The Complexes of Aromatic Amines with Iodine or Iodine Monochloride in Carbon Tetrachloride*

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(Received October 5, 1967)

방향족아민과 요오드 또는 일염화요오드 사이의 錯物에 관한 연구

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(1967. 10. 5 受理)

요 약

사염화탄소 용액에 대하여 分光光度法으로 연구한 결과 아닐린, N, N-디메틸아닐린 및 N, N-디에틸아닐린 과 요오드 또는 일염화요오드 사이에 1 : 1 錯物이 형성됨을 알았다. 이들 錯物형성에 대한 실온에서의 평형 상수는 다음과 같다. $C_6H_5NH_2 \cdot I_2$ 2.05, $C_6H_5N(CH_3)_2 \cdot I_2$ 15.2, $C_6H_5N(C_2H_5)_2 \cdot I_2$ 35.5, $C_6H_5NH_2 \cdot ICl$ 18.5, $C_6H_5N(CH_3)_2 \cdot ICl$ 25.6, 및 $C_6H_5N(C_2H_5)_2 \cdot ICl$ 42.0 l mole^{-1}.

Abstract

The systems of aromatic amines such as aniline, N, N-dimethylaniline and N, N-diethylaniline with iodine or iodine monochloride in carbon tetrachloride have been examined spectrophotometrically. The results indicate the formation of one to one molecular complexes. The equilibrium constants obtained at room temperature for formation of the complexes are as follows: $C_6H_5NH_2 \cdot I_2$ 2.05, $C_6H_5N(CH_3)_2 \cdot I_2$ 15.2, $C_6H_5N(C_2H_5)_2 \cdot I_2$ 35.5, $C_6H_5NH_2 \cdot ICl$ 18.5, $C_6H_5(CH_3)_2 \cdot ICl$ 25.6 and $C_6H_5N(C_2H_5)_2 \cdot ICl$ 42.0 l mole^{-1}.

Introduction

The complex formation between aromatic amines and iodine or iodine monochloride in various solvents has been studied by several investigators. For example, formation of the complex of N, N-dimethylaniline with iodine in such solvents as cyclohexane[1], n-heptane[2], chloroform[3] and n-hexane[4] was examined by means of spectrophotometric measurements. The formation of the complex of aniline with iodine was also examined in chloroform solution[3]. These results indicated that iodine formed more stable complex with N, N-dimethylaniline than with aniline. It appeared of interest, therefore, to extend studies to the N, N-diethylaniline-iodine system. We undertook the present studies on the complexes of aniline, N, N-dimethylaniline and N, N-diethylaniline with iodine or iodine monochloride in carbon tetrachloride.

Experimental Part

Aniline (Reagent Grade, Merck, Germany), N, N-dimethylaniline(Analytical Reagent, Chameleon, Japan), N, N-diethylaniline(Reagent grade, Merck, Germany) were treated with an aqueous solution of potassium hydroxide, dried with calcium chloride and distilled under reduced pressure. All the other materials used

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* The Molecular Complexes. Ⅸ·

in the present study were prepared and/or purified by the method described previously[5].

Experimental procedures for preparation of stock solutions and ultraviolet spectrophotometric measurements were described previously[5]. Absorbancy measurements were complete within a few hours after a solution of aromatic amine-iodine mixture was freshly prepared, in order to prevent photochemical reactions of aromatic amines with iodine in the presence of oxygen[6].

Results

The Complexes of Iodine with Aniline, N, N-Dimethylaniline and N, N, -Diethylaniline. —

