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The Complexes of Benzene with Halogens and Interhalogens in Carbon Tetrachloride[*, **]

by

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벤젠과 할로겐 또는 할로겐間化合物 사이의 錯物에 관한 연구

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要　　約

벤젠과 요오드, 브롬, 염소 또는 일브롬화요오드와의 각 系를 사염화탄소 용액에서 分光光度法에 의하여 연구한 결과 $C_6H_6 \cdot X_2$ 또는 $C_6H_6 \cdot IX$형의 錯物이 형성됨을 알았다(X는 할로겐 原子를 표시함). 이들 錯物의 생성에 대한 25°에서의 평형상수는 다음과 같다. $C_6H_6 \cdot I_2$　0.173 l mole^{-1}, $C_6H_6 \cdot Br_2$　0.137 l mole^{-1}, $C_6H_6 \cdot Cl_2$　0.0643 l mole^{-1}, $C_6H_6 \cdot IBr$　0.341 l mole^{-1}. 이 결과와 다른 사람들의 결과를 종합하면 벤젠과의 錯物의 상대적 안정도가 다음 순서로 감소함을 알 수 있다.

$ICl > IBr > I_2 > Br_2 > Cl_2$

이 순서는 그들의 상대적 산도를 의미하며 할로겐 분자의 편극율 및 할로겐 원자의 전기음성도의 차이에 의하여 설명할 수 있다.

Abstract

Ultraviolet spectrophotometric investigations have been carried out on the systems of benzene with iodine, bromine, chlorine and iodine monobromide in carbon tetrachloride. The results reveal the formation of one to one molecular complexes of the type, $C_6H_6 \cdot X_2$ or $C_6H_6 \cdot IX$ (X denotes halogen atoms). The equilibrium constants obtained at 25° for the complex formation are 0.173, 0.137, 0.0643 and 0.341 l mole^{-1} for $C_6H_6 \cdot I_2$, $C_6H_6 \cdot Br_2$, $C_6H_6 \cdot Cl_2$ and $C_6H_6 \cdot IBr$, respectively. These results combined with those obtained by other workers indicate that the relative stabilities of the benzene complexes decrease in the order,

$ICl > IBr > I_2 > Br_2 > Cl_2$.

This order may be a measure of their relative acidities toward benzene, which is explained in terms of the relative polarizabilities of halogen molecules and the relative electronegativities of halogen atoms.

Introduction

After Benesi and Hildebrand[1] first demonstrated the formation of the one to one molecular

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[*] The Molecular Complexes. III.

[**] Based partly on M. S. thesis submitted by Suck Joo Chang and by Shoon Ja Kwon to the Graduate School of Seoul National University.

complex between benzene and iodine in carbon tetrachloride solution, studies were extended to other systems by a number of workers.[2,3] Among the various experimental techniques used,[4] spectrophotometric measurement was one of the most common methods. Utilizing spectrophotometric data, the equilibrium constants for the formation of the molecular complexes were calculated by the method proposed by Benesi and Hildebrand[1] or the methods modified by other investigators.[5]

Benesi and Hildebrand[1] observed that the solution of a mixture of benzene with iodine in carbon tetrachloride had the maximum absorption at 2970 Å, and attributed it to the formation of the one to one molecular complex, $C_6H_6 \cdot I_2$, in solution. They determined both the molar absorptivity, a, of the complex at 2970 Å, and the corresponding equilibrium constant *, K_x, in which the concentration of benzene was expressed by mole fractions and the concentrations of other species by molar concentrations. The values obtained at room temperature were as follows:

$$a=15400, \quad K_x=1.72.$$

As the results of similar studies, however, Keefer and Andrews[2d] observed the absorption maximum of the benzene—iodine complex at 2920 Å, and determined both the molar absorptivity of the complex at 2920 Å and the corresponding equilibrium constant **, K, in which the concentrations of all species were expressed in terms of molar concentrations. The values obtained at 25° were as follows:

$$a=16400, \quad K=0.15\ l\ \text{mole}^{-1}.$$

Thus, the results reported by the two groups of authors did not agree well with each other. It appeared of interest, therefore, to reinvestigate spectrophotometrically the system of benzene—iodine in carbon tetrachloride.

