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오르토 치환 아닐린과 요오드 사이의 착물에 관한 연구

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The Complexes of Iodine with Ortho-Substituted Anilines in Carbon Tetrachloride*

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요 약 아닐린, o-톨루이딘, o-에틸아닐린, o-클로로아닐린등과 I_2 사이의 상호작용을 자외선 분광광도법으로 조사한 결과 CCl_4 용액내에서 아닐린 또는 상기 o-치환 아닐린과 I_2 사이에 1:1 착물이 형성됨을 알았다. 이들 착물의 실온에서의 형성상수를 구한 결과 다음과 같은 값을 얻었다. C_6H_5-$NH_2 \cdot I_2$, 12.8 l mole^{-1}; o-$CH_3C_6H_4NH_2 \cdot I_2$, 9.31 l mole^{-1}; o-$C_2H_5C_6H_4NH_2 \cdot I_2$, 3.15 l mole^{-1}; o-$ClC_6H_4NH_2 \cdot I_2$, 0.576 l mole^{-1}. 본실험결과를 전 실험의 결과와 비교하면 $I_2 \cdot$ 아민 착물의 안정도가 다음 순으로 감소함을 알 수 있다
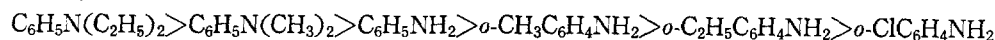
$$C_6H_5N(C_2H_5)_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2 > o\text{-}C_2H_5C_6H_4NH_2 > o\text{-}ClC_6H_4NH_2$$

이들 착물의 상대적 안정도는 치환기의 유발효과와 입체효과에 의하여 설명될 수 있다.

Abstract The interactions of aniline, o-toluidine, o-ethylaniline and o-chloroaniline with iodine in carbon tetrachloride solution have been examined through spectrophotometric measurements. The results indicate that both aniline and the o-substituted anilines examined form one-to-one complexes with I_2 in solution. The formation constants of the complexes measured at room temperature are 12.8, 9.31, 3.15 and 0.576 l mole^{-1}, respectively. Comparison of these results with previous experimental results indicates that the relative stabilities of the I_2-amine complexes decrease in the

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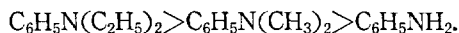
following order:

$$C_6H_5N(C_2H_5)_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2 > o\text{-}C_2H_5C_6H_4NH_2 > o\text{-}ClC_6H_4NH_2$$

This may support the conclusion that the relative stabilities of these complexes are explained by the inductive effect and steric hindrance of the substituents.

Introduction

The formation of the molecular complexes of aromatic amines with iodine was reported by Tsubomura,[1] Senkowski[2] and Chandra.[3] In previous paper of this series,[4] we reported that iodine and iodine monochloride formed one-to-one complexes with aromatic amines in carbon tetrachloride solution, and that relative stabilities of the complexes decreased in the order,

$$C_6H_5N(C_2H_5)_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2.$$

The observed relative stabilities of the complexes were explained by the electron-releasing power of alkyl groups under the assumption that these complexes were formed through Lewis acid-base interaction. The electron-releasing nature of the alkyl groups might affect the electron density of nitrogen atoms to increase the basicity of the aromatic amines toward the complex formation.

It appeared of interest to extend studies to the systems of ortho-substituted anilines with iodine, in order to see, if any, the effect of o-substituents on the formation of molecular complexes with I_2. The present study was undertaken on the complexes of aniline, o-toluidine, o-ethylaniline and o-chloroaniline formed with iodine in carbon tetrachloride.

Experimental Part

Aniline (Reagent grade, Sargent), o-toluidine (Reagent grade, Eastman Organic Chemical Co.), o-ethylaniline (Reagent grade, Aldrich Chemical Co.) and o-chloroaniline (Reagent grade, Eastman Organic Chemical Co.) were treated with aqueous solution of potassium hydroxide, dried with calcium chloride and fractionated under reduced pressure. The middle fractions were taken and used for the experiment. All the other materials used in the present study were prepared and/or purified by the methods described previously.[4,5]

Experimental procedures for preparation of the stock solutions and U. V. spectrophotometric measurements were described previously.[4,5] Absorbancy measurements were carried out in about 20 minutes after a solution of aromatic amine was mixed with iodine solution. In all cases except the aniline-iodine system, no change in absorbancy at the wave lengths of maximum absorption was observed upon standing.

