

고진공 상태에서 니트로벤젠과 *m*-크실렌용액 중 요오드화갈륨과 1-요오드화프로판과의 상호작용

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The Interaction of Gallium Iodide with *n*-Propyl Iodide in Nitrobenzene and *m*-Xylene on High Vacuum

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요 약. 니트로벤젠 및 *m*-크실렌 용액내에서 1-요오드화프로판의 용해도를 8°, 15° 및 25°C에서 요오드화갈륨이 존재할 때와 존재하지 않을 때의 두 경우에 대하여 각각 측정하여 보았다. 요오드화갈륨이 존재하지 않을 때에 *m*-크실렌에서 1-요오드화프로판의 용해도가 니트로벤젠에서 보다 크다. 이것은 1-요오드화프로판과 *m*-크실렌의 상호작용이 니트로벤젠보다 더 강하다는 것을 나타낸다. 그리고 요오드화갈륨이 존재할 경우에는 용액내에서 1-요오드화프로판과 요오드화갈륨이 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 $n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3$ 가 형성됨을 알았으며, 이 착물은 용액내에서 다음 평형식에 의해서 이루어 진다고 본다. $n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3 \rightleftharpoons n\text{-C}_3\text{H}_7\text{I} + 1/2\text{Ga}_2\text{I}_6$ 요오드화갈륨과 1-요오드화프로판의 착물의 불안정도를 이와 대응하는 요오드화메틸과 비교하여 보았다. 또한 이 착물의 해리에 대한 엔탈피, 자유에너지 및 엔트로피 변화도 산출하였다.

ABSTRACT. The solubilities of the *n*-propyl iodide in nitrobenzene and *m*-xylene have been measured at 8°, 15° and 25°C in the presence and the absence of gallium iodide. When gallium iodide does not exist in the system, the solubility of *n*-propyl iodide in *m*-xylene is greater than in nitrobenzene, indicating a stronger interaction of *n*-propyl iodide with *m*-xylene than that with nitrobenzene. It could be thought that *n*-propyl iodide forms unstable complex with gallium iodide in the presence of gallium iodide in the system. This complex has been assumed in various ways and evaluated, that instability constant (*K* value) is relatively certain under the assumption of 1:1 complex, $n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3$. Therefore, the complex would form the following equilibrium in the solution: $n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3 \rightleftharpoons n\text{-C}_3\text{H}_7\text{I} + 1/2\text{Ga}_2\text{I}_6$, the instability of the complex of *n*-propyl iodide with gallium iodide is compared with similar complexes of gallium iodide with methyl iodide. The changes of enthalpy, free energy and entropy for the dissociation of the complex are also calculated.

INTRODUCTION

It has been reported that the systematic studies¹⁻⁷ of the interaction between gallium bromide and alkyl bromide in nitrobenzene and 1,2,4-trichlorobenzene are made and also that the interac-

tion between gallium iodide and alkyl iodide in nitrobenzene and *m*-xylene at 8°C is expressed as



In this study an attempt has been made to closely examine the latter interaction mentioned above by measuring the solubilities of *n*-propyl iodide in nitrobenzene and *m*-xylene at 8°, 15° and 25°C in the presence and absence of gallium iodide. From this result, the instability constant *K* of the complex, $\text{RI} \cdot \text{GaI}_3$ on the occasion dissociation of complex in equilibrium is evaluated and

compared with the previously obtained one¹⁻⁹.

The changes of enthalpy, free energy and entropy and calculated from the relation between *K* and temperature. The stability of the complex is compared with that of methyl iodide¹⁰.

EXPERIMENTAL

Material. The gallium iodide was prepared by

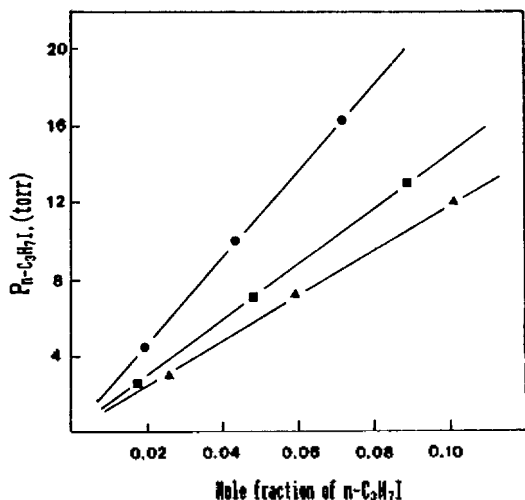


Fig. 1. Solubilities of *n*-propyl iodide in nitrobenzene at the several temperatures in the absence of gallium iodide. (—▲—: 8°C, —■—: 15°C, —●—: 25°C).

