

The Complexes of Iodobenzene with Halogens and Interhalogens in Carbon Tetrachloride*

by

SANG UP CHOI AND EUNG RYUL KIM

Department of Chemistry, Sogang Jesuit College, Seoul, Korea

(Received September 23, 1967)

요오도벤젠과 할로젠 또는 할로겐間化合物 사이의錯物에 관한 연구

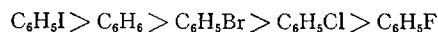
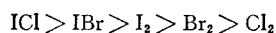
西江大學 化學科

崔 相 業 · 金 應 洙

(1967. 9. 23 受理)

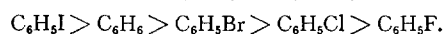
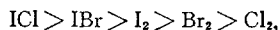
要 約

요오도벤젠과 요오드, 일브롬화요오드, 일염화요오드 또는 염소와의 각 系를 사염화탄소 용액에서 分光光度法에 의하여 연구한 결과, $C_6H_5I \cdot I_2$, $C_6H_5I \cdot IBr$, $C_6H_5I \cdot ICl$ 또는 $C_6H_5I \cdot Cl_2$ 의 錯物이 형성됨을 알았다. 이들 錯物형성에 대한 실온(약 $21^\circ C$)에서의 평형상수는 각각 0.23, 0.73, 1.2 및 $0.070 \text{ l mole}^{-1}$ 이다. 이 결과와 문헌에 보고된 결과를 종합하면 이러한 錯物의 상대적 안정도가 다음 순서로 감소함을 알 수 있다.



Abstract

The interactions of iodobenzene with iodine, iodine monobromide, iodine monochloride and chlorine in carbon tetrachloride solution have been investigated by means of ultraviolet spectrophotometric measurements. The results reveal the formation of one to one molecular complexes, $C_6H_5I \cdot I_2$, $C_6H_5I \cdot IBr$, $C_6H_5I \cdot ICl$ and $C_6H_5I \cdot Cl_2$, in solution. The equilibrium constants obtained at room temperature (about $21^\circ C$) for the formation of these four complexes are 0.23, 0.73, 1.2 and $0.070 \text{ l mole}^{-1}$, respectively. Comparison of these results with those reported in the literature on other complexes of similar type indicates that the relative stabilities of these complexes decrease in the following orders:



Introduction

We investigated earlier the interactions of aromatics with halogens and interhalogens in carbon tetrachloride, through ultraviolet spectrophotometric measurements⁽¹⁾. We reported the formation of one to one molecular

complexes, $Ar \cdot X_2$ and $Ar \cdot IX$ (Ar =benzene, bromobenzene, chlorobenzene or fluorobenzene; X =halogen atoms) in solution. It appeared of importance to examine the behavior of iodobenzene toward complex formation with halogens. We undertook the present investigation on the systems of iodobenzene with iodine, iodine monobromide, iodine monochloride and chlorine in carbon tetrachloride.

* The Molecular Complexes. VIII.

Experimentals

Iodobenzene was synthesized by the reaction of aniline with sodium nitrite in the presence of hydrochloric acid at the temperature lower than 5°C, followed by the addition of aqueous solution of potassium iodide⁽²⁾. The reaction products were steam-distilled after being made alkaline by adding strong sodium hydroxide solution, and steam-distilled again after being acidified with concentrated sulfuric acid. The steam-distillate was then dried with calcium chloride, and distilled under reduced pressure. The observed boiling point of the compound was 72°C at 15 mm Hg and the observed refractive index was $n_D^{20}=1.620$ (literature value⁽³⁾, $n_D^{20}=1.621$).

All the other materials used in the present study were prepared and/or purified by the methods described previously⁽¹⁾.

The experimental procedures for the preparation of stock solutions and for the ultraviolet spectrophotometric measurements of the solutions were reported in previous papers⁽¹⁾.

Results

The Complex of Iodobenzene with Iodine.

Absorbancies of carbon tetrachloride solutions of iodine and iodobenzene were measured over the range of wave lengths from 3100 to 4000 Å, using carbon tetrachloride as blank. The absorbancy measurements were repeated with a solution of iodobenzene-iodine mixture in carbon tetrachloride, using as blank the carbon tetrachloride solution of iodobenzene of the same concentration as that of the mixture solution. The absorption spectra obtained at room temperature are shown in Figure 1*.