Results

The Complexes of o-Substituted Anilines with Iodine. The systems of o-toluidine, o-ethylaniline and o-chloroaniline with iodine in carbon tetrachloride were examined through the U. V. spectrophotometric measurements at room temperature. The absorption spectra of the systems showed absorption maxima in the wave length region of 3490–3610 Å. This phenomenon was attributed to the complex formation in solution, as was discussed previously.[4,5] The complexes were assumed to be the one-to-one molecular complexes, $(XC_6H_4NH_2) \cdot I_2$, and the equilibrium constants, K, for the complex formation were calculated by the method used previously.[4,5] The results obtained

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Table I Formation of o-toluidine-I_2 in CCl_4 at 19°C.

o-Toluidine, mole/l $[D]_0$	I_2, 10^{-5} mole/l $[B]_0$	Absorbancy at 3600 Å A	$\dfrac{[D]_0[B]_0{}^*}{A-a_0[B]_0}$ 10^{-5} mole/l	Average
0.107	2.65	0.126	2.25	2.24
	5.30	0.255	2.23	
	7.95	0.382	2.23	
0.312	2.65	0.183	4.52	4.46
	5.30	0.367	4.51	
	7.95	0.546	4.36	
0.418	2.65	0.193	5.74	5.62
	5.30	0.404	5.49	
	7.95	0.589	5.65	
0.634	2.65	0.214	7.86	7.82
	5.30	0.434	7.75	
	7.95	0.641	7.86	

*a_0=10. K=9.31 l mole.$^{-1}$

Table II Formation of o-ethylaniline-I_2 in CCl_4 at 19°C.

o-Ethylaniline mole/l $[D]_0$	I_2, 10^{-5} mole/l $[B]_0$	Absorbancy at 3610Å A	$\dfrac{[D]_0[B]_0{}^*}{A-a_0[B]_0}$ 10^{-5} mole/l	Average
0.095	2.83	0.095	2.84	2.76
	5.65	0.200	2.69	
	8.51	0.294	2.75	
0.201	2.83	0.151	3.77	3.78
	5.65	0.302	3.76	
	8.51	0.450	3.81	
0.281	2.83	0.187	4.26	4.25
	5.65	0.370	4.30	
	8.51	0.567	4.22	
0.461	2.83	0.234	5.58	5.37
	5.65	0.502	5.19	
	8.51	0.732	5.36	

*a_0=10. K=3.15 l mole^{-1}.

for o-toluidine-iodine, o-ethylaniline-iodine and o-chloroaniline-iodine systems are summarized in *Tables* I , II and III, where each symbol denotes the followings:

$[D]_o$: initial concentrations of the amines

$[B]_o$: initial concentrations of iodine

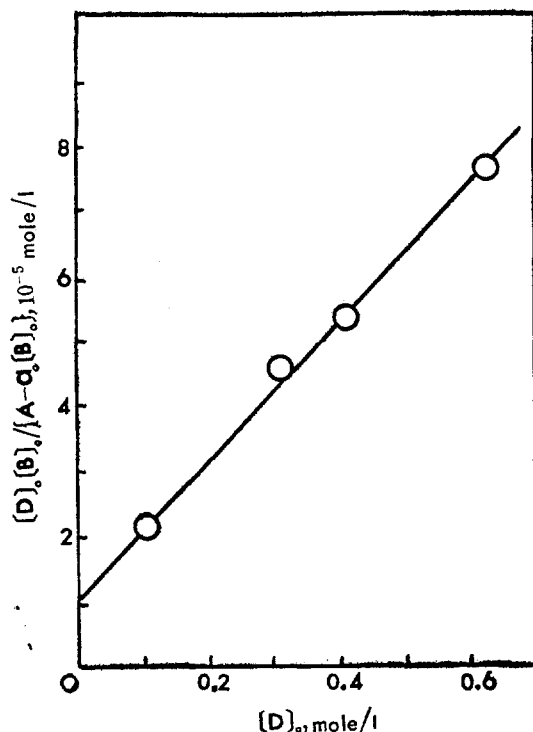A: absorbancy of the mixture solution measured at its absorption maximum

a_o: molar absorptivity of iodine in CCl_4.