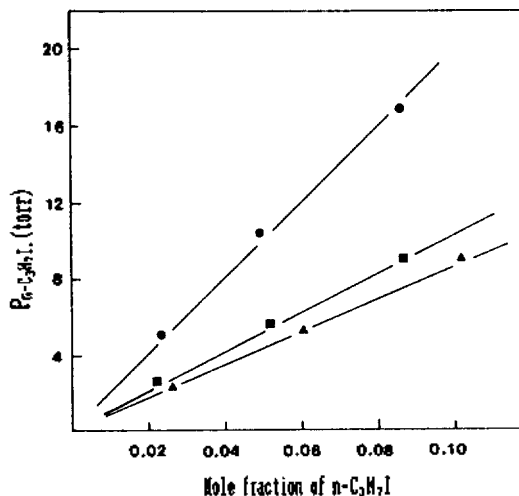


Fig. 3. Solubilities of *n*-propyl iodide in nitrobenzene at the several temperatures in the presence of gallium iodide. (—▲—: 8°C, —■—: 15°C, —●—: 25°C).

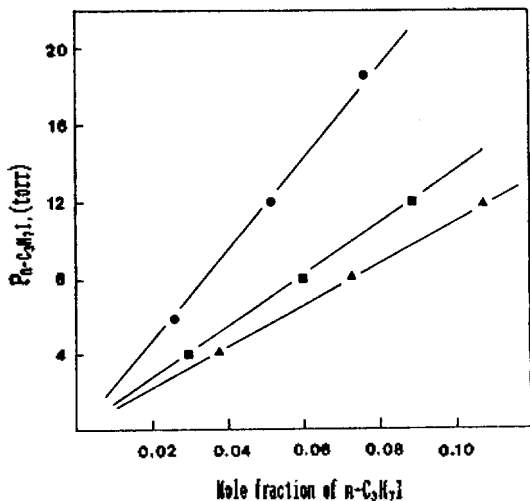


Fig. 2. Solubilities of *n*-propyl iodide in *m*-xylene at the several temperatures in the absence of gallium iodide. (—▲—: 8°C, —■—: 15°C, —●—: 25°C).

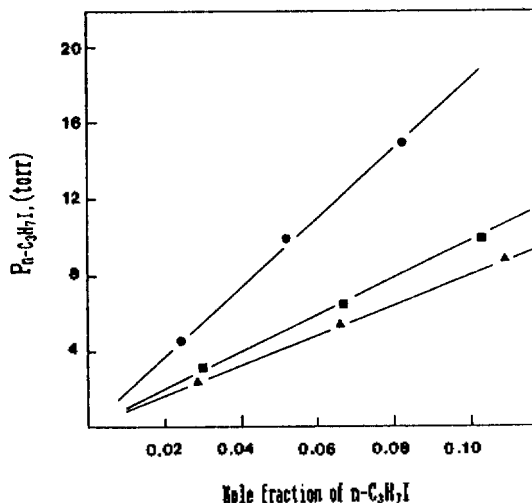


Fig. 4. Solubilities of *n*-propyl iodide in *m*-xylene at the several temperatures in the presence of gallium iodide. (—▲—: 8°C, —■—: 15°C, —●—: 25°C).

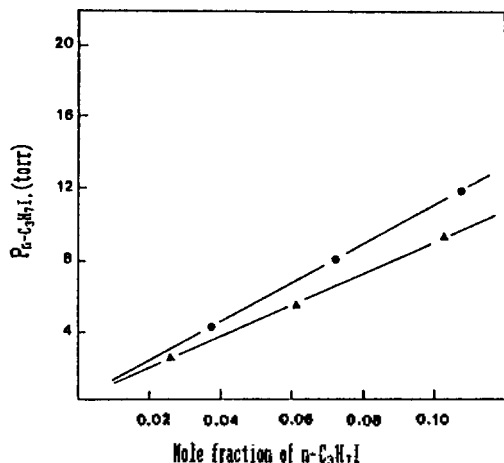


Fig. 5. Solubilities of *n*-propyl iodide in nitrobenzene at 8°C in the presence and absence of gallium iodide.
 —▲—: $n\text{-C}_3\text{H}_7\text{I}\cdot\text{C}_6\text{H}_5\text{NO}_2\cdot\text{GaI}_3$ (ca. $0.111\text{ mole}\cdot\text{l}^{-1}$)
 —●—: $n\text{-C}_3\text{H}_7\text{I}\cdot\text{C}_6\text{H}_5\text{NO}_2$.