Keefer and Andrews evaluated also the equilibrium constants, K_x, for the formation of the complexes of benzene with bromine[2a], chlorine[2c] and iodine monochloride[2b] in carbon tetrachloride.

The K_x values obtained at 25° were as follows:

Benzene—bromine, $K_x=1.04$.
Benzene—chlorine, $K_x=0.33$.
Benzene—iodine monochloride, $K_x=4.76$.

The relative magnitudes of the K_x values may be a measure of relative stabilities of the complexes. Since all of the complexes mentioned above are the benzene-complexes, the relative complexing power of the halogens and the interhalogen with benzene presumably decreases in the order,

$$ICl > I_2 > Br_2 > Cl_2.$$

It then appeared of interest to extend the studies to the system of benzene—iodine monobromide in carbon tetrachloride, in order to determine the relative complexing power of iodine monobromide with benzene. Thus, the present study involved the spectrophotometric investigations of the systems of benzene with iodine, bromine, chlorine, and iodine monobromide in carbon tetrachloride.

Experimental

Materials.—Benzene(reagent grade, Wako, Japan) was treated with concentrated sulfuric acid, and washed successively with water, 10% aqueous solution of sodium carbonate, and again water.[6] It was then dried over metallic sodium, and distilled through a 100-cm. distillation column packed with glass helices. The reflux ratio was controlled at approximately 1:15. The middle fraction of the distillate was collected and the boiling point observed was 80.2°.

Carbon tetrachloride(reagent grade, Katayama, Japan) was dried over calcium chloride and distilled through a 100-cm. distillation column at the reflux ratio of about 1:15. The middle

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* This equilibrium constant has no dimensions and will be referred to as K_x hereafter in this paper.

** This equilibrium constant has the dimensions of l mole^{-1}, and will be referred to as K hereafter in this paper.

portion of the distillate was collected and the boiling point observed was 76.8°.

Iodine (reagent grade, Merck, Germany) was purified by sublimation of a mixture of iodine with potassium iodide (about 3:1 by weight), followed by resublimation of the product.[7] It was stored over phosphorus pentoxide in a desiccator.

Bromine (Wako, Japan) was used without further purification.

Chlorine was prepared by dissolving potassium dichromate into hydrochloric acid. The evolving chlorine gas was washed successively with water and concentrated sulfuric acid in order to remove contaminated hydrogen chloride.

Preparation of Stock Solutions.—The solution of iodine in carbon tetrachloride was prepared by weighing an appropriate quantity of iodine into a volumetric flask, and adding carbon tetrachloride solvent to make up to volume. The solution thus prepared was diluted further to suitable concentrations.

The solutions of bromine or chlorine in carbon tetrachloride were perpared by pipetting a small amount of bromine or bubbling chlorine gas into carbon tetrachloride in volumetric flasks. The concentrations of the solutions were then deterimined by titration with 0.1 normal sodium thiosulfate solution in the presence of excess potassium iodide.[8] After the concentrations were determined, the solutions were diluted to appropriate concentrations.

The solution of iodine monobromide in carbon tetrachloride was prepared by dissolving an equivalent quantity of elemental iodine into bromine solutions whose concentrations had already been determined.

The solution of benzene in carbon tetrachloride was prepared by weighing an appropriate quantity of benzene into a volumetric flask and adding carbon tetrachloride to make up to volume.

All the stock solutions were brought to 25° by placing in a thermostat prior to the spectrophotometric measurements. The temperature of the thermostat was kept at 25±0.5°.

The Spectrophotometric Measurements.—The absorbancies of the stock solutions of iodine, bromine, chlorine, iodine monobromide or benzene in carbon tetrachloride were measured over the region of wave lengths from 2700 to 6000 Å, using the pure solvent, carbon tetrachloride, as the blank.

