

## The Complexes of Bromobenzene with Halogens and Interhalogens in Carbon Tetrachloride\*\*

by

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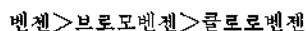
브로모벤젠과 할로젠 또는 할로겐間化合物  
사이의 錯物에 관한 연구

西江大學 化學科 崔相燾·張石柱

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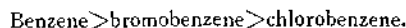
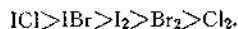
### 要 約

브로모벤젠과 염소 또는 일브롬화요오드의 각 시스템을 사염화탄소 용액에서 분광光度法에 의하여 연구한 결과  $C_6H_5Br \cdot Cl_2$  또는  $C_6H_5Br \cdot IBr$ 의 錯物이 형성됨을 알았다. 이들 錯物의 생성에 대한  $25^\circ$ 에서의 평형 상수는 각각 0.0485 및  $0.183 \text{ l} \cdot \text{mole}^{-1}$ 이다. 이 결과와 文獻에 있는 연구결과를 종합하면 芳香族化合物과 할로젠 또는 할로겐間化合物 사이에 형성되는 錯物의 상대적 안정도가 다음 순서로 감소함을 알 수 있다.



### Abstract

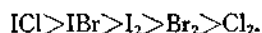
The systems of bromobenzene with chlorine and iodine monobromide in carbon tetrachloride have been investigated at  $25^\circ$  by means of ultraviolet spectrophotometric measurements. The results indicate the formation of one to one molecular complexes,  $C_6H_5Br \cdot Cl_2$  and  $C_6H_5Br \cdot IBr$ , in solution. The equilibrium constants obtained at  $25^\circ$  for the formation of these two complexes are 0.0485 and  $0.183 \text{ l} \cdot \text{mole}^{-1}$ , respectively. Comparison of these results with those reported in the literature on other complexes of similar type shows that the relative stabilities of the complexes decrease in the following orders:



### Introduction

In a paper of this series<sup>(1)</sup>, we reported the formation of one to one molecular complexes,  $C_6H_6 \cdot X_2$  and  $C_6H_5 \cdot IX$  (X: halogen atoms), in carbon tetrachloride solution at  $25^\circ$ , based on the ultraviolet spectrophotometric studies. By

comparing the values of the equilibrium constant for the complex formation, the following order was established for the relative stabilities of the complexes formed with benzene:



As the results of similar studies with chlorobenzene<sup>(2)</sup> we observed not only that chlorobenzene also formed one to one molecular complexes,  $C_6H_5Cl \cdot X_2$  and  $C_6H_5Cl \cdot IX$ , in carbon tetrachloride at  $25^\circ$ , but that the relative stabilities of the

\* The Molecular Complexes. VI.

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complexes decreased in the order written above. We also reported that the halogens and interhalogens listed above formed less stable complexes with chlorobenzene than with benzene in carbon tetrachloride<sup>(2)</sup>.

It seemed then of interest to see if the similar order to the one written above could be observed with bromobenzene and to compare the behavior of bromobenzene with that of benzene or chlorobenzene. Keefer and Andrews reported the existence of the 1:1 complexes of bromobenzene with iodine, bromine and iodine monochloride in carbon tetrachloride<sup>(3)</sup>. The relative stabilities of the bromobenzene complexes observed by them decreased in the order,  $\text{ICl} > \text{I}_2 > \text{Br}_2$ . We have, therefore, undertaken the spectrophotometric studies on the systems of bromobenzene with chlorine and iodine monobromide, in order to examine the behavior of chlorine and iodine monobromide toward complex formation with bromobenzene.

### Experimental

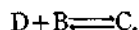
Bromobenzene (reagent grade, Wako, Japan) was distilled through a 100 cm. Todd column packed with glass helices. The reflux ratio was kept at about 1:15. The boiling point of the middle fraction of the distillate was 157°. All the other materials used in the present study were prepared and/or purified by the procedures described previously<sup>(1)</sup>.

