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

by

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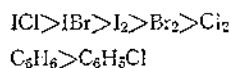(Received September 17, 1965)

클로로벤젠과 할로겐 또는 할로겐間化合物 사이의 錯物에 관한 연구

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要　約

클로로벤젠과 요오드, 염소 또는 일브롬화오오드와의 각 系를 사염화탄소 용액에서 分光光度法에 의하여 연구한 결과 $C_6H_5Cl \cdot I_2$, $C_6H_5Cl \cdot Cl_2$ 및 $C_6H_5Cl \cdot IBr$ 의 錯物이 형성됨을 알았다. 이들 錯物의 생성에 대한 $25°$에서의 평형상수는 각각 0.106, 0.0400 및 0.109 l $mole^{-1}$ 였다. 이 결과와 文献에 있는 실험결과를 綜合하면 芳香族化合物과 할로겐 또는 할로겐間化合物과의 錯物의 상대적 안정도가 다음 순서로 감소함을 알 수 있다.

$$ICl > IBr > I_2 > Br_2 > Cl_2$$
$$C_6H_6 > C_6H_5Cl$$

Abstract

The results of ultraviolet spectrophotometric investigations on the system of chlorobenzene with iodine, chlorine and iodine monobromide in carbon tetrachloride at $25°$ indicate the formation of one to one molecular complexes, $C_6H_5Cl \cdot I_2$, $C_6H_5Cl \cdot Cl_2$ and $C_6H_5Cl \cdot IBr$. The equilibrium constants obtained at $25°$ for the complex formations are 0.106, 0.0400 and 0.109 l $mole^{-1}$, respectively. These results combined with those reported in the literature reveal the following order as the relative stabilities of complexes with aromatics and with halogens or interhalogens, respectively.
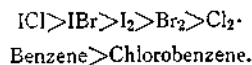
$$ICl > IBr > I_2 > Br_2 > Cl_2 \cdot$$
$$\text{Benzene} > \text{Chlorobenzene}.$$

Introduction

As the results of our previous study on ultraviolet spectrophotometric investigations of the

systems of benzene with halogens and interhalogens in carbon tetrachloride at 25°,[1] it was found that the one to one molecular complexes of the type $C_6H_6 \cdot X_2$ ($X_2 = I_2$, Br_2 and Cl_2) or $C_6H_6 \cdot IX$ (IX = ICl and IBr) were present in solution. The equilibrium constants for the formation of the complexes were calculated, and the following order was established for relative complexing abilities with benzene:

$$ICl > IBr > I_2 > Br_2 > Cl_2.$$
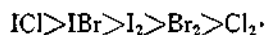
In a previous study of this series,[2] we also investigated the effect of solvents on the stabilities of the $C_6H_6 \cdot I_2$ complex and the $C_6H_6 \cdot ICl$ complex. The results observed were correlated with dielectric constants of the solvents, supporting a conclusion that a dative, ionic structures, $C_6H_6^+ \cdots I_2^-$ and $(C_6H_6I)^+ \cdots Cl^-$, would contribute greatly to the resonance stabilization[3] of the complexes. Thus, it appeared that complexes of this type were formed through a charge transfer between Lewis acid and Lewis base in solution.

Therefore, the order of the halogens and the interhalogens mentioned above might be the decreasing order of their relative acidities toward benzene, a Lewis base. It then appeared of interest to examine the systems of chlorobenzene with the halogens and the interhalogens in order to see if the similar tendency could be observed with chlorobenzene, and to compare the relative stability of chlorobenzene complex with that of benzene complex.

The present study involved the spectrophotometric investigations at 25° on the systems of chlorobenzene with iodine, chlorine and iodine monobromide in carbon tetrachloride.

Experimental

Materials. —Chlorobenzene (reagent grade, Wako, Japan) was distilled through a 100-cm. column packed with glass helices. The reflux ratio was controlled at approximately 1:15. The middle portion of the distillate was collected. The boiling point observed was 132°. All the other materials used in the present study were prepared and/or purified by the method reported previously.[1]

Spectrophotometric Measurements. — The experimental procedures utilized for both the preparation of stock solutions and the spectrophotometric measurements of the solutions were described previously,[1] and will not repeated in this paper. A Beckman DU Spectrophotometer and a set of 1-cm. quartz cells were used.