Then, the stock solution of benzene was mixed at various ratio with the solutions of the halogens or the interhalogen*. The absorbancies of the resulting solutions were immediately measured. The prolonged keeping of the mixture solutions was avoided for otherwise slow chemical changes might have occurred. The blank in this case was the carbon tetrachloride solution of benzene with the same concentrations as those of the solutions containing the halogens or the interhalogen.

A Beckman DU Spectrophotometer and a set of 1-cm. quartz cells were used for the absorbancy measurements.

Results and Discussion

Calculation of Equilibrium Constants for the Complex Formation.—The absorption spectra of the individual stock solutions of iodine, bromine, chlorine, iodine monobromide or benzene in carbon tetrachloride did not indicate the presence of maximum absorption peaks in the vicinity of 2900 Å. When the absorption spectra of the solutions of a mixture of benzene with iodine, bromine, chlorine or iodine monobromide in carbon tetrachloride were measured, however, absorption maxima were observed in the region of wave lengths near 2900 Å.

The maximum absorptions observed are attri-

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* The total volume after mixing the two solutions was assumed to be the sum of those of the two solutions in the calculation of concentrations of the resulting solutions.

buted to the formation of the complexes of benzene with the halogens or the interhalogen in solution. The complexes of this type are assumed to be the one to one molecular complexes, as was first proposed by Benesi and Hildebrand for the system of benzene—iodine in carbon tetrachloride.[1)]

$$\mathrm{D} + \mathrm{B} \rightleftharpoons \mathrm{C} \qquad (1),$$

where D denotes the benzene molecules, B the molecules of iodine, bromine, chlorine or iodine monobromide, and C the one to one molecular complexes D·B.

The absorbancies, A, measured at the maximum absorption peaks are due to both the complexes and the free halogens or interhalogen present in solution.

$$A = a[\mathrm{C}] + a_0\{[\mathrm{B}]_0 - [\mathrm{C}]\} \qquad (2),$$

where a and a_0 denote respectively the molar absorptivities of the complexes and the free halogens or interhalogen at the wave lengths corresponding to the absorption maxima of the complexes, $[\mathrm{B}]_0$ molar concentrations of the halogens or the interhalogen present initially, and $[\mathrm{C}]$ molar concentrations of the complexes.

The equilibrium constant, K, for equilibrium (1) is expressed by

$$K = \frac{[\mathrm{C}]}{\{[\mathrm{D}]_0 - [\mathrm{C}]\}\{[\mathrm{B}]_0 - [\mathrm{C}]\}} \qquad (3),$$

where $[\mathrm{D}]_0$ denotes molar concentrations of benzene present initially. Combining equations (2) and (3), it follows that*

$$\frac{[\mathrm{D}]_0[\mathrm{B}]_0}{A - a_0[\mathrm{B}]_0} = \frac{[\mathrm{D}]_0 + [\mathrm{B}]_0}{a - a_0} + \frac{1}{a - a_0}\left\{\frac{1}{K} - \frac{A - a_0[\mathrm{B}]_0}{a - a_0}\right\} \qquad (4).$$

In the present study, $[\mathrm{D}]_0 \gg [\mathrm{B}]_0$. If it is assumed, therefore, that

$$\frac{1}{K} \gg \frac{A - a_0[\mathrm{B}]_0}{a - a_0} \qquad (5),$$

the following equation is obtained:

$$\frac{[\mathrm{D}]_0[\mathrm{B}]_0}{A - a_0[\mathrm{B}]_0} = \frac{1}{a - a_0}[\mathrm{D}]_0 + \frac{1}{(a - a_0)K} \qquad (6).$$

This assumption (equation 5) was found to be reasonable from the values of K, a, a_0, A and $[\mathrm{B}]_0$ obtained on all the systems in the present study. (Tables Ⅱ, Ⅲ, Ⅳ and Ⅵ)