Figure 1 shows that the spectrum of the mixture solution (spectrum 3 of Fig. 1) has no absorption maxima in the region of wave lengths investigated. Figure 1 indicates, however, that the mixture solution (spectrum 3 of Fig. 1) shows much stronger absorption than the solutions of component materials (spectra 1 and 2 of Fig. 1). This phenomenon is attributed to

an interaction of iodobenzene with iodine in the mixture solution. The formation of the one to one molecular complex, $C_6H_5I \cdot I_2$, is assumed.

The equilibrium constant, K , for the complex formation were calculated from data obtained at 3550, 3600 and 3650 Å, utilizing the method reported previously.⁽¹⁾ The molar absorptivities, a , of the complex at 3550, 3600 and 3650 Å were also calculated. For these calculations, it was required to know the values of the molar absorptivities of iodine in carbon tetrachloride at 3550, 3600 and 3650 Å (Table 1). The results of these calculations are summarized in Table 2. Good linearities observed between $[D]_0 \cdot [B]_0 / \{A - a_0[B]_0\}$ and $[D]_0$ (Fig. 2) indicate the assumption of the formation of one to one complex, $C_6H_5I \cdot I_2$, being correct.* The K values obtained at the three different wave lengths agree with each other within experimental error. The average value is 0.23 l mole⁻¹.

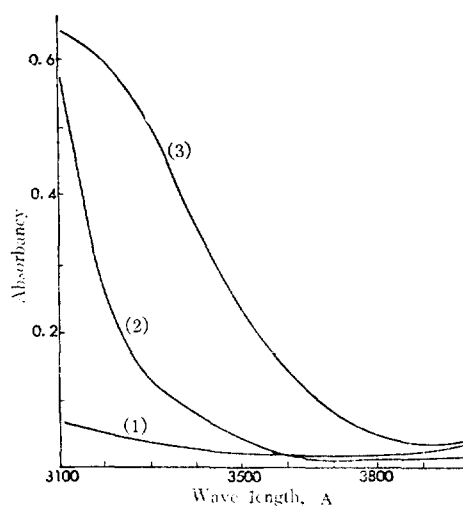


Figure 1. Absorption Spectra of (1) $I_2 \cdot CCl_4$ (CCl_4 as blank), (2) $C_6H_5I \cdot CCl_4$ (CCl_4 as blank), and (3) $I_2 \cdot C_6H_5I \cdot CCl_4$ ($C_6H_5I \cdot CCl_4$ as blank).

The Complexes of Iodobenzene with Iodine Monobromide, Iodine Monochloride and Chlorine.

Absorbancies of the solutions of mixtures of iodobenzene with iodine monobromide, iodine monochloride or chlorine in carbon tetrachloride were measured.

* The absorbancies of the mixture solution were unable to be measured at the wave lengths below 3100 Å, due to strong absorption of iodobenzene.

* The symbols written here imply the same meanings as those described in previous papers (ref. 1).

Table 1. Molar Absorptivities of Halogens and Interhalogens in Carbon Tetrachloride Solution at Room Temperature

Halogen	Concn., 10 ⁻³ mole l ⁻¹	Wave length, Å	Absorbancy (A)	Molar Absorptivity (a _o)	Average
I ₂	3.91	3550	0.045	12	12
	8.87	"	0.104	12	
	3.91	3600	0.043	11	11
	8.87	"	0.094	11	
IBr	3.91	3650	0.039	10	10
	8.87	"	0.088	10	
	11.2	3550	0.095	8.5	8.5
	15.0	"	0.128	8.5	
ICl	28.2	"	0.238	8.4	
	4.16	3550	0.038	9.1	8.7
Cl ₂	7.98	"	0.066	8.3	
	2.77	3550	0.134	48	48
	5.81	"	0.272	47	
	8.32	"	0.378	46	
	16.63	"	0.852	51	

