

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

by

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플루오로벤젠과 할로겐 또는 할로겐間化合物 사이의錯물에 관한 연구

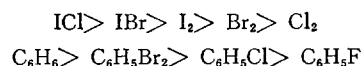
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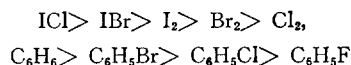
요 약

플루오로벤젠과 일염화요오드, 일브롬화요오드, 브롬 또는 염소의 각 시스템을 사염화탄소 용액에서 分光光度法에 의하여 연구한 결과, $C_6H_5F \cdot ICl$, $C_6H_5F \cdot IBr$, $C_6H_5F \cdot Br_2$, 또는 $C_6H_5F \cdot Cl_2$ 의錯물이 형성됨을 알았다. 이들錯物형성에 대한 실온에서의 평형상수는 각각 0.161, 0.072, 0.045 및 0.035 $l \text{ mole}^{-1}$ 이다. 이 결과와 문헌에 보고된 연구결과를 종합함으로써 이러한錯物の 상대적 안정도가 다음 순으로 감소함을 알 수 있었다.



Abstract

The interactions of fluorobenzene with iodine monochloride, iodine monobromide, bromine and chlorine in carbon tetrachloride solution have been examined through ultraviolet spectrophotometric measurements. The results indicate the formation of one to one molecular complexes, $C_6H_5F \cdot ICl$, $C_6H_5F \cdot IBr$, $C_6H_5F \cdot Br_2$ and $C_6H_5F \cdot Cl_2$, in solution. The equilibrium constants obtained at room temperature for the formation of these four complexes are 0.161, 0.072, 0.045 and 0.035 $l \text{ mole}^{-1}$, respectively. Comparison of these results with those reported in the literature on other complexes of similar type reveals that the relative stabilities of these complexes decrease in the following orders:



Introduction

In previous papers of this series⁽¹⁾, we reported the formation of one to one molecular complexes of aromatics with halogens or interhalogens, $Ar \cdot X_2$ or $Ar \cdot IX$ (Ar =benzene, chlorobenzene or bromobenzene;

X =halogen atoms), in carbon tetrachloride solution at 25°C. These results were obtained by means of ultraviolet spectrophotometric measurements. It seemed of interest to extend the studies to the corresponding fluorobenzene systems in order to see if fluorobenzene formed similar complexes with halogens or interhalogens and if so, to compare the stabilities of the fluorobenzene complexes with those of other halo-

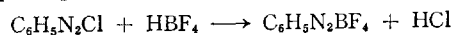
* The Molecular Complexes. VI.

benzene complexes. Thus, the present study involved the spectrophotometric investigations on the systems of fluorobenzene with iodine monochloride, iodine monobromide, bromine and chlorine in carbon tetrachloride.

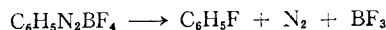
Experimentals

Materials.—Fluorobenzene was prepared by D. T. Flood's method⁽²⁾. Aniline hydrochloride was diazotized with aqueous nitrite solution at the temperatures below 5°C.

$\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} + \text{HNO}_2 \longrightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} + 2\text{H}_2\text{O}$
Fluoroboric acid was prepared concurrently with the diazotization by adding boric acid to hydrofluoric acid. The ice-cold solution of fluoroboric acid was then poured into the diazonium chloride solution prepared previously.



The resulting crystalline was washed successively with water, methanol and ethyl ether, and dried in open air. The solid thus obtained was decomposed by gentle heating with small flame.



The distillate was washed with sodium hydroxide solution and then with water. It was dried with calcium chloride and distilled again. The observed boiling point of the compound was 85°C, and the observed refractive index was $n_D^{19.5} = 1.4638$ (literature value⁽³⁾, $n_D^{20} = 1.4646$).

Chlorine gas was prepared by the reaction of conc. hydrochloric acid with potassium permanganate⁽⁴⁾. It was then purified by passing successively through aqueous solution of potassium permanganate, conc. sulfuric acid, and phosphorus pentoxide column.

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

Experimental Procedures.—The experimental procedures for preparation of all the solutions and for ultraviolet spectrophotometric measurements were described in previous papers⁽¹⁾. The method of calculation of the equilibrium constants for the complex formation was also described in previous papers⁽¹⁾.