After the values of a_0 were determined experimentally, the quantities of $[\mathrm{D}]_0[\mathrm{B}]_0/\{A - a_0[\mathrm{B}]_0\}$ were plotted against $[\mathrm{D}]_0$. The plots indicated good linearity between the two quantities in all the systems examined. (Figs. 1 to 4) Hence, the values of $1/(a - a_0)$ and $1/\{K(a - a_0)\}$ were calculated from the slopes and the intercepts of the straight lines. The least square method was utilized to determine the slopes and the intercepts of the plots. Knowing the values of $(a - a_0)$ and $K(a - a_0)$, the values of K and a were calculated, since the values of a_0 were determined already. (Table Ⅰ)

Since linearities were observed between $[\mathrm{D}]_0[\mathrm{B}]_0/\{A - a_0[\mathrm{B}]_0\}$ and $[\mathrm{D}]_0$ experimentally, not only the values of K and a were able to be calculated, but it could be concluded that the assumption of the formation of one to one complexes should be correct.

Table Ⅰ

Molar Absorptivities of Halogens and Interhalogen in Carbon Tetrachloride Solution at 25°.

Halogen	Concn., 10^{-3} mole l^{-1}	Wave length, Å	Absorbancy(A)	Molar absorptivity (a_0)	Average
I_2	0.0850	2930	—	42.7 (1)	
	0.124	〃	—	42.8 (1)	
	0.130	〃	—	42.8 (1)	42.8
Br_2	3.97	2860	0.123	31.0	
	7.95	〃	0.248	31.2	
	19.9	〃	0.604	30.4	30.9
Cl_2	14.9	2760	0.078	5.24	
	74.4	〃	0.391	5.25	
	112	〃	0.568	5.08	5.19
IBr	1.27	2900	0.166	131	
	2.54	〃	0.323	127	
	3.82	〃	0.487	128	
	5.09	〃	0.662	130	129

(1) Estimated from the literature value. (ref. 9)

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* This equation is identical to that reported by Rose and Drago (ref. 5). But the method of calculating thevalues of K and a in the present study is different fromtheir method.

The Benzene-Halogen Complexes. — Data obtained at 25° on the systems of benzene with iodine, bromine and chlorine in carbon tetrachloride are summarized in Tables Ⅱ, Ⅲ and Ⅳ, and shown graphically in Figs. 1, 2 and 3.

The results of the present study are now compared with those reported in the literature. Benesi and Hildebrand reported a value of 1.72 as the K_x for the complex, $C_6H_6 \cdot I_2$.[1] Rose and Drago recalculated the K_x value, utilizing the data obtained by Benesi and Hildebrand but using a modified method of calculation, and

Table Ⅱ

Formation of $C_6H_6 \cdot I_2$ in Carbon Tetrachloride at 25°.

C_6H_6, mole l^{-1} ($[D]_o$)	I_2, 10^{-3} mole l^{-1} ($[B]_o$)	Absorbancy at 2930 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$ 10^{-3} mole l^{-1}
2.57	0.0850	0.409	0.538
3.22	0.124	0.684	0.588
5.38	0.130	0.974	0.722

$K = 0.173$ l mole^{-1}
$a = 15500$

Table Ⅲ

Formation of $C_6H_6 \cdot Br_2$ in Carbon Tetrachloride at 25°.

C_6H_6, mole l^{-1} ($[D]_o$)	Br_2, 10^{-4} mole l^{-1} ($[B]_o$)	Absorbancy at 2860 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$, 10^{-3} mole l^{-1}	Average, 10^{-3} mole l^{-1}
2.20	0.04	0.189	1.23	
	1.91	0.352	1.21	
	3.83	0.736	1.16	
	5.75	1.20	1.07	1.17
4.33	1.04	0.309	1.47	
	1.91	0.568	1.47	
	3.83	1.14	1.47	1.47
6.41	1.04	0.395	1.70	
	1.91	0.715	1.73	
	3.83	1.39	1.78	1.74
9.39	1.04	0.471	2.09	
	1.91	0.881	2.05	
	3.83	1.75	3.07	2.07

$K = 0.137$ l mole^{-1}
$a = 8030$

Table Ⅳ

Formation of $C_6H_6 \cdot Cl_2$ in Carbon Tetrachloride at 25°.

C_6H_6, mole l^{-1} ($[D]_o$)	Cl_2, 10^{-3} mole l^{-1} ($[B]^{\circ}$)	Absorbancy at 2760 Å (A)	$\frac{[D]_o[B]_o}{A-a_o [B]_o}$ 10^{-3} mole l^{-1}	Average, 10^{-3} mole l^{-1}
1.12	1.07	0.262	4.68	
	1.16	0.275	4.83	
	1.54	0.366	4.79	
	1.92	0.478	4.59	4.73
2.22	0.580	0.261	4.99	
	0.660	0.295	5.02	
	1.02	0.416	5.51	
	1.07	0.478	5.03	
	1.16	0.523	4.98	5.11
3.32	0.580	0.358	5.42	
	0.660	0.408	5.41	
	1.02	0.627	5.44	
	1.07	0.637	5.63	
	1.16	0.736	5.28	5.44
4.36	0.580	0.446	5.71	
	0.660	0.523	5.53	
	1.02	0.800	5.59	
	1.07	0.863	5.44	5.57
5.41	0.660	0.590	6.08	
	1.02	0.901	6.16	
	1.07	0.980	5.94	
	1.16	1.08	5.84	6.01

$K = 0.0643$ l mole^{-1}
$a = 3520$

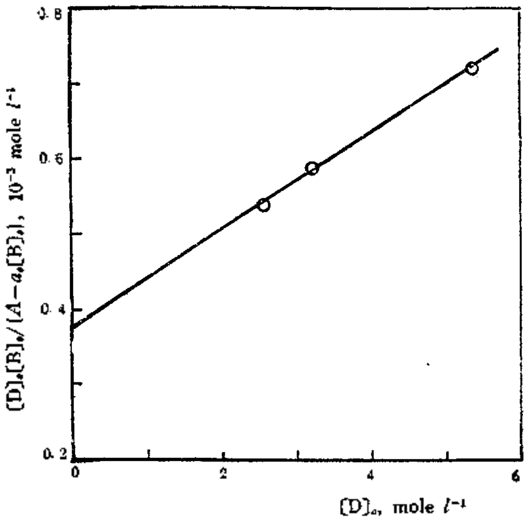

Fig. 1 Plot of $[D]_o$ $[B]_o/\{A-a_o[B]_o\}$ versus $[D]_o$ of the benzene—iodine system at 25°C.

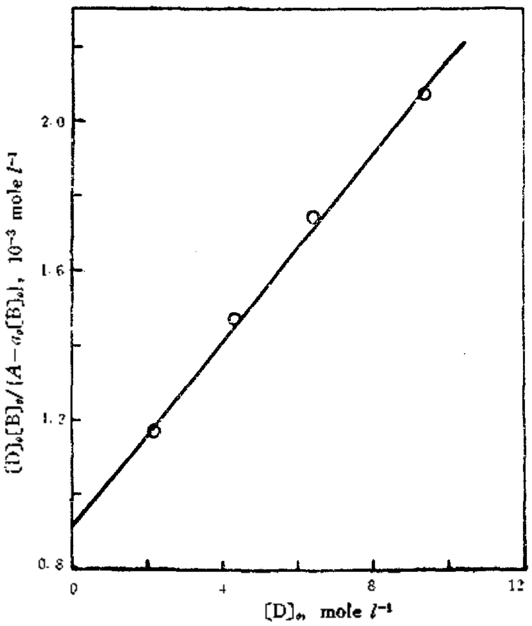

Fig. 2 Plot of $[D]_0[B]_0/\{A-a_0[B]_0\}$ versus $[D]_0$ of the benzene—bromine system at 25°C.