Table 2. Formation of C₆H₅I·I₂ in Carbon Tetrachloride at 21°C

C ₆ H ₅ I, mole l ⁻¹ ([D] _o)	I ₂ , 10 ⁻⁴ mole l ⁻¹ ([B] _o)	Absorbancy at 3550 Å			Absorbancy at 3600 Å			Absorbancy at 3650 Å		
		(A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$	Average,	(A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$	Average,	(A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$	Average,
0.143	5.51	0.087	9.85	9.85	0.064	13.6	13.8	0.050	17.9	18.1
	13.8	0.216	9.91		0.158	13.8		0.124	17.9	
	19.3	0.304	9.80		0.218	14.0		0.168	18.4	
	27.6	0.434	9.84		0.312	13.9		0.244	18.1	
0.274	5.51	0.153	10.3	10.2	0.115	13.8	13.7	0.088	18.4	18.5
	13.8	0.388	10.2		0.290	13.7		0.217	18.6	
	19.3	0.544	10.1		0.408	13.7		0.302	18.7	
	27.6	0.778	10.2		0.581	13.7		0.435	18.5	
0.397	5.51	0.215	10.5	10.5	0.157	14.5	14.4	0.120	19.2	19.2
	13.8	0.541	10.5		0.398	14.3		0.300	19.2	
	19.3	0.758	10.4		0.560	14.2		0.420	19.1	
	27.6	1.08	10.4		0.792	14.4		0.598	19.2	
0.512	5.51	0.268	10.9	10.8	0.200	14.7	14.6	0.150	19.6	19.5
	13.8	0.675	10.7		0.498	14.6		0.376	19.5	
	19.3	0.946	10.7		0.685	14.3		0.526	19.5	
	27.6	1.35	10.7		0.995	14.6		0.750	19.5	

 $K=0.26 \text{ l mole}^{-1}, a=4060$ $K=0.21 \text{ l mole}^{-1}, a=3570$ $K=0.23 \text{ l mole}^{-1}, a=2490$

Although these mixture solutions did not indicate absorption maxima, the mixture solutions revealed much stronger absorption than the solutions of component materials in the region of wave lengths from 3100 to 3700Å, as observed on the iodine-iodobenzene system. Thus, the formation of one to one molecular complexes, C₆H₅I·IBr, C₆H₅I·ICl and C₆H₅I·Cl₂, was assumed.

Since the K values for the formation of C₆H₅I·I₂ calculated from the data obtained at the three different wave lengths, 3550, 3600 and 3650Å, agreed

with each other, only the data at 3550Å were used for the calculation of K values for the complexes, C₆H₅I·IBr, C₆H₅I·ICl and C₆H₅I·Cl₂ (Tables 3, 4 and 5). Again good linearities were observed between $[D]_o[B]_o/[A-a_o[B]_o]$ and $[D]_o$ (Fig. 3, 4 and 5), which indicated the assumption of the one to one complex formation being correct in these systems. The K values obtained for these three complexes at room temperature are 0.73, 1.2 and 0.070 l mole⁻¹, respectively.

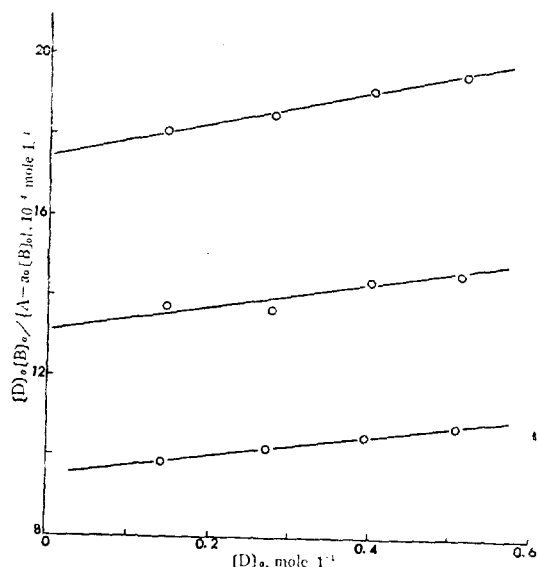


Figure 2. Plot of $[D]_0[B]_0 / \{A - a_0[B]_0\}$ Versus $[D]_0$ of the Iodobenzene-Iodine System at 21°C