Absorbancies of carbon tetrachloride solution of aniline-iodine mixture were measured in the range of wave lengths from 3100Å to 4000Å*. The obtained spectra did not indicate absorption maxima. However, the mixture solution showed much stronger absorption than the solution of each component material in the wave length region examined. This phenomenon was similar to that observed on the system of iodobenzene-iodine in carbon tetrachloride, and attributed to complex formation in solution as discussed previously[7]. The complex was assumed to be one to one molecular complex, $C_6H_5NH_2 \cdot I_2$. The equilibrium constant, K, for the complex formation was calculated by the method reported previously[6,7]. The results of the calculation are summarized in Table 1 and
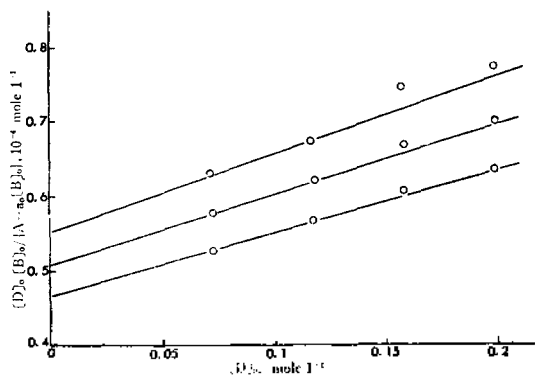
shown in Figure 1. The K values obtained at three different wave lengths agree with each other within experimental error. The average K value at 28°C is 2.05 l mole^{-1}.

Similar studies were carried out on the system of N, N-dimethylaniline with iodine in carbon tetrachloride. In this system, again no maxima were observed in the absorption spectrum of the N, N-dimethylaniline-iodine mixture solution. But the mixture solution indicated again much stronger absorption than the solution of each component material in the wave length region
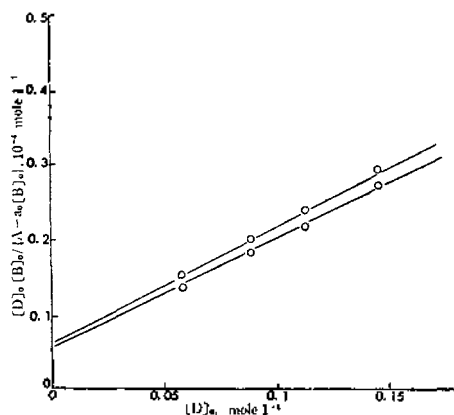

Figure 2. Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ Versus $[D]_o$ of the N, N-dimethylaniline-iodine System Obtained from Data at 3600Å (upper line) and 3570Å (lower line) at 28°C

Figure 1. Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ Versus $[D]_o$ of the Aniline-iodine System Obtained from Data at 3650Å (upper line), 3600Å(middle line) and 3550Å(lower line) at 28°C
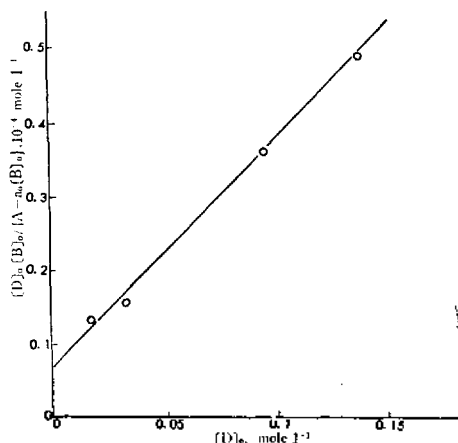

Figure 3. Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ Versus $[D]_o$ of the N, N-Dimethylaniline-iodine System at 20°C

* The blank solution was the carb on tetrachloride solution of aniline of the same concentration as that of the mixture solution.

Table 1. Formation of $C_6H_5NH_2 \cdot I_2$ in Carbon Tetrachloride at 28°C

$C_6H_5NH_2$, mole/l ([D]o)	I_2, 10^{-4} mole/l ([B]o)	Absorbancy at 3550 Å (A)	$\frac{[D]_o[B]_o^{(1)}}{A-a_o[B]_o}$ 10^{-4}mole/l	Average	Absorbancy at 3600 Å (A)	$\frac{[D]_o[B]_o^{(1)}}{A-a_o[B]_o}$ 10^{-4}mole/l	Average	Absorbancy at 3650 Å	$\frac{[D]_o[B]_o^{(1)}}{A-a_o[B]_o}$ 10^{-4}mole/l	Average
0.0734	1.01	0.161	0.461	0.501	0.148	0.502	0.547	0.136	0.546	0.633
	1.69	0.254	0.488		0.232	0.536		0.211	0.590	
	2.36	0.333	0.522		0.308	0.565		0.281	0.620	
	3.04	0.419	0.534		0.383	0.586		0.348	0.645	
0.118	1.01	0.208	0.576	0.571	0.192	0.624	0.624	0.176	0.681	0.681
	1.69	0.354	0.567		0.322	0.623		0.301	0.667	
	2.36	0.493	0.568		0.453	0.620		0.408	0.688	
	3.04	0.632	0.571		0.573	0.630		0.525	0.689	
0.161	1.01	0.264	0.611	0.616	0.244	0.669	0.670	0.216	0.756	0.753
	1.69	0.443	0.617		0.407	0.672		0.363	0.754	
	2.36	0.617	0.619		0.572	0.668		0.508	0.752	
	3.04	0.804	0.611		0.734	0.670		0.654	0.735	
0.200	1.01	0.317	0.639	0.636	0.290	0.700	0.704	0.263	0.771	0.773
	1.69	0.537	0.632		0.480	0.707		0.440	0.772	
	2.36	0.744	0.637		0.673	0.704		0.613	0.774	
	3.04	0.960	0.636		0.869	0.703		0.787	0.776	

$K=1.95$ l mole^{-1}, $a=11.1\times10^3$　　　　$K=2.04$ l mole^{-1}, $a=9.8\times10^3$　　　$K=2.16$ l mole^{-1}, $a=8.54\times10^3$

[1]The values of molar absorptivity, a_o, of iodine in carbon terachloride were taken from ref. (7).

Table 2. Formation of $C_6H_5N(CH_3)_2 \cdot I_2$ in Carbon Tetrachloride at 28°C

$C_6H_5N(CH_3)_2$, mole/l ([D]o)	I_2, 10^{-4} mole/l ([B]o)	Absorbancy at 3570 Å (A)	$\frac{[D]_o[B]_o^{(1)}}{A-a_o[B]_o}$ 10^{-4} mole/l	Average	Absorbancy at 3600 Å (A)	$\frac{[D]_o[B]_o^{(1)}}{A-a_o[B]_o}$ 10^{-4} mole/l	Average
0.0542	1.04	0.392	0.144	0.147	0.359	0.157	0.156
	1.73	0.632	0.148		0.602	0.156	
	2.42	0.883	0.148		0.843	0.156	
	3.11	1.13	0.149		1.08	0.156	
0.0847	1.04	0.470	0.186	0.189	0.425	0.206	0.208
	1.73	0.772	0.189		0.702	0.208	
	2.42	1.08	0.189		0.978	0.208	
	3.11	1.36	0.193		1.25	0.210	
0.115	1.04	0.511	0.235	0.240	0.501	0.239	0.245
	1.73	0.850	0.235		0.813	0.245	
	2.42	1.15	0.243		1.13	0.247	
	3.11	1.46	0.246		1.43	0.251	
0.143	1.04	0.545	0.273	0.274	0.524	0.284	0.280
	1.73	0.908	0.273		0.887	0.280	
	2.42	1.26	0.270		1.25	0.275	
	3.11	1.63	0.273		1.58	0.282	

$K=15.6$ l mole^{-1}, $a=7.72\times10^2$　　　　　$K=14.8$ l mole^{-1}, $a=7.72\times10^3$

[1] a_o at 3570Å$=14$ (the present study).

examined. Therefore, the obtained data were treated in a similar way to that mentioned above. The results are shown in Table 2 and Figure 2.

The study was extended further to the system of N, N-diethylaniline with iodine in carbon tetrachloride. Contrary to the two system mentioned above, in this system carbon tetrachloride solution of the N, -N diethylaniline-iodine mixture showed a maximum at 3600Å in its absortion spectrum. This was attributed to formation of one to one complex, $C_6H_5N(C_2H_5)_2 \cdot I_2$, and the equilibrium constant for the complex formation was calculated (Table 3 and Fig. 3).