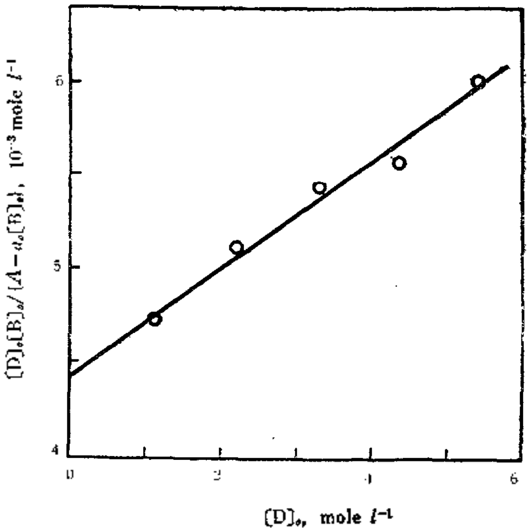

Fig. 3. Plot of $[D]_0[B]_0/\{A-a_0[B]_0\}$ versus $[D]_0$ of the benzene—chlorine system at 25°C.

reported a value of 1.78 as the K_x value.[5] On the other hand, Keefer and Andrews obtained a value of 0.15 l mole^{-1} as the K value.[2d] For closer examination, the K_x values mentioned above are converted to the K values with the aid of the following approximation, and are listed in Table V.

$$K=K_x\cdot\frac{MW}{10^3d} \tag{7}$$

where MW and d denote the molecular weight and the density of carbon tetrachloride, respectively. A value of 1.595 was used as the density of carbon tetrachloride[10] for this conversion. It can be seen from Table V that the results of the present study agree generally well with those of other investigators, although fairly significant discrepancy exists in some cases.

Larger values of K indicate greater stabilities of the corresponding complexes. Hence, it is concluded that among the halogens examined, iodine forms the most stable complex with benzene, bromine the less stable one and chlorine the least stable one. Since these complexes are explained in terms of an interaction between Lewis base(benzene) and Lewis acids (halogens), it appears that the relative acidity toward benzene decreases in the order,

$$I_2>Br_2>Cl_2.$$

According to Mulliken,[11] these complexes should be stabilized by resonance between a non-bonded structure,

$$(C_6H_6)\cdots\cdots\cdots(X-X) \qquad \text{(I)}$$

Table V

Data Obtained on the $C_6H_6\cdot I_2$, $C_6H_6\cdot Br_2$ and $C_6H_6\cdot Cl_2$ Complexes in Carbon Tetrachloride by Different Authors.

Halogen	Wave length of absorption maxima, Å (λ_{max})	Molar absorptivity (a)	Equilibrium const., l mole^{-1} (K)	Ref.
I_2	2930	15500	0.173	This study
	2970	15400	0.166$^{(2)}$	Ref. 1
	(2970)$^{(1)}$	15400	0.172$^{(2)}$	Ref. 5
	2920	16400	0.15	Ref. 2d
Br_2	2860	8030	0.137	This study
	2920	13400	0.100$^{(2)}$	Ref. 2a
Cl_2	2760	3520	0.0643	This study
	2780	2220	0.032$^{(2)}$	Ref. 2c

(1) Value reported in Ref. 1.

(2) Estimated with the aid of equation (7) from the K_x values in the literature.

and a dative structure,

$$(C_6H_6)^+\cdots\cdots\cdots(X-X)^- \qquad (\text{II}),$$

the latter becoming increasingly important with stronger interaction (X denotes halogen atoms). The relative stabilities of the halogen complexes of benzene may therefore be affected by the relative magnitudes of contribution of structure II to the resonance, which in turn could be correlated with the abilities of the halogen molecules to accomodate an electronic charge. Thus, it appears that among the three halogens studied, iodine has the greatest contribution of structure II to the resonance, probably due to its highest polarizability, whereas chlorine has the least contribution due to its lowest polarizability.

The Benzene-Iodine Monobromide Complex. —The results obtained at 25° on the system of benzene with iodine monobromide in carbon tetrachloride are summarized in Table VI, and shown graphically in Fig. 4.