Table 4. Formation of $C_6H_5I \cdot ICl$ in Carbon Tetrachloride at 21°C

C_6H_5I , mole l^{-1} ($[D]_0$)	ICl , 10^{-3} mole l^{-1} ($[B]_0$)	Absorbancy at 3550 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$, 10^{-3} mole l^{-1}	Average
0.123	1.19	0.091	1.81	1.82
	2.38	0.182	1.82	
	4.75	0.364	1.81	
	7.13	0.544	1.82	
0.263	1.19	0.167	1.99	2.01
	2.38	0.328	2.04	
	4.75	0.670	1.99	
	7.13	0.990	2.02	
0.409	1.19	0.220	2.31	2.34
	2.38	0.435	2.35	
	4.75	0.900	2.32	
	7.13	1.29	2.37	
0.523	1.19	0.259	2.49	2.51
	2.38	0.520	2.49	
	4.75	1.02	2.53	
	7.13	1.54	2.53	
$K=1.2 \text{ l mole}^{-1}, a=560$				

Table 3. Formation of $C_6H_5I \cdot IBr$ in Carbon Tetrachloride at 21°C

C_6H_5I , mole l^{-1} $([D]_0)$	IBr , 10^{-3} mole l^{-1} $([B]_0)$	Absorbancy at 3550 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$, 10^{-3} mole l^{-1}	Average
0.128	0.857	0.108	1.09	1.07
	1.71	0.222	1.06	
	2.57	0.329	1.07	
	3.43	0.442	1.06	
0.283	0.857	0.209	1.20	1.17
	1.71	0.429	1.17	
	2.57	0.654	1.15	
	3.43	0.863	1.16	
0.332	0.857	0.246	1.19	1.21
	1.71	0.475	1.23	
	2.57	0.723	1.22	
	3.43	0.968	1.21	
0.425	0.857	0.285	1.31	1.28
	1.71	0.582	1.28	
	2.57	0.873	1.28	
	3.43	1.18	1.27	

Table 5. Formation of $C_6H_5I \cdot Cl_2$ in Carbon Tetrachloride at 21°C

C_6H_5I , mole l^{-1} ($[D]_0$)	Cl_2 , 10^{-3} mole l^{-1} ($[B]_0$)	Absorbancy at 3550 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$, 10^{-3} mole l^{-1}	Average
0.123	2.37	0.135	13.6	13.9
	5.94	0.336	14.1	
	8.32	0.475	13.5	
	11.9	0.673	14.2	
0.263	2.37	0.160	13.8	14.0
	5.94	0.393	14.3	
	8.32	0.555	14.0	
	11.9	0.795	13.9	
0.409	2.37	0.183	14.0	14.1
	5.94	0.457	14.1	
	8.32	0.646	13.8	
	11.9	0.910	14.3	
0.523	2.37	0.200	14.4	14.3
	5.94	0.501	14.3	
	8.32	0.711	13.9	
	11.9	0.995	14.6	

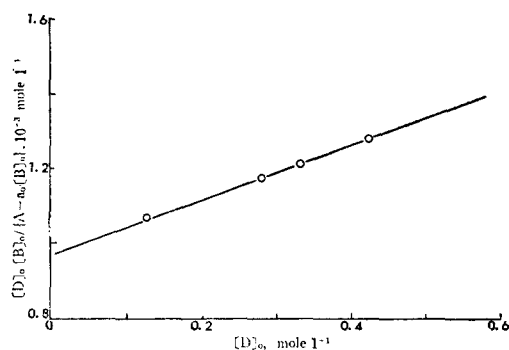


Figure 3. Plot of $[D]_0[B]_0/[A-a_e[B]_0]$ Versus $[D]_0$ of the Iodobenzene-iodine Monobromide System at 21°C

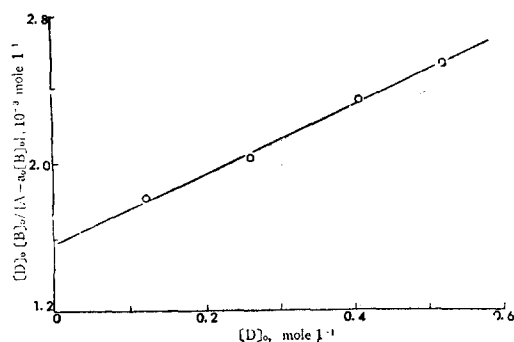


Figure 4. Plot of $[D]_0[B]_0/[A-a_e[B]_0]$ Versus $[D]_0$ of the Iodobenzene-iodine Monochloride System at 21°C