Results

The absorption spectra of the solutions of iodine, chlorine, iodine monobromide or chlorobenzene in carbon tetrachloride were measured. The results showed no absorption maxima in the vicinity of 2840 Å. When the spectra of the carbon tetrachloride solutions of chlorobenzene with the halogens or the interhalogens were measured, however, absorption maxima were observed at 2840 Å.

This phenomenon is similar to that observed on the corresponding benzene systems.[1] Thus, the absorption maxima are attributed to the formation of one to one molecular complexes (D·B) between chlorobenzene (D) and the halogens or the interhalogen (B).

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

where C denotes the complexes, D·B. If the assumption of the one to one complex formation (equilibrium 1) is correct, the plots of $[D]_o [B]_o / \{A - a_o [B]_o\}$ versus $[D]_o$ should exhibit linearities. (A denotes the absorbancies measured at the maximum absorption peaks, a_o the molar absorptivities of the free halogens or interhalogen at wave length corresponding to the absorption maxima, of the complexes, and $[\ ]_o$ the initial molar concentrations.) From slopes and intercept of the straight lines, the equilibrium constants, K, for the complex formation

and the molar absorptivities, a, of the complexes at their absorption maxima were evaluated by

Table I

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

Halogen	Concn., 10^{-3} mole l^{-1}	Wave length, (Å)	Absorbancy	Molar absorptivity (a_o)	Average
I₂ [1]	0.252	2840	—	43.5	
	0.316	"	—	43.7	
	0.441	"	—	44.0	
	0.567	"	—	44.2	43.9
Cl₂	22.3	2840	0.247	11.1	
	37.2	"	0.465	12.5	
	74.4	"	0.887	11.9	
	112	"	1.23	11.0	11.6
IBr	1.27	2840	0.193	152	
	2.54	"	0.382	150	
	3.82	"	0.575	151	
	5.09	"	0.782	154	152

[1] Ref. 4

Table II

Formation of $C_6H_5Cl \cdot I_2$ in Carbon Tetrachloride at 25°.

C_6H_5Cl, mole l^{-1} [D]$_o$	I₂, 10^{-2} mole l^{-1} [B]$_o$	Absorbancy at 2840 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$ 10^{-4} mole l^{-1}	Average, 10^{-4} mole l^{-1}
0.902	2.52	0.242	9.84	
	3.16	0.276	10.9	
	4.41	0.343	12.3	
	5.67	0.480	11.2	11.1
1.79	2.52	0.396	11.7	
	3.16	0.494	11.8	
	4.41	0.676	12.1	
	5.67	0.897	11.7	11.8
2.72	2.52	0.550	12.7	
	3.16	0.720	12.2	
	4.41	0.920	12.3	
	5.67	1.26	12.5	12.4
3.52	2.52	0.632	14.3	
	3.16	0.900	12.6	
	4.41	1.21	13.0	13.3
4.58	2.52	0.795	14.7	
	3.16	0.987	14.9	
	4.41	1.40	14.7	14.8

$K = 0.106$ l mole^{-1}

$a = 9650$

the method described previously,[1] after the values of a_o were determined experimentally (Table I).

Data obtained at 25° are summarized in Tables II, III and IV. The results exhibit good linearities between $[D]_o[B]_o / \{A-a_o[B]_o\}$ and $[D]_o$ in all the systems examined (Figs. 1 to 3), indicating the assumption of the formation of one to one molecular complexes being correct.

Discussion

As the results of the present study, it is concluded that iodine, chlorine and iodine monobromide form one to one molecular complexes, $C_6H_5Cl \cdot I_2$, $C_6H_5Cl \cdot Cl_2$ and $C_6H_5Cl \cdot IBr$, with chlorobenzene in carbon tetrachloride.

Comparing the K values for these complexes with those for the benzene complexes,[1] it is

Table III

Formation of $C_6H_5Cl \cdot Cl_2$ in Carbon Tetrachloride at 25°.

C_6H_5Cl, mole l^{-1} [D]$_o$	Cl₂, 10^{-3} mole l^{-1} [B]$_o$	Absorbancy at 2840 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$ 10^{-3} mole l^{-1}	Average, 10^{-3} mole l^{-1}
4.01	0.770	0.462	6.82	
	1.07	0.630	6.91	
	1.16	0.693	6.84	
	1.54	0.920	6.82	6.86
5.03	0.770	0.557	7.07	
	1.07	0.775	7.24	
	1.16	0.831	7.13	
	1.54	1.10	7.16	7.15
6.12	0.770	0.657	7.27	
	1.07	0.890	7.46	
	1.16	0.992	7.25	
	1.54	1.35	7.08	7.27
7.38	0.770	0.752	7.65	
	1.07	1.02	7.83	
	1.16	1.31	6.60	
	1.54	1.49	7.72	7.45
8.20	0.770	0.812	7.86	
	1.07	1.10	8.06	
	1.16	1.23	7.82	7.91

$K = 0.0400$ l mole^{-1}

$a = 4270$

also concluded that these chlorobenzene compl-
exes are less stable than the corresponding
benzene complexes. This might be explained
by assuming that both the chlorobenzene com-
plexes and the benzene complexes are formed
through the utilization of π-electrons of the

Table IV

Formation of $C_6H_5Cl \cdot IBr$ in Carbon Tetrachloride at 25°.

C_6H_5Cl, mole l^{-1} ($[D]_o$)	IBr. 10^{-4} mole l^{-1} $[B]_o$	Absorbancy at 2840 Å (A)	$\dfrac{[D]_o[B]_o}{A-a_o[B]_o}$ 10^{-4} mole l^{-1}	Average. 10^{-4} mole l^{-1}
0.902	2.25	0.205	11.9	
	3.13	0.330	9.98	
	3.92	0.360	11.8	
	7.84	0.820	10.1	10.9
1.79	2.25	0.385	11.5	
	3.13	0.529	11.6	
	3.92	0.610	12.7	
	7.84	1.25	12.4	12.1
2.72	1.96	0.445	12.8	
	2.25	0.523	12.5	
	3.13	0.710	12.8	12.7
3.52	1.96	0.520	13.9	
	2.25	0.632	13.2	
	3.13	0.796	14.7	
	3.92	1.12	13.0	13.7
4.58	1.96	0.600	15.8	
	2.25	0.730	14.8	
	3.13	1.05	14.3	
	3.92	1.25	15.1	15.0

$K=0.109$ l mole^{-1}
$a=9630$

aromatic nuclei. Since chlorine has greater ele-
ctronegativity than hydrogen, the π-electron
cloud of the chlorobenzene nucleus is less dense
than that of benzene, and hence chlorobenzene
has weaker interaction with the halogens or
the interhalogen than benzene does. Thus, it is
concluded that chlorobenzene is weaker Lewis
base than benzene toward the halogens or the
interhalogen.

The K values for these chlorobenzene com-
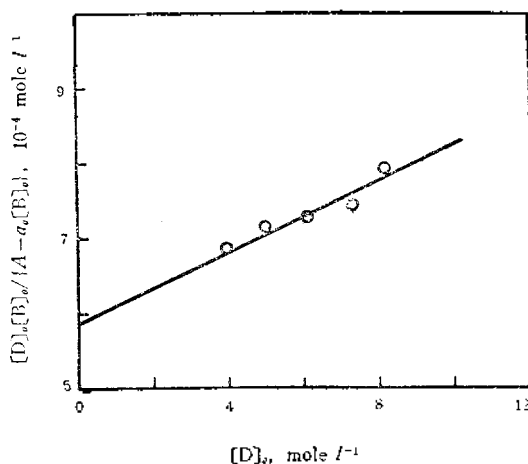plexes are now compared with those for the

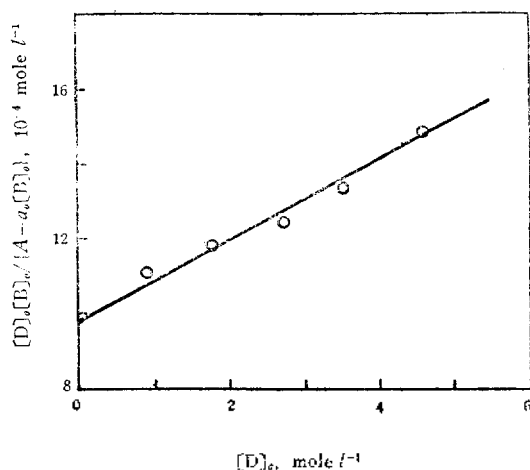**Fig. 2** Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ versus $[D]_o$ of the chlorobenzene—chlorine system at 25°C.

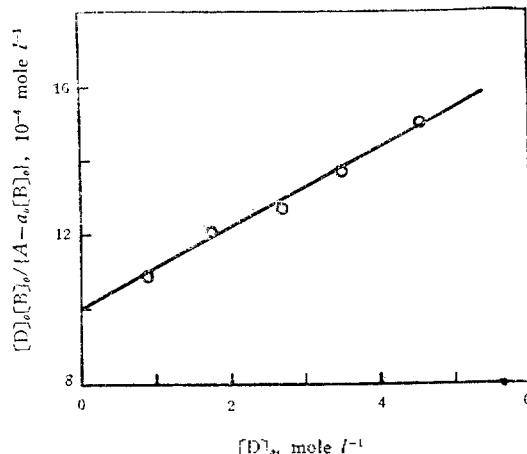**Fig. 1** Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ versus $[D]_o$ of the chlorobenzene—iodine system at 25°C.

Fig. 3 Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ versus $[D]_o$ of the chlorobenzene—iodine monobromide system at 25°C.

$C_6H_5Cl \cdot Br_2$ complex [5] and the $C_6H_5Cl \cdot ICl$ complex. [6] Keefer and Andrews reported a value of 0.90 as the equilibrium constant, K_x, at 25° for the $C_6H_5Cl \cdot Br_2$ complex, in which the aromatic concentration was expressed by mole fractions and all other species by molar concentrations. [5] Keefer and Andrews also reported a value of 2.24 as the K_x value at 25° for the $C_6H_5Cl \cdot ICl$ complex. [6] These K_x values are converted to K values with acid of the following approximation:

$$K = K_x \cdot \frac{MW}{10^3 d} \qquad (2),$$

where MW and d denote the molecular weight and the density of carbon tetrachloride, respectively. The results of this conversion are included in Table V.

Table V

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

Halogen	Wave length of absorption maxima, Å (λ_{max})	Molar absorptivity (a)	Equilibrium const., l mole^{-1} (K)
ICl [1]	2870	5650	0.216 [3]
IBr	2840	9330	0.109
I_2	2840	9650	0.106
Br_2 [2]	2860	7300	0.087 [3]
Cl_2	2840	4270	0.0400

[1] Ref. 6
[2] Ref. 5
[3] Evaluated from K_x values by equation (2).

It is seen from Table V that the relative stabilites of the chlorobenzene complexes decrease in the order,

$$ICl > IBr > I_2 > Br_2 > Cl_2.$$
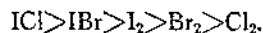
Since these complexes are considered to be formed through Lewis acid-base interaction, this must be the decreasing order of their relative acidities toward chlorobenzene. This order is exactly the same as that observed on the corresponding benzene complexes. Hence, as was discussed previously, [1] it appears that the relative acidities of the halogens and the interhalogens toward chlorobenzene also may be explained in terms of the relative polarizabilities of halogen molecules and the relative electronegativities of halogen atoms.

The values of λ_{max} and a listed in Table V do not reveal any gradual changes with increasing K values. Hence the relative values of both λ_{max} and a should be accounted for probably by some additional factors, besides the relative acidities of the halogens and the interhalogens.

References

1) Sang Up Choi, Suck Joo Chang and Shoon Ja Kwon, *This Journal*, **9**, 153 (1965).

2) Sang Up Choi and Bu Yong Lee, *ibid.*, **9**, 161 (1965).

3) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

4) Bong Joo Han, M. S. Thesis, Hanyang Univ. Library, 1964.

5) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950).

6) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).