Table 3. Formation of $C_6H_5N(C_2H_5)_2 \cdot I_2$ in Carbon Tetrachloride at 20°C

$C_6H_5N(C_2H_5)_2$, mole/l ([D]$_o$)	I_2, 10^{-4} mole/l ([B]$_o$)	Absorbancy at 3600 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$ 10^{-4} mole/l	Average
0.0163	1.23	0.128	0.155	0.153
	1.59	0.177	0.145	
	2.27	0.243	0.151	
	2.72	0.277	0.159	
0.0337	1.23	0.251	0.163	0.159
	1.59	0.352	0.150	
	2.27	0.469	0.160	
	2.72	0.568	0.159	
0.0952	1.23	0.311	0.377	0.365
	1.59	0.428	0.355	
	2.27	0.592	0.366	
	2.72	0.717	0.360	
0.137	1.23	0.332	0.509	0.496
	1.59	0.457	0.479	
	2.27	0.639	0.489	
	2.72	0.737	0.507	

$$K=35.5 \; l \; \text{mole}^{-1}, \quad a=2.46 \times 10^3$$

Table 5. Formation of $C_6H_5N(CH_3)_2 \cdot ICl$ in Carbon Tetrachloride at 19°C

$C_6H_5N(CH_3)_2$, mole/l ([D]$_o$)	ICl, 10^{-4} mole/l ([B]$_o$)	Absorbancy at 3500 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$[1] 10^{-4} mole/l	Average
0.0392	0.623	0.183	0.134	0.135
	1.04	0.300	0.136	
	1.45	0.438	0.130	
	1.87	0.532	0.139	
0.0771	0.623	0.223	0.216	0.219
	1.04	0.365	0.220	
	1.45	0.516	0.218	
	1.87	0.655	0.221	
0.0960	0.623	0.244	0.246	0.247
	1.04	0.416	0.241	
	1.45	0.557	0.251	
	1.87	0.729	0.248	
0.160	0.623	0.278	0.359	0.359
	1.04	0.462	0.361	
	1.45	0.653	0.357	
	1.87	0.833	0.360	

$$K=25.6 \; l \; \text{mole}^{-1}, \quad a=5670$$

[1]a_o at 3500 Å=11 (the present study).

Table 4. Formation of $C_6H_5NH_2 \cdot ICl$ in Carbon Tetrachloride at 19°C

$C_6H_5NH_2$, mole/l ([D]$_o$)	ICl, 10^{-4} mole/l ([B]$_o$)	Absorbancy at 3250 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$[1] 10^{-4} mole/l Average	
0.0361	0.812	0.117	0.252	0.254
	2.03	0.287	0.256	
	2.84	0.410	0.251	
	3.65	0.515	0.257	
0.0673	0.812	0.151	0.363	0.362
	2.03	0.376	0.363	
	2.84	0.533	0.360	
	3.65	0.680	0.361	
0.118	0.812	0.194	0.497	0.491
	2.03	0.489	0.491	
	2.84	0.686	0.490	
	3.65	0.899	0.485	
0.176	0.812	0.216	0.665	0.670
	2.03	0.535	0.670	
	2.84	0.762	0.659	
	3.65	0.938	0.687	

$$K=18.5 \; l \; \text{mole}^{-1} \quad a=3,440$$

[1]a_o at 3250 Å=7.4 (the present study).

Table 6. Formation of $C_6H_5N(C_2H_5)_2 \cdot ICl$ in Carbon Tetrachloride at 19°C

$C_6H_5N(C_2H_5)_2$, mole/l ([D]$_o$)	ICl, 10^{-4} mole/l ([B]$_o$)	Absorbancy at 3600 Å (A)	$\frac{[D]_o[B]_o}{A-a_o[B]_o}$[1] 10^{-4} mole/l Average	
0.0502	0.826	0.292	0.142	0.139
	1.65	0.603	0.137	
	2.48	0.894	0.139	
	3.30	1.18	0.139	
0.0765	0.826	0.319	0.197	0.195
	1.65	0.660	0.191	
	2.48	0.997	0.190	
	3.30	1.24	0.203	
0.110	0.826	0.356	0.256	0.257
	1.65	0.698	0.264	
	2.48	1.09	0.251	
	3.30	1.41	0.258	
0.157	0.826	0.364	0.357	0.349
	1.65	0.762	0.341	
	2.48	1.11	0.351	
	3.30	1.50	0.347	

$$K=42.0 \; l \; \text{mole}^{-1}, \quad a_o=5070$$

[1]a_o at 3600 Å=17 (the present study).

The Complexes of Iodine Monochloride with Aniline, N, N-Dimethylaniline and N, N-Diethylaniline.

Similar studies were carried out on the systems of iodine monochloride with aromatic amines in carbon tetrachloride. Absorption spectra of the solutions of the iodine monochloride-aromatic amine mixtures showed maxima at 3250~3600Å. This phenomenon was attributed to formation of one to one complexes,

$C_6H_5NH_2 \cdot ICl$, $C_6H_5N(CH_3)_2 \cdot ICl$ and $C_6H_5N(C_2H_5)_2 \cdot$ ICl. The equilibrium constants for formation of these complexes were calculated (Tables 4~6 and Fig. 4).

Discussion

The results of the present study indicate that aniline, N, N-dimethylaniline and N, N-diethylaniline form one to one molecular complexes, (amine)$\cdot I_2$ and (amine)$\cdot ICl$, with iodine and iodine monochloride in carbon tetrachloride solution. The results of the present study are now compared with those reported in the literature (Table. 7).

By comparing the K values in Table 7, it is concluded that the aromatic amines form more stable complexes with iodine monochloride than with iodine. This is what we have noticed earlier on the systems of benzene and halobenzene with the halogens[6,7]. Table 7 also show that the relative stabilities of both

Table 7. Equilibrium Constants for the Formation of One to One Molecular Complexes

Comlpex	K l mole^{-1}	Solvent	Temperature (°C)	Reference
Aniline-I_2	2.05	CCl_4	28	(a)
	12.0	$CHCl_3$	25	3
DMA-I_2	15.2	CCl_4	28	(a)
	15	$CHCl_3$	25	3
	19.7	n-Heptane	27	2
	19.1	Cyclohexane	25	1
DEA-I_2	35.5	CCl_4	20	(a)
Aniline-ICl	18.5	CCl_4	19	(a)
	22	$CHCl_3$	25	3
DMA-ICl	25.6	CCl_4	19	(a)
	20	$CHCl_3$	25	3
DEA-ICl	42.0	CCl_4	19	(a)

(a) The present study

iodine-and iodine monochloride-complexes decrease in the order,

$$C_6H_5N(C_2H_5)_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2.$$
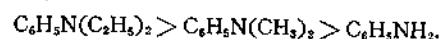
If these complexes are considered to be formed through Lewis acid-base interactions in solution, it must be concluded that iodine monochloride is a stronger acid than iodine, and that the relative basicities of the three aromatic amines decrease in the order written above.

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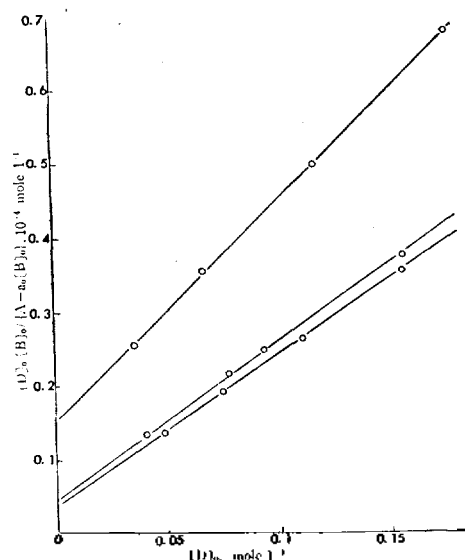Figure 4. Plot of $[D]_o[B]_o/\{A-a_o[B]_o\}$ Versus$[D]_o$ of the Aniline-Iodine Monochloride System(upper line), N, N-Dimethylaniline-iodine Monochloride System (middle line) and N, N-Diethylaniline-Iodine Monochloride System (lower line) at 19°C