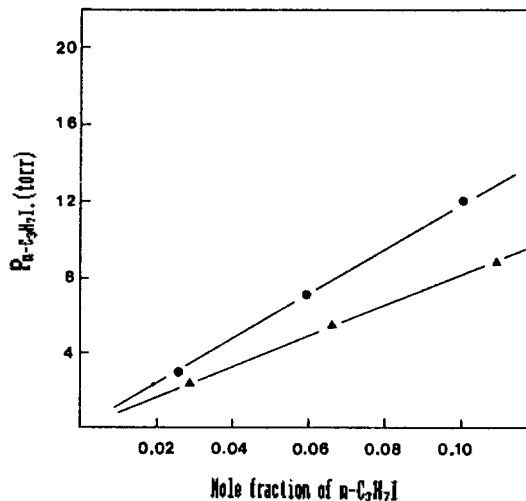


Fig. 6. Solubilities of *n*-propyl iodide in *m*-xylene at 8°C in the presence and absence of gallium iodide.
 —▲—: $n\text{-C}_3\text{H}_7\text{I}\cdot\text{C}_6\text{H}_4(\text{CH}_3)_2\cdot\text{GaI}_3$ (ca. $0.140\text{ mole}\cdot\text{l}^{-1}$)
 —●—: $n\text{-C}_3\text{H}_7\text{I}\cdot\text{C}_6\text{H}_4(\text{CH}_3)_2$.

Table 1. Solubilities of *n*-propyl iodide in nitrobenzene in the presence and absence of gallium iodide

Temp.(°C)	GaI_3 ($\text{mole}\cdot\text{l}^{-1}$)	Henry's law const. ^a (torr)
8	0	117
	0	118
		Av. 118
	0.088	98
	0.111	99
	Av. 99	
15	0	146
	0	147
		Av. 147
	0.086	127
	0.102	127
	Av. 127	
25	0	229
	0	232
		Av. 231
	0.087	218
	0.091	217
	Av. 218	

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

a direct reaction between gallium and iodide under high vacuum^{11,13}. Nitrobenzene and *m*-xylene

Table 2. Solubilities of *n*-propyl iodide in *m*-xylene in the presence and absence of gallium iodide

Temp.(°C)	GaI_3 ($\text{mole}\cdot\text{l}^{-1}$)	Henry's law const. ^a (torr)
8	0	110
	0	111
		Av. 111
	0.104	91
	0.140	90
	Av. 91	
15	0	136
	0	136
		Av. 136
	0.102	115
	0.113	113
	Av. 114	
25	0	227
	0	227
		Av. 227
	0.088	207
	0.098	206
	Av. 207	

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

(reagent grade, Merck, Germany) were used without further purification. The sample of *n*-propyl

iodide (special grade, Wako, Japan) was purified under high vacuum.

Apparatus and Measurement of Solubility. The equipment used in this experiment is similar to that described previously^{1,2,4}.

The solubility measurements of *n*-propyl iodide in nitrobenzene and *m*-xylene in the presence and absence of gallium iodide are based on those presented by Corbett *et al.*¹¹.

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

Solvent	CH ₃ I ^a		<i>n</i> -C ₃ H ₇ I ^b	
	<i>K</i> _{obs} (torr)	<i>K</i> _{obs} / <i>K</i> _{id}	<i>K</i> _{obs} (torr)	<i>K</i> _{obs} / <i>K</i> _{id}
C ₆ H ₅ NO ₂	421	1.91	118	5.90
C ₆ H ₄ (CH ₃) ₂	302	1.31	111	5.55

^areference 10, ^bthe present study.

RESULTS AND DISCUSSION

The solubilities of *n*-propyl iodide in nitrobenzene and *m*-xylene are measured at 8°, 15° and 25°C, respectively. In this case, adding *n*-propyl iodide to the solvents and measuring pressures of the system, the relation between mole fraction and partial pressure of *n*-propyl iodide in solution are plotted to Henry's law constant. These results are shown in Fig. 1 to 4; the first two figures show the results of the solvents without gallium iodide and the last ones those with it.