It is concluded from the present study that benzene forms more stable complex with iodine monobromide than with the elemental halogens examined. This may be explained by considering an additional resonance structure,

$$(C_6H_6I)^+\cdots\cdots\cdots Br^- \qquad (\text{III}).$$

Thus, the positive end of IBr molecules may interact with the π-electrons of benzene nucleus, whereas the halogen molecules do not have such interaction.

Table VI

Formation of $C_6H_6\cdot IBr$ in Carbon Tetrachloride at 25°.

C_6H_6, mole l^{-1} ($[D]_o$)	IBr, 10^{-4} mole l^{-1} ($[B]_o$)	Absorbancy at 2900 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$, 10^{-4} mole l^{-1}	Average 10^{-4}mole l^{-1}
0.985	0.778	0.207	3.89	
	1.55	0.482	3.31	
	3.11	0.790	4.08	
	3.89	1.18	3.39	3.66
1.97	0.778	0.325	4.87	
	1.55	0.640	4.93	
	3.11	1.33	4.75	4.85
2.92	0.778	0.407	5.72	
	1.55	0.840	5.52	
	3.11	1.66	5.61	5.62
3.89	0.778	0.468	6.61	
	1.55	0.950	6.49	6.55

$K=0.341\ l\ \text{mole}^{-1}$

$a=10500$

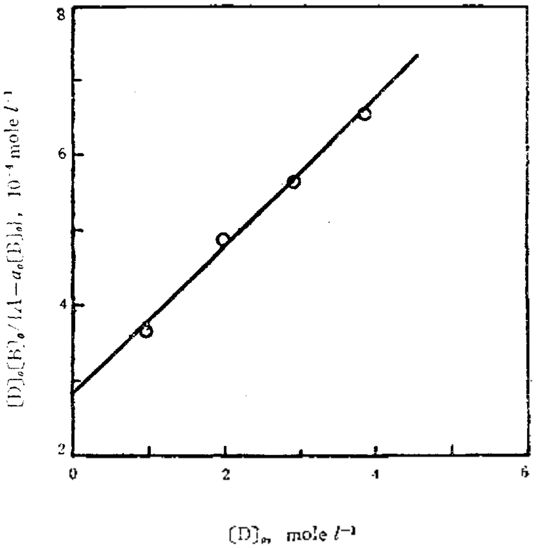

Fig. 4 Plot of $[D]_o[B]_o/(A-a_o[B]_o)$ versus $[D]_o$ of the benzene—iodine monobromide system at 25°C.

In view of the greater K value for the system of benzene with iodine monobromide than with iodine, bromine or chlorine, the K value for the $C_6H_6\cdot ICl$ complex reported in the literature is compared with that for the $C_6H_6\cdot IBr$ complex (Table VII). The fact that iodine monochloride exhibits greater K value than iodine monobromide is attributed to greater importance of resonance structure III in the ICl system than in the IBr system. This might be rationalized by considering the electronegativities of chlorine and bromine. Since chlorine has greater electronegativity than bromine, ICl molecules are more polarized than IBr molecules, and hence the positive end of ICl molecules has greater positive charge than that of IBr molecules.

Comparing the K values listed in Table VII,

Table Ⅶ

Summary of Data Obtained on the Halogen Complexes of Benzene in Carbon Tetrachloride at 25°.

Halogen	Wave length of absorption maxima, Å (λ_{max})	Molar absorptivity (a)	Equilibrium const., (K) l mole^{-1}
ICl(1)	2820	8130	0.54
IBr	2900	10500	0.341
I_2	2930	15500	0.173
Br_2	2860	8030	0.137
Cl_2	2760	3520	0.0643

(1) Ref. 2d.

the following order can be established for the relative acidities of the halogens and the interhalogens toward benzene.

$$ICl > IBr > I_2 > Br_2 > Cl_2 \cdot$$

On the other hand, the values of λ_{max}, and a shown in Table Ⅶ do not exhibit any gradual changes with increasing K values. Hence, it appears that the values of λ_{max} and a may be affected by some additional factors, besides the relative acidities of the halogens and the interhalogens.

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