Results

Absorption spectra of the solutions of mixtures of fluorobenzene with iodine monochloride, iodine monobromide, bromine or chlorine in carbon tetrachloride were determined, using as blank the solutions of the halogens or the interhalogens of the same concentrations as those of the mixture solutions. The results indicated that each spectrum had maximum absorption peak in the vicinity of 2800Å, where none of the components had strong absorption. This phenomenon was attributed to formation of a complex in solution, and the complex was assumed to be one to one molecular complex, $\text{C}_6\text{H}_5\text{F} \cdot \text{ICl}$, $\text{C}_6\text{H}_5\text{F} \cdot \text{IBr}$, $\text{C}_6\text{H}_5\text{F} \cdot \text{Br}_2$ or $\text{C}_6\text{H}_5\text{F} \cdot \text{Cl}_2$, as discussed in previous papers⁽¹⁾.

The equilibrium constants, K , for the complex formation were calculated by the method reported previously⁽¹⁾. These calculations involved the evaluation of slopes and intercepts of the linear plots of $\{D\}_o \cdot [B]_o / \{A - a_o[B]_o\}$ versus $\{D\}_o$, where A denoted the absorbancies measured at absorption maxima, a_o the molar absorptivities of the halogens or interhalogens in carbon tetrachloride solution (Table 1), $\{D\}_o$ the initial concentration of fluorobenzene, and $[B]_o$ the initial concentrations of halogens or interhalogens. The results of these calculations are summarized in Tables 2~5. The linearities observed between $\{D\}_o \cdot [B]_o / \{A - a_o[B]_o\}$ and $\{D\}_o$ indicate the assumption of the formation of one to one complexes, $\text{C}_6\text{H}_5\text{F} \cdot \text{ICl}$, $\text{C}_6\text{H}_5\text{F} \cdot \text{IBr}$, $\text{C}_6\text{H}_5\text{F} \cdot \text{Br}_2$ and $\text{C}_6\text{H}_5\text{F} \cdot \text{Cl}_2$, being correct (Figs. 1~4).

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)
ICl ^a	4.16	2850	0.227	54.5
IBr ^b	13.4	2820	0.946	70.5
Br ₂ ^b	96.6	2820	1.10	11.4
Cl ₂ ^b	35.9	2820	0.403	11.2

a : 21°C, b : 29°C.

Table 2. Formation of $C_6H_5F \cdot ICl$ in Carbon Tetrachloride at 21°C

C_6H_5F , mole l^{-1} ([D] ₀)	ICl , 10^{-3} mole l^{-1} ([B] ₀)	Absorbancy at 2820 Å (A)	$\frac{[D]_e [B]_e}{A - a_e[B]_e}$, 10^{-3} mole l^{-1}
0.568	0.456	0.292	0.967
	0.760	0.487	0.969
	1.14	0.732	0.966
	1.90	1.219	0.968
	average		0.968
0.696	0.456	0.345	0.989
	0.760	0.589	0.966
	1.14	0.870	0.982
	1.90	1.408	1.01
	average		0.987
0.930	0.456	0.451	0.995
	0.760	0.692	1.09
	1.14	1.130	0.993
	1.90	1.834	1.02
	average		1.02

$$K=0.161 \text{ l mole}^{-1}, a=7.05 \times 10^3$$

Table 3. Formation of $C_6H_5F \cdot IBr$ in Carbon Tetrachloride at 29°C

C_6H_5F , mole l^{-1} ([D] ₀)	IBr , 10^{-4} mole l^{-1} ([B] ₀)	Absorbancy at 2820 Å (A)	$\frac{[D]_e [B]_e}{A - a_e[B]_e}$, 10^{-4} mole l^{-1}
0.441	5.37	0.272	10.1
	6.71	0.339	10.1
	8.05	0.410	10.1
	9.39	0.470	10.2
	average		10.1
0.771	5.37	0.446	10.2
	6.71	0.555	10.2
	8.05	0.665	10.2
	9.39	0.778	10.2
	average		10.2
1.17	5.37	0.635	10.5
	6.71	0.779	10.7
	8.05	0.938	10.7
	9.39	1.081	10.8
	average		10.7
1.50	5.37	0.781	10.8
	6.71	0.982	10.8
	8.05	1.174	10.8
	9.39	1.398	10.6
	average		10.8