The experimental techniques utilized for the preparation of stock solutions and for the ultraviolet spectrophotometric measurements of the solutions were reported in a previous paper of this series<sup>(1)</sup>. A Beckman DU spectrophotometer and a set of 1 cm quartz cells were used for absorbancy measurements.

### Results

Absorption spectra of the carbon tetrachloride solutions of the mixture of bromobenzene with chlorine or iodine monobromide measured at 25°

revealed the presence of maximum absorption peak at 2860 Å, where none of the component materials had strong absorption. This phenomenon is analogous to that observed on the systems of halogens or interhalogens with benzene<sup>(1)</sup> and with chlorobenzene<sup>(2)</sup> in carbon tetrachloride. Thus, the absorption maxima at 2860 Å are ascribed to the formation of one to one molecular complexes,  $\text{C}_6\text{H}_5\text{Br}\cdot\text{Cl}_2$  and  $\text{C}_6\text{H}_5\text{Br}\cdot\text{IBr}$ . These complexes are additional examples of the complexes (C) formed through interaction between Lewis bases (D) and Lewis acids (B).



The equilibrium constants,  $K$ , for the complex formation and the molar absorptivities,  $a$ , of the complexes at their absorption maxima were calculated from spectrophotometric data, by the method reported previously<sup>(1)</sup>. This involved the evaluation of slopes and intercepts of the linear plots of  $[\text{D}]_0[\text{B}]_0 / \{A - a_0[\text{B}]_0\}$  versus  $[\text{D}]_0$ , where  $A$  denotes the absorbancy measured at 2860 Å,  $a_0$  the molar absorptivity at 2860 Å of chlorine or iodine monobromide in carbon tetrachloride, and  $[\ ]_0$  the initial concentrations. The values of  $a_0$  observed are shown in Table I. The results obtained at 25° on the systems of bromobenzene with chlorine and with iodine monobromide in

Table I  
Molar Absorptivities of Chlorine and Iodine Monobromide in Carbon Tetrachloride at 25°.

Halo- gen	Conc., $10^{-2}$ mole l <sup>-1</sup>	Wave length, Å	Absor bancy	Molar absorp- tivity( $a_0$ )	Average
Cl <sub>2</sub>	2.23	2860	0.283	12.7	
	3.72	"	0.532	14.3	
	7.44	"	1.03	13.9	
	11.2	"	1.43	12.8	13.4
IBr	0.127	2860	0.178	140	
	0.254	"	0.368	145	
	0.382	"	0.549	144	
	0.509	"	0.726	143	143

carbon tetrachloride are summarized in Tables II and III. The linearities observed between  $[\text{D}]_0[\text{B}]_0 / \{A - a_0[\text{B}]_0\}$  and  $[\text{D}]_0$  (Figs. 1 and 2)

indicate the assumption of the formation of one to one complexes,  $C_6H_5Br \cdot Cl_2$  and  $C_6H_5Br \cdot IBr$ , being correct. The  $K$  values obtained for these two complexes at  $25^\circ$  are  $0.0485$  and  $0.183$   $l \cdot \text{mole}^{-1}$ , respectively.

**Table I**  
Formation of  $C_6H_5Br \cdot Cl_2$  in Carbon Tetrachloride at  $25^\circ$ .

$C_6H_5Br$ , mole $\cdot l^{-1}$ ( $[D]_0$ )	$Cl_2$ , $10^{-3}$ mole $\cdot l^{-1}$ ( $[B]_0$ )	Absor- bancy at $2860 \text{ \AA}$ ( $A$ )	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-3}$ mole $\cdot l^{-1}$	Average, $10^{-3}$ mole $\cdot l^{-1}$
3.93	0.790	0.485	6.54	6.43
	1.19	0.745	6.42	
	1.58	0.992	6.39	
	2.38	1.50	6.37	
4.97	0.790	0.592	6.75	6.72
	1.19	0.900	6.69	
	1.58	1.19	6.72	
6.01	0.790	0.690	6.98	6.98
	1.19	1.04	6.98	
	1.58	1.38	6.99	
7.06	0.790	0.780	7.24	7.24
	1.19	1.17	7.28	
	1.58	1.57	7.20	