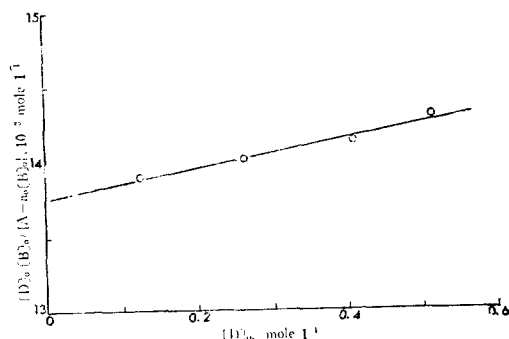
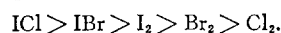


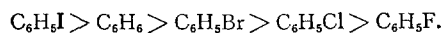
Figure 5. Plot of $[D]_0[B]_0/[A-a_e[B]_0]$ Versus $[D]_0$ of the Iodobenzene-chlorine System at 21°C

Discussion

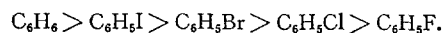
The results of the present investigation are compared with those reported in the literature^{(1), (4)} (Table 6). It is seen that the relative stabilities of any given aromatic complexes decrease in the order,



As discussed previously⁽¹⁾, this order might be considered as relative acidities of the halogens and interhalogens toward complex formation with the aromatics, and explained in terms of the relative polarizabilities of halogen molecules and the relative electronegativities of halogen atoms in the interhalogen molecules. It is also seen in Table 6 that the relative stabilities of given halogen or interhalogen complexes decrease in the order,



If it is assumed that these complexes are formed only through the interaction of π -electrons of aromatic ring with halogens or interhalogens, the following order would be expected for relative stabilities of the complexes, since this is the decreasing order of π -electron density of the aromatics:



It should be concluded therefore that some additional factors other than the utilization of π -electrons of aromatic nuclei must be considered for the formation of the iodobenzene complexes.

Table 6. Equilibrium Constants for the Formation of One to One Molecular Complexes at Room Temperature

Halogen	$K, l \text{ mole}^{-1}$				
	$\text{C}_6\text{H}_5\text{I}^{(1)}$	$\text{C}_6\text{H}_6^{(2)}$	$\text{C}_6\text{H}_5\text{Br}^{(2)}$	$\text{C}_6\text{H}_5\text{Cl}^{(2)}$	$\text{C}_6\text{H}_5\text{F}^{(2)}$
ICl	1.2	0.54	0.32	0.216	0.161
IBr	0.73	0.341	0.183	0.109	0.072
I ₂	0.23	0.173	0.13	0.106	0.064
Br ₂	0.15 ⁽³⁾	0.137	0.11	0.087	0.045
Cl ₂	0.070	0.0643	0.0485	0.040	0.035

(1) The present study except otherwise indicated. The K values at room temperature (about 21°C).

(2) See ref. 1 and papers referenced therein. The K values except for $\text{C}_6\text{H}_5\text{F}$ complexes were obtained at 25°.

(3) Ref. 4. Evaluated from K_x values by the method reported previously (ref. 1).

References

- (1) (a) Sang Up Choi, Suck Joo Chang and Shoon Ja Kwon, This Journal, **9**, 153 (1965); (b) Sang Up Choi and Bu Yong Lee, *ibid.*, **9**, 161 (1965); (c) Sang Up Choi and Suck Joo Chang, *ibid.*, **9**, 169 (1965); (d) *ibid.*, **10**, 46 (1966); (e) Sang Up Choi and Bong Joo Han, *ibid.*, **11**, 89(1967)
- (2) A.H. Blatt, Organic Syntheses Vol. II (John Wiley and Sons, Inc., New York. 1957) p.351.
- (3) International Critical Tables, Vol. I (McGraw-Hill Co., New York, 1926) p.278.
- (4) R.M. Keefer and L.J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950).