$$K=0.072 \text{ l mole}^{-1}, a=1.44 \times 10^4$$

Table 4. Formation of $C_6H_5F \cdot Br_2$ in Carbon Tetrachloride at 29°C

C_6H_5F , mole l^{-1} ([D] ₀)	Br_2 , 10^{-4} mole l^{-1} ([B] ₀)	Absorbancy at 2820 Å (A)	$\frac{[D]_e [B]_e}{A - a_e[B]_e}$, 10^{-4} mole l^{-1}
0.515	6.04	0.176	18.4
	9.06	0.274	17.7
	12.1	0.357	18.1
	15.1	0.448	18.1
	average		18.1
0.816	6.04	0.277	18.3
	9.06	0.412	18.4
	12.1	0.545	18.6
	15.1	0.692	18.2
	average		18.4
1.28	6.04	0.426	18.5
	9.06	0.634	18.6
	12.1	0.844	18.6
	15.1	1.053	18.7
	average		18.6
1.58	6.04	0.518	18.7
	9.06	0.768	18.9
	12.1	1.013	19.4
	15.1	1.274	19.0
	average		19.0

$$K=0.045 \text{ l mole}^{-1}, a=1.25 \times 10^4$$

Table 5. Formation of $C_6H_5F \cdot Cl_2$ in Carbon Tetrachloride at 29°C

C_6H_5F , mole l^{-1} ([D] ₀)	Cl_2 , 10^{-3} mole l^{-1} ([B] ₀)	Absorbancy at 2820 Å (A)	$\frac{[D]_e [B]_e}{A - a_e[B]_e}$, 10^{-3} mole l^{-1}
0.392	3.59	0.132	15.3
	5.39	0.196	15.4
	7.18	0.263	15.4
	8.98	0.327	15.4
	average		15.4
0.787	3.59	0.223	15.4
	5.39	0.332	15.5
	7.18	0.490	15.5
	8.98	0.550	15.6
	average		15.5
1.19	3.59	0.312	15.7
	5.39	0.462	15.9
	7.18	0.662	15.8
	8.98	0.769	15.9
	average		15.8
1.58	3.59	0.401	15.7
	5.39	0.590	16.0
	7.18	0.784	16.1
	8.98	0.989	15.9
	average		15.9

$$K=0.035 \text{ l mole}^{-1}, a=1.92 \times 10^3$$

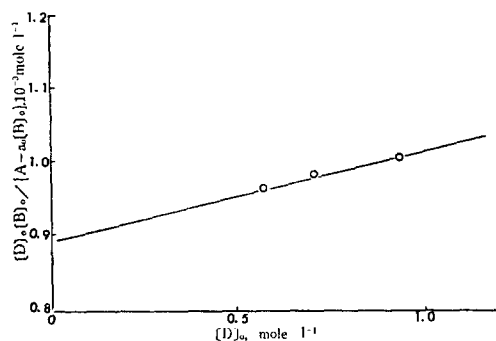


Figure 1. Plot of $[D]_0[B]_0/[A-\alpha_s[B]_0]$ Versus $[D]_0$ of the Fluorobenzene-iodine Monochloride System at 21°C

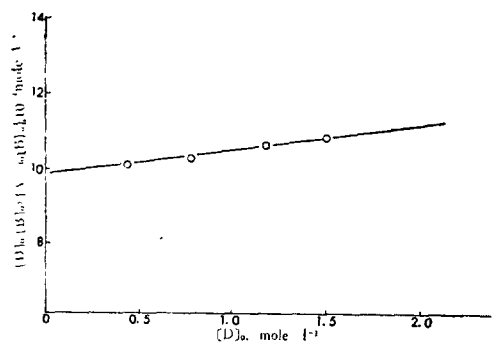


Figure 2. Plot of $[D]_0[B]_0/[A-\alpha_s[B]_0]$ Versus $[D]_0$ of the Fluorobenzene-iodine Monobromide System at 29°C

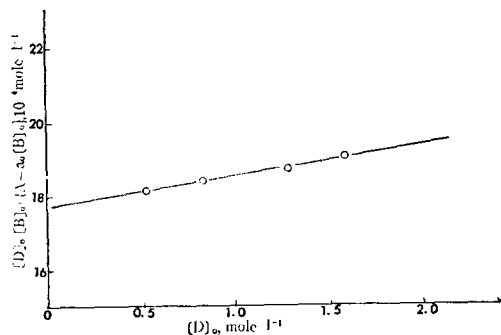


Figure 3. Plot of $[D]_0[B]_0/[A-\alpha_s[B]_0]$ Versus $[D]_0$ of the Fluorobenzene-bromine System at 29°C

Table 6. Summary of Data Obtained on the Complexes of Aromatics with Halogens or Interhalogens in Carbon Tetrachloride at 25°C^(a)

Halogen	C ₆ H ₆ ^(b)	C ₆ H ₅ Br ^(c)	C ₆ H ₅ Cl ^(d)	C ₆ H ₅ F ^(e)
Wave length of max. absorption (Å)				
ICl	2820	2860	2870	2850
IBr	2900	2860	2840	2820
I ₂	2930	2900	2840	2880 ^(f)
Br ₂	2860	2880	2860	2820
Cl ₂	2760	2860	2840	2820
Molar absorptivity of complex				
ICl	8130	5910	5650	6950
IBr	10500	8990	9330	14400
I ₂	15500	10400	9650	—
Br ₂	8030	7600	7300	12500
Cl ₂	3520	3830	4270	1920
Equil. const. of complex formation (l mole ⁻¹)				
ICl	0.54	0.32	0.216	0.161
IBr	0.341	0.183	0.109	0.072
I ₂	0.173	0.13	0.106	0.064 ^(f, g)
Br ₂	0.137	0.11	0.087	0.045
Cl ₂	0.0643	0.0485	0.0400	0.035

(a) Except the case of C₆H₅F complexes (the present study).

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

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

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

(e) The present study except otherwise indicated.

(f) Ref. 5.

(g) Evaluated from K_x value by the method described in ref. 1(a).

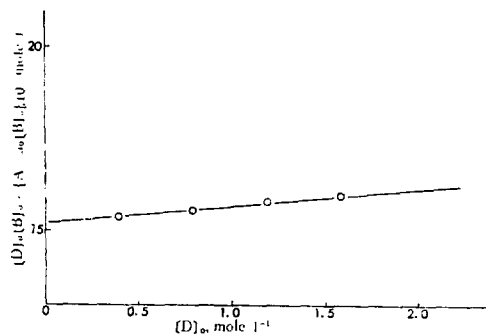


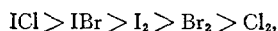
Figure 4. Plot of $[D]_0[B]_0/[A-\alpha_s[B]_0]$ Versus $[D]_0$ of the Fluorobenzene-chlorine System at 29°C

Discussion

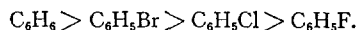
As a result of the present study, it is concluded that fluorobenzene interacts with iodine monochloride,

iodine monobromide, bromine or chlorine in carbon tetrachloride solution to form one to one complexes, $C_6H_5F \cdot ICl$, $C_6H_5F \cdot IBr$, $C_6H_5F \cdot Br_2$ or $C_6H_5F \cdot Cl_2$. The results of the present study are compared with those reported in the literature on other aromatic complexes of similar type (Table 6).

By comparing the K values in Table 6, it can be concluded that relative stabilities of the complexes of any given aromatics decrease in the order,



and that relative stabilities of the complexes of given halogens or interhalogens decrease in the order,



These orders indicate relative acidities of the halogens and the interhalogens and relative basicities of the aromatics toward complex formation. As discussed in previous papers,⁽¹⁾ these can be explained in terms of polarizabilities of halogen molecules and electronegativities of halogen atoms in both interhalogen and aromatic molecules.

The wave lengths (λ_{max}) of maximum absorption of the complexes R and the molar absorptivities (α)

of the complexes at their absorption maxima do not reveal any gradual change with increasing K values. The values of λ_{max} and α might be affected by some additional factors besides the relative acidities of halogens and interhalogens and the relative basicities of the aromatics.

References

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