The values of $[D]_o[B]_o/\{A-a_o[B]_o\}$ shown in *Tables* I-III were plotted against $[D]_o$. The

results indicated good linearity in each case examined. A typical example of the plots is shown in *Fig.* 1. The linearities observed between $[D]_o[B]_o/\{A-a_o[B]_o\}$ and $[D]_o$ indicate the assumption of one-to-one complex formation being correct, as discussed previously.[4,5] From the slopes and intercepts of the linear plots, the formation constants, K, of the complexes were calculated by the method described previously.[4,5] The K values obtained at 19°C are as follows:

Table III   Formation of o-chloroaniline- I_2 in CCl_4 at 19°C.

o-Chloroaniline mole/l [D]_o	I_2, 10^{-5} mole/l [B]_o	Absorbancy at 3490 Å A	$\frac{[D]_o[B]_o*}{A-a_0[B]_0}$ 10^{-5} mole/l	Average
0. 333	3. 42	0. 078	14. 6	14. 6
	6. 84	0. 159	14. 3	
	10. 3	0. 229	14. 9	
0. 654	3. 42	0. 141	15. 9	16. 5
	6. 84	0. 267	16. 8	
	10. 3	0. 397	16. 9	
0. 978	3. 42	0. 169	19. 8	20. 1
	6. 84	0. 330	20. 3	
	10. 3	0. 492	20. 4	
1. 25	3. 42	0. 205	21. 5	21. 8
	6. 84	0. 447	21. 9	
	10. 3	0. 604	22. 0	

a_o=9.

K=0. 576 l mole$^{-}_{1}$.

Fig. 1. — Plots of $[D]_o[B]_o/\{A-a_0[B]_o\}$ *versus* $[D]_o$ of the o-toluidine-iodine system at 19°C.

(o-Toluidine)·I_2, K=9. 31 l mole^{-1}
(o-Ethylaniline)·I_2, K=3. 15 l mole^{-1}
(o-Chloroaniline)·I_2, K =0. 576 l mole^{-1}

The Complex of Aniline with Iodine. In a previous paper of this series,[4] we reported that aniline formed one-to-one complex with iodine in carbon tetrachloride solution. The absorbancy measurements were carried out soon after the mixture solution was prepared, due to the fact that absorbancy of the mixture solution gradually decreased upon standing. This system has been re-examined by observing time dependence of the absorbancy of the mixture solution. Absorption spectra of the mixture solution measured at different time intervals after the mixing are shown in *Fig.* 2, which reveals that absorbancy at the absorption maximum increases during the first 20-minute period and then decreases gradually upon standing. This might be explained by assuming that one-to-one complex formed during the first 20-minute period undergoes some decomposition reactions to give unidentified products.

$$C_6H_5NH_2+I_2 \rightleftharpoons C_6H_2NH_2·I_2 \rightarrow X+Y$$

In order to obtain the formation constant of the complex, absorbancy measurements were

Table IV   Formation of aniline-I_2 in CCl_4 at 19°C.

Aniline mole/l $[D]_o$	I_2, 10^{-5} mole/l $[B]_o$	Absorbancy at 3630Å A	$\dfrac{[D]_o[B]_o*}{A-a_0\,[B]_0}$ 10^{-5}mole/l	Average
0.073	4.45	0.215	1.51	1.51
	6.68	0.325	1.51	
	8.90	0.433	1.50	
0.185	4.45	0.376	2.19	2.17
	6.68	0.561	2.21	
	8.90	0.782	2.11	
0.270	4.45	0.388	3.10	3.05
	6.68	0.587	3.07	
	8.90	0.826	3.00	
0.410	4.45	0.403	4.53	4.45
	6.68	0.603	4.54	
	8.90	0.852	4.28	

$*a_o=10.$ $K=12.8\ l$ mole^{-1}.

carried out in about 20 minutes after the mixing with varying concentrations of aniline. The results are summarized in *Table* IV. From

Fig. 2. — Variation of absorption spectra of aniline-iodine system with time.

the slope and intercept of the linear plots of $[D]_o[B]_o/\{A-a_o[B]_o\}$ versus $[D]_c$, the formation constant, K, of the $C_6H_5NH_2 \cdot I_2$ complex was calculated to be 12.8 l mole^{-1} at 19°C.