The typical results obtained from the above two cases are compared and revealed in Fig. 5 and 6. It is found that the solubilities measured with gallium iodide are greater than those without it. This is because of the formation of the complex between gallium iodide and *n*-propyl iodide. The

Table 4. Instability constants of *n*-C₃H₇I·GaI₃ in nitrobenzene

Temp. (°C)	GaI ₃ initial (mole·l ⁻¹)	P(<i>n</i> -C ₃ H ₇ I) (torr)	[<i>n</i> -C ₃ H ₇ I] ^a (mole·l ⁻¹)×10	Mole fract. of <i>n</i> -C ₃ H ₇ I×10 ²	[<i>n</i> -C ₃ H ₇ I] ^b free (mole·l ⁻¹)×10 ²	[1:1 complex] (mole·l ⁻¹)×10	<i>K</i> (mole ^{1/2} ·l ^{1/2})	
8	0.088	2	2.07	2.07	1.91	1.56	2.33	
		4.5	5.24	5.08	4.87	3.68	2.12	
		7	9.80	9.10	9.20	6.02	1.80	
	0.111	2.5	2.55	2.54	2.34	2.07	2.40	
		5.5	6.28	6.02	5.80	4.83	2.12	
		8	11.14	10.22	10.40	7.38	1.92	
								Av. 2.12
								(± 10.9%)
15	0.086	2.5	2.34	2.33	2.21	1.34	3.15	
		5.5	5.80	5.58	5.49	3.06	2.97	
		8	10.22	9.45	9.75	4.65	2.95	
	0.102	2.5	2.34	2.33	2.20	1.38	3.35	
		5.5	5.29	5.12	4.98	3.17	2.95	
		8	9.43	8.78	8.95	4.79	3.08	
								Av. 3.07
								(± 5.1%)
25	0.087	5	2.29	2.29	2.20	0.94	4.61	
		10.5	5.20	5.04	4.99	2.06	4.41	
		17	9.40	8.75	9.05	3.53	4.12	
	0.091	3.5	1.83	1.84	1.75	0.80	4.48	
		7.5	4.03	4.12	3.85	1.77	4.18	
		12	7.35	6.97	7.05	2.94	4.22	
								Av. 4.34
								(± 4.4%)

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

Table 5. Instability constants of *n*-C₃H₇I·GaI₃ in *m*-xylene

Temp. (°C)	GaI ₃ initial (mole·l ⁻¹)	P(<i>n</i> -C ₃ H ₇ I) (torr)	[<i>n</i> -C ₃ H ₇ I] ^a (mole·l ⁻¹)×10	Mole fract. of <i>n</i> -C ₃ H ₇ I×10 ²	[<i>n</i> -C ₃ H ₇ I] ^b free (mole·l ⁻¹)×10 ²	[1:1 complex] (mole·l ⁻¹)×10	<i>K</i> (mole ^{1/2} ·l ^{1/2})	
8	0.104	3	2.40	2.84	2.18	2.25	1.95	
		6	5.70	6.49	5.22	4.79	1.83	
		8.5	10.11	10.96	9.40	7.17	1.67	
	0.140	3	2.42	2.86	2.17	2.51	2.06	
		6	5.73	6.52	5.20	5.35	2.02	
		9	10.16	11.0	9.30	8.55	1.80	
								Av. 1.89
								(± 7.8%)
	15	0.102	3	2.54	3.00	2.37	1.73	2.84
6			5.74	6.57	5.38	3.61	2.71	
8.5			9.64	10.51	9.11	5.33	2.67	
0.113		2.5	2.66	3.13	2.48	1.85	2.91	
		5	5.87	6.68	5.49	3.83	2.75	
		7	9.71	10.57	9.15	5.58	2.77	
							Av. 2.78	
							(± 3.2%)	
25	0.088	5	2.03	2.41	1.94	0.91	4.25	
		10.5	4.61	5.31	4.41	2.00	4.07	
		16	7.40	8.26	7.07	3.20	3.70	
	0.098	4.5	2.06	2.45	1.97	0.91	4.44	
		10	4.60	5.30	4.38	2.18	3.92	
		15	7.41	8.27	7.07	3.41	3.70	
							Av. 4.01	
							(± 7.5%)	

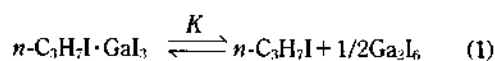
^aTotal mole of liquid and gas phase in reaction vessel, ^bTotal mole of liquid and gas phase, not complexed.

experimental data shown in these figures (Figs. 5 and 6) correspond to the law mention above and its constant determined at the respective temperatures are listed in Table 1 and 2.

Consequently and results of the above two tables show that the interaction of *n*-propyl iodide in the solvents with gallium iodide is stronger than that without it, and moreover that the interaction of *n*-propyl iodide in *m*-xylene is stronger than one in nitrobenzene. Table 3 exhibits experimental Henry's law constant of *n*-propyl iodide *K*_{obs} for each solvents, computation value *K*_{id} for ideal solutions and its ratios *K*_{obs}/*K*_{id}. *K*_{id} value is equal to vapor pressure in that temperature. The less a ratio of *K*_{obs}/*K*_{id} is, the more soluble *n*-propyl iodide is in the solvent. Then, the interaction of *n*-propyl iodide with *m*-xylene is stronger than with nitrobenzene. If it is assume that

the interaction is electron donor-acceptor interaction, acid-base reaction, between alkyl iodide and solvent, *m*-xyiene is stronger base than nitrobenzene. Also, it is noticed that the table shown a stronger interaction of methyl iodide than *n*-propyl iodide in *m*-xylene and nitrobenzene.

If *n*-propyl iodide is considered to be similar to methyl iodide,¹⁰ it is expected that one to one molecular complex, *n*-C₃H₇I·GaI₃, is formed and dissociated according to the following equation:



where *K* is given by

$$K = \frac{[n\text{-C}_3\text{H}_7\text{I free}][1/2(\text{GaI}_3 \text{ initial}-1:1 \text{ complex})]^{1/2}}{[1:1 \text{ complex}]} \quad (2)$$

The instability constant K of the complex is calculated by eq. (2). Its calculated results are listed

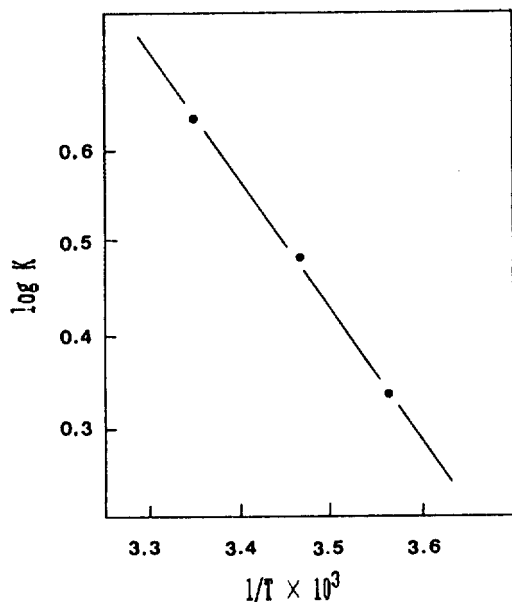


Fig. 7. Temperatures dependence of $\log K$ for the interaction of gallium iodide with n -propyl iodide in nitrobenzene.

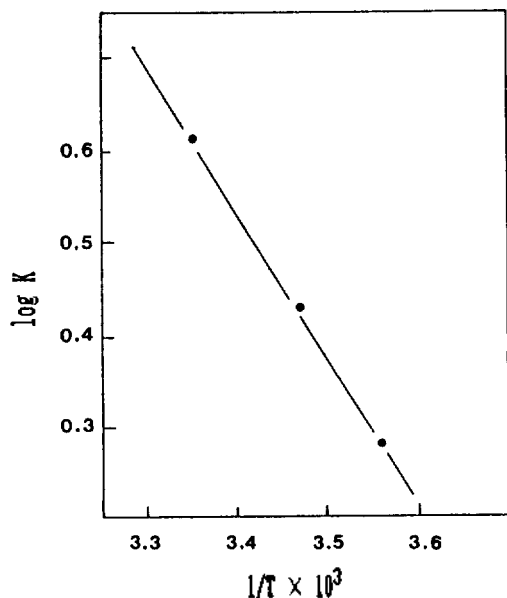
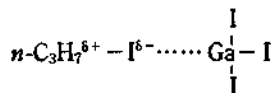


Fig. 8. Temperatures dependence of $\log K$ for the interaction of gallium iodide with n -propyl iodide in m -xylene.

in Table 4 and 5. From this it can be that they are a good agreement with those of the one to one complex shown by Brown *et al*^{14,15}.