$K = 0.0485$   $l \cdot \text{mole}^{-1}$ ,  $a = 3830$

**Table II**  
Formation of  $C_6H_5Br \cdot IBr$  in Carbon Tetrachloride at  $25^\circ$ .

$C_6H_5Br$ , mole $\cdot l^{-1}$ ( $[D]_0$ )	$IBr$ , $10^{-4}$ mole $\cdot l^{-1}$ ( $[B]_0$ )	Absor- bancy at $2860 \text{ \AA}$ ( $A$ )	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $\cdot l^{-1}$	Average, $10^{-4}$ mole $\cdot l^{-1}$
0.889	1.96	0.305	6.29	7.06
	2.25	0.350	6.29	
	3.13	0.417	7.48	
	3.92	0.485	8.12	
	7.84	1.09	7.13	
1.77	1.96	0.442	8.38	8.36
	2.25	0.520	8.16	
	3.13	0.700	8.46	
	3.92	0.880	8.42	
2.68	1.96	0.586	9.41	9.21
	2.25	0.710	8.89	
	3.13	0.960	9.17	
	3.92	1.18	9.35	
3.63	1.96	0.705	10.5	10.2
	2.25	0.860	9.9	
	3.13	1.15	10.3	

$K = 0.183$   $l \cdot \text{mole}^{-1}$ ,  $a = 8990$

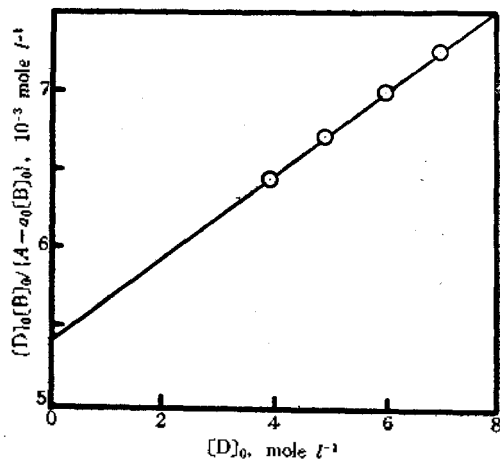


Fig. 1. Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the bromobenzene-chlorine system at  $25^\circ$ .

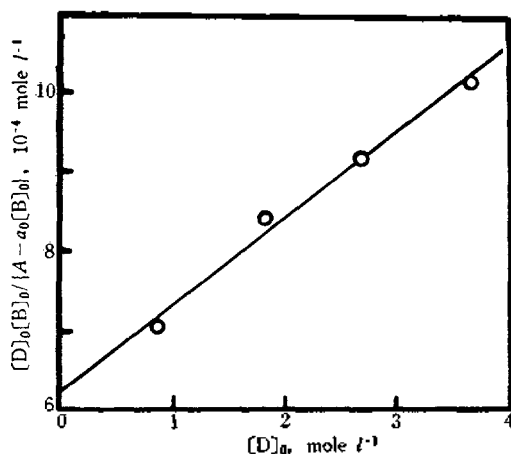


Fig. 2. Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of bromobenzene-iodine monobromide system at  $25^\circ$ .

### Discussion

The results of the present study reveal that chlorine and iodine monobromide form one to one molecular complexes,  $C_6H_5Br \cdot Cl_2$  and  $C_6H_5Br \cdot Br_2$ , with bromobenzene in carbon tetrachloride. The experimental results of the present investigation are now compared with those reported in the literature<sup>(1-3)</sup>. This comparison is shown in Table IV.

Some of the values of the equilibrium constants for the complex formation reported by Keefer and Andrews were  $K_x$  values in which the concentration of the aromatic was expressed by

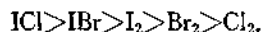
mole fractions and those of all the other species by molar concentrations<sup>(3a)</sup>. The  $K_x$  value is converted to  $K$  value with the aid of the following approximation, as reported previously<sup>(1)</sup>:

$$K = K_x \cdot \frac{MW}{10^3 d},$$

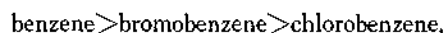
where  $MW$  and  $d$  denote the molecular weight and the density of carbon tetrachloride, respectively. The values thus converted are listed in

Table *W*.

By comparing the  $K$  values in Table *W*, it is seen that the relative stabilities of any given aromatic complexes decrease in the order,



and that the relative stabilities of any given halogen or interhalogen complexes decrease in the order,



**Table *V***  
Summary of Data Obtained on the Complexes of Benzene and Halobenzene with Halogens and Interhalogens in Carbon Tetrachloride at 25°.

Halogen	Wavelength of max. absorption, (Å)			Molar absorptivity of complex			Equil. const. of complex formation, ( <i>l</i> ·mole <sup>-1</sup> )		
	C <sub>6</sub> H <sub>6</sub> <sup>(1)</sup>	C <sub>6</sub> H <sub>5</sub> Br <sup>(2)</sup>	C <sub>6</sub> H <sub>5</sub> Cl <sup>(3)</sup>	C <sub>6</sub> H <sub>6</sub> <sup>(1)</sup>	C <sub>6</sub> H <sub>5</sub> Br <sup>(2)</sup>	C <sub>6</sub> H <sub>5</sub> Cl <sup>(3)</sup>	C <sub>6</sub> H <sub>6</sub> <sup>(1)</sup>	C <sub>6</sub> H <sub>5</sub> Br <sup>(2)</sup>	C <sub>6</sub> H <sub>5</sub> Cl <sup>(3)</sup>
ICl	2820	2860 <sup>(4)</sup>	2870	8130	5910 <sup>(4)</sup>	5650	0.54	0.32 <sup>(4)</sup>	0.216
IBr	2900	2860	2840	10500	8990	9330	0.341	0.183	0.109
I <sub>2</sub>	2930	2900 <sup>(4)</sup>	2840	15500	10400 <sup>(4)</sup>	9650	0.173	0.13 <sup>(4)</sup>	0.106
Br <sub>2</sub>	2860	2880 <sup>(5)</sup>	2860	8030	7600 <sup>(5)</sup>	7300	0.137	0.11 <sup>(5,6)</sup>	0.087
Cl <sub>2</sub>	2760	2860	2840	3520	3830	4270	0.0643	0.0485	0.0400

(1) See ref. 1 and papers referenced therein.

(2) The present study except otherwise indicated.

(3) See ref. 2 and papers referenced therein.

(4) Ref. 3b.

(5) Ref. 3a.

(6) Evaluated from  $K_x$  values.

Since these complexes are considered to be formed through Lewis acid-base interactions in solution, the orders shown above must be the decreasing orders of their relative acidities and basicities, respectively. As discussed previously,<sup>(1,2,4)</sup> it appears that the relative acidities of the halogens and interhalogens written above may be explained in terms of the relative polarizabilities of halogen molecules and the relative electronegativities of halogen atoms in the interhalogen molecules, and that the relative acidities of the aromatics shown above in terms of the relative electronegativities of hydrogen and halogen atoms in the aromatic molecules.

The values of both the wave lengths ( $\lambda_{\text{max}}$ ) of maximum absorption of the complexes and the molar absorptivities ( $a$ ) of the complexes at their absorption maxima do not reveal any gradual changes with increasing  $K$  values. Hence, the relative values of both  $\lambda_{\text{max}}$  and  $a$

may be considered to be affected by some additional factors other than the relative acidities of halogens or interhalogens and the relative basicities of the aromatic compounds involved.

#### Acknowledgment.

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#### References

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