Discussion

As the results of the present study, it is concluded that iodine forms one-to-one molecular complexes, $C_6H_5NH_2 \cdot I_2$, o-$CH_3C_6H_4NH_2 \cdot I_2$, o-$C_2H_5C_6H_4NH_2 \cdot I_2$ and o-$ClC_6H_4NH_2 \cdot I_2$, with the aromatic amines in carbon tetrachloride solution. The relative value of the formation constants of the complexes could be considered as a measure of the relative stability of the complexes. Comparing the K values for the formation of these complexes, it is concluded that the relative stabilities of the complexes decrease in the order: aniline$>$$o$-toluidine$>$ o-ethylaniline$>$$o$-chloroaniline.

The results of the present study are compared with those reported in the literature on other similar systems. [4] The K values for the formation of one-to-one complexes of various aromatic amines with iodine are summarized in *Table* V.
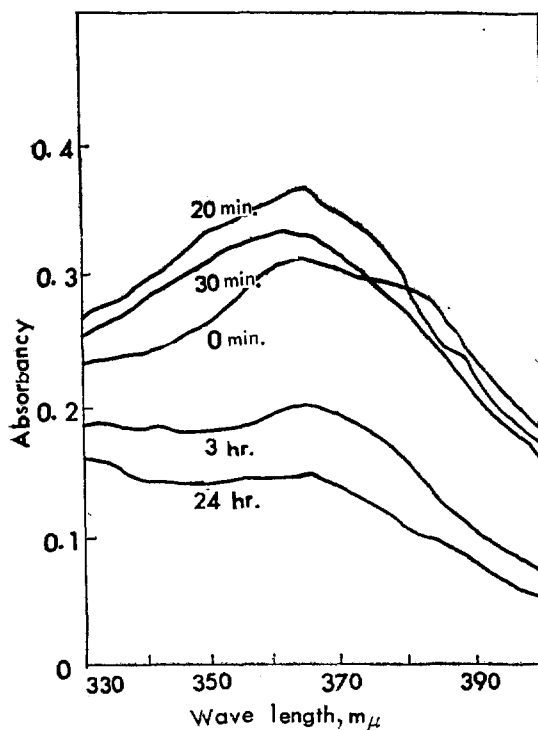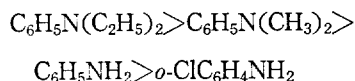
Table V   Equilibrium constant for the formation of 1 : 1 complexes in CCl_4 at room temperature

Complex	Formation const., l mole^{-1}	Reference
$C_6H_5N(C_2H_5)_2 \cdot I_2$	35. 5	(4)
$C_6H_5N(CH_3)_2 \cdot I_2$	15. 2	(4)
$C_6H_5NH_2 \cdot I_2$	12. 8	(a)
$o\text{-}CH_3C_6H_4NH_2 \cdot I_2$	9. 31	(a)
$o\text{-}C_2H_5C_6H_4NH_2 \cdot I_2$	3. 15	(a)
$o\text{-}ClC_6H_4NH_2 \cdot I_2$	0. 576	(a)

(a) Present study.

If these complexes are assumed to be formed through Lewis acid-base interaction or charge transfer interaction at the nitrogen atoms, the relative stabilities of the N, N-diethylaniline-, N, N-dimethylaniline-, aniline-, and o-chloro-aniline-complexes could be explained by electron-releasing nature of the ethyl and methyl groups and by electron-withdrawing character of the chlorine atoms.

$$C_6H_5N(C_2H_5)_2 > C_6H_5N(CH_3)_2 >$$
$$C_6H_5NH_2 > o\text{-}ClC_6H_4NH_2$$

If the inductive effect of the substituents is the only factor to affect the relative stabilities of the complexes formed with same I_2-molecules, the following relative stabilities of the aniline-, o-methylaