallium bromide with alkyl bromide (methyl bromide, ethyl bromide, *n*-propyl bromide, *i*-propyl bromide, *n*-butyl bromide and *t*-butyl bromide) in nitrobenzene and 1,2,4-trichlorobenzene¹⁰⁻¹⁵, to aluminium bromide with alkyl bromide²⁰ and to gallium chloride with alkyl chloride^{21,22}.

Solubility of ethyl bromide in *o*-chloroaniline with gallium bromide. Adding gradually ethyl

bromide to *o*-chloroaniline in the presence of gallium bromide, the solution appear light brown color. Table 5 reveals that Henry's law constants have value in increasing 5°C to 25°C, and this indicates that the solubilities of ethyl bromide are reduced with rising temperatures. The typical results obtained at 5, 15° and 25°C are shown in Fig. 5. As same as before, it is noticed that the solubilities in the solution with gallium bromide and greater than that with no it (Fig. 6), and it is also expected that the complex $\text{C}_2\text{H}_5\text{Br} \cdot \text{GaBr}_3$ is formed and dissociated according to equation (2). The instability constant of complex is calculated and summarized in Table 5. Because of constancy of instability constant K , we can say that 1:1 complex exist in the solvent as mentioned before¹⁰⁻¹⁵.

Using the data listed in Table 4 and 5, a good linearity is obtained from the plots of $\log K$ versus

Table 5. Instability constantss of $\text{C}_2\text{H}_5\text{Br} \cdot \text{GaBr}_3$ in *o*-chloroaniline

Temp. (°C)	GaBr_3 initial (mole·l ⁻¹)	P($\text{C}_2\text{H}_5\text{Br}$) (torr)	$[\text{C}_2\text{H}_5\text{Br}]^a$ (mole·l ⁻¹)	Mole fract. of $\text{C}_2\text{H}_5\text{Br} \times 10$	$[\text{C}_2\text{H}_5\text{Br}]^b$ free (mole·l ⁻¹)	[1:1 complex] (mole·l ⁻¹) × 10	K (mole ^{1/2} ·l ^{1/2})	
5	0.178	9	0.22	0.24	0.25	0.20	3.52	
		18	0.55	0.54	0.51	0.38	3.49	
		29	0.88	0.87	0.82	0.59	3.67	
	0.243	10	0.29	0.30	0.27	0.23	3.20	
		23.5	0.73	0.71	0.67	0.55	3.75	
		38.5	1.20	1.16	1.11	0.89	3.45	
								Av. 3.47 (± 5.5%)
	15	0.162	11.	0.19	0.19	0.17	0.11	4.25
			26	0.45	0.45	0.42	0.25	4.40
44			0.76	0.76	0.72	0.40	4.46	
0.284		11.5	0.19	0.20	0.18	0.15	4.40	
		23	0.37	0.40	0.34	0.27	4.51	
		38	0.63	0.65	0.59	0.45	4.53	
						Av. 4.43 (± 2.3%)		
25	0.215	15.5	0.20	0.20	0.19	0.11	5.52	
		30.5	0.40	0.40	0.38	0.22	5.37	
		48.5	0.66	0.66	0.63	0.35	5.40	
	0.228	17.5	0.23	0.23	0.21	0.13	5.30	
		30.5	0.40	0.40	0.38	0.22	5.54	
		46	0.60	0.60	0.57	0.33	5.40	
						Av. 5.42 (± 1.7%)		

^aTotal mole of liquid and gas phase in reaction vessel, ^bTotal mole of liquid and gas phase, not complexed.

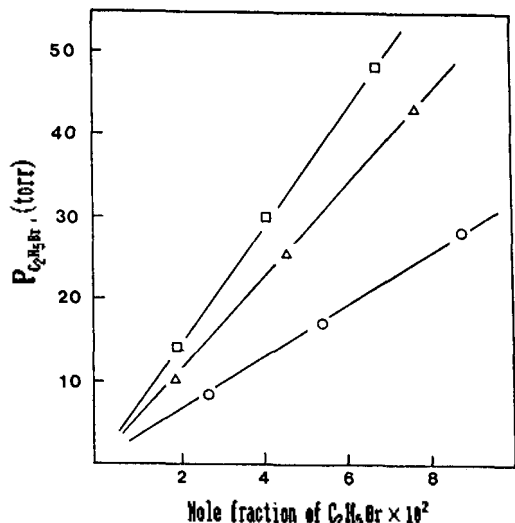


Fig. 5. Solubilities of ethyl bromide in aniline in the presence of gallium bromide at various temperatures. (—○—: 5°C, —△—: 15°C, —□—: 25°C).

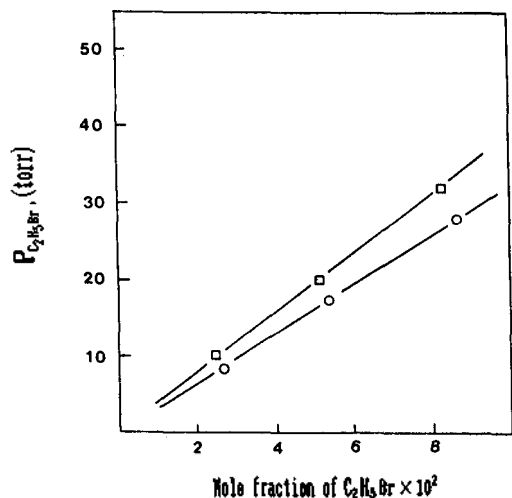


Fig. 6. Solubilities of ethyl bromide *o*-chloroaniline at 5°C in the presence and absence of gallium bromide. (—○—: $C_2H_5Br \cdot C_6H_4NH_2Cl \cdot GaBr_3$ (Ca. 0.178 mole $\cdot l^{-2}$), —□—: $C_2H_5Br \cdot C_6H_4NH_2Cl$).

the reciprocal of temperature as shown in Fig. 7. From the slope of the linearity, the change of enthalpy, ΔH , of the complex formation is calculated. The changes of free energy and entropy, ΔG and ΔS , are calculated at the given respective temperatures. The calculated results were listed

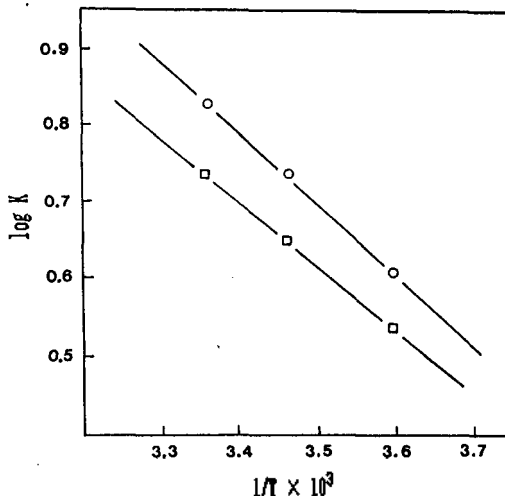


Fig. 7. Temperatures dependence of $\log K$ for the complex of gallium bromide with ethyl bromide in aniline and *o*-chloroaniline. (—○—: aniline, —□—: *o*-chloroaniline).

Table 6. The value of thermodynamic parameter for the dissociation of ethyl bromide-gallium bromide complex

Solvent	Temp. (°C)	ΔH (KJ \cdot mol $^{-1}$)	ΔG (KJ \cdot mol $^{-1}$)	ΔS (J \cdot mol $^{-1} \cdot$ K $^{-1}$)
$C_6H_5NH_2$	5		-3.26	74.8
	15	17.56	-4.07	75.2
	25		-4.74	74.8
$C_6H_4NH_2Cl$	5		-2.88	67.2
	15	15.38	-3.57	65.9
	25		-4.20	65.5

in Table 6.

The value of ΔG at each temperature indicates that the stability of the complex decreases as the temperature increases from 5°C to 25°C. The comparison between the results of the present study and those previously studied on methyl bromide¹⁶ is shown in Table 7. In result, the stability is greater in *o*-chloroaniline than in aniline and also ethyl bromide is formed more stable complex than methyl bromide.

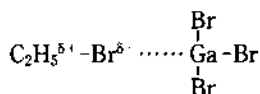
It seems that the structure of one to one complex $RBr \cdot GaBr_3$ between alkyl bromide and gallium bromide is the same as the one between alkyl iodide and gallium iodide⁷⁻⁹, alkyl bromide and al-

Table 7. Comparison of instability constant of $\text{CH}_3\text{Br}\cdot\text{GaBr}_3$ and $\text{C}_2\text{H}_5\text{Br}\cdot\text{GaBr}_3$ at 5°C

Solvent	K ($\text{mole}^{1/2}\cdot\text{l}^{1/2}$)	
	$\text{CH}_3\text{I}\cdot\text{GaBr}_3^d$	$\text{C}_2\text{H}_5\text{Br}\cdot\text{GaBr}_3^b$
$\text{C}_6\text{H}_5\text{NH}_2$	4.67	4.09
$\text{C}_6\text{H}_4\text{NH}_2\text{Cl}$	4.20	3.47

^dreference 16, ^bthe present study.

luminium bromide²⁰ and alkyl chloride and gallium chloride^{21,22}.



Also as shown Table 7, it is seen that the stability of the complex of alkyl bromide in aniline is $\text{CH}_3\text{Br}\cdot\text{GaBr}_3 < \text{C}_2\text{H}_5\text{Br}\cdot\text{GaBr}_3$. It has been thought that carbonium ion stabilities of the complex, methyl bromide and ethyl bromide, do not have influence on the stability of one to one complex¹¹, however on the contrary they do on the 1:1 complex as shown in the present and the previous result of methyl bromide¹⁶. The reason for this is that instability constant of complex are $\text{CH}_3\text{Br} > \text{C}_2\text{H}_5\text{Br}$ and furthermore that the stability of carbonium ion is $\text{CH}_3^+ < \text{CH}_3\text{CH}_2^+$. Therefore, the tendency of more stable complex formation of $\text{C}_2\text{H}_5\text{Br}$ than CH_3Br indicates that, besides the stability of carbonium ion, the other factor contributes to the stability of complex but the stability of alkyl ion contributes more to the stability of complex.

REFERENCES

1. C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245 (1956).
2. H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955).
3. H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).
4. H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6249 (1956).
5. S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 3315 (1965).
6. O. C. Kwun and S. U. Choi, *J. Phy. Chem.*, **72**, 3148 (1968).
7. C. S. Kim, H. J. An, and Y. C. Kim, "Research review of Chungbuk National University (Chunbuk, Korea)" **29**, 99 (1985).
8. Y. C. Kim and B. C. Heo, *J. Basic Science* (Hanyang Univ.), **5**, 75 (1986).
9. Y. C. Kim and D. J. Koo, *J. Korean Chem.*, **6**, 77 (1962).
10. S. U. Choi, *J. Korean Chem. Soc.*, **6**, 77 (1962).
11. S. U. Choi, *J. Korean Chem. Soc.*, **7**, 65 (1963).
12. O. C. Kwun, Y. C. Kim, and S. D. Lee, *J. Korean Chem. Soc.*, **24**, 302 (1980).
13. O. C. Kwun, D. S. Lee, and Y. H. Lee, *J. Korean Soc.*, **29**, 9 (1985).
14. J. H. Namkung, "The thesis of the graduate school of Hanyang University", 1970.
15. H. M. Kwun, "The thesis of the graduate school of Hanyang University", 1971.
16. Y. C. Kim, B. H. Kang, and B. C. Heo, *J. Basic Science* (Hanyang Univ.), **6**, 97 (1987).
17. S. U. Choi and J. E. Millard, *J. Am. Chem. Soc.*, **87**, 3072 (1965).
18. I. D. Corbett and R. K. McMullan, *J. Am. Chem. Soc.*, **77**, 4217 (1955).
19. R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).
20. H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6279 (1962).
21. H. C. Brown and L. P. Eddy, and R. Wang, *ibid.*, **75**, 6275 (1953).
22. R. Wang and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).