Using the data listed in the above two tables, a good linearity is obtained from the plots of $\log K$ versus the reciprocal of temperature as shown in Fig. 7 and 8. 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 in Table 6. The value of ΔG at each temperature indicates that the stability of the complex decreases as the temperature increases from 8°C to 25°C.

The comparison between the results of the present study and those¹⁰ previously studied on methyl iodide is shown in Table 7. In result, the stability of the complex between alkyl iodide and gallium iodide shows $\text{CH}_3\text{I} < n\text{-C}_3\text{H}_7\text{I}$. It seems that the structure of one to one complex $\text{RI} \cdot \text{GaI}_3$ between alkyl chloride and gallium bromide¹⁻⁹, alkyl bromide and aluminium bromide¹⁴ and alkyl chloride and gallium bromide¹⁵.



Also as shown Table 7, it is seen that the stability of the complex of alkyl iodide in nitrobenzene is $\text{CH}_3\text{I} \cdot \text{GaI}_3 < n\text{-C}_3\text{H}_7\text{I} \cdot \text{GaI}_3$.

It has been thought that carbonium ion stabilities of the complex, methyl bromide and ethyl bromide, do not have influence on the stability

Table 6. Summary of data obtained for dissociation of complex

Solvent	Temp. (°C)	ΔH (kcal/mole)	ΔG (kcal/mole)	ΔS (cal/mole·deg)
$\text{C}_6\text{H}_5\text{NO}_2$	8		-0.42	21.03
	15	5.51	-0.64	21.35
	25		-0.87	21.40
$\text{C}_6\text{H}_4(\text{CH}_3)_2$	8		-0.36	27.47
	15	7.34	-0.58	27.60
	25		-0.82	27.48

Table 7. Comparison of instability constant of $\text{CH}_3\text{I}\cdot\text{GaI}_3$ and $n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3$ at 8°C

Solvent	K (mole ^{1/2} ·l ^{1/2})	
	$\text{CH}_3\text{I}\cdot\text{GaI}_3^a$	$n\text{-C}_3\text{H}_7\text{I}\cdot\text{GaI}_3^b$
$\text{C}_6\text{H}_5\text{NO}_2$	2.60	2.12
$\text{C}_6\text{H}_4(\text{CH}_3)_2$	2.40	1.89

^areference 10, ^bthe present study.

of one to one complex,² however on the contrary they do on the 1:1 complex as shown in the presence study and the previous result of methyl iodide¹⁰. The reason for this is that instability constant of complex are $\text{CH}_3\text{I} > n\text{-C}_3\text{H}_7\text{I}$ and furthermore that the stability of carbonium ion is $\text{CH}_3^+ < \text{CH}_3\text{CH}_2\text{CH}_2^+$. Therefore, the tendency of more stable complex formation of $n\text{-C}_3\text{H}_7\text{I}$ than CH_3I 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. S. U. Choi, *J. Korean Chem. Soc.*, **6**, 77 (1962).
2. S. U. Choi, *ibid.*, **7**, 65 (1963).
3. S. U. Choi and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 3072 (1965).
4. O. C. Kwun and S. U. Choi, *J. Phy. Chem.*, **72**, 3148 (1968).
5. J. H. Namkung, "The thesis of the graduate school of Hanyang University", 1970.
6. H. M. Kwun, "The thesis of the graduate school of Hanyang University", 1971.
7. O. C. Kwun and Y. C. Kim, *J. Korean Chem. Soc.*, **15**, 228 (1971).
8. O. C. Kwun, Y. C. Kim, and D. S. Lee, *ibid.*, **24**, 302 (1980).
9. O. C. Kwun, D. S. Lee, and Y. C. Lee, *ibid.* **29**, 9 (1985).
10. C. S. Kim, H. J. An, and Y. C. Kim, "Research review of Chungbuk National University (Chunbuk, Korea)" **29**, 99 (1985).
11. I. D. Corbett and R. K. McMullan, *J. Am. Chem. Soc.*, **77**, 4217 (1955).
12. W. Klemm and W. Tilk, *Z. anorg. allg. Chem.*, **207**, 161 (1932).
13. W. Fischer and O. Juber mann, *Z. anorg. allg. Chem.*, **227**, 227 (1936).
14. H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6279 (1953).
15. H. C. Brown, L. P. Eddy, and R. Wang, *ibid.*, **75**, 6275 (1953).
16. R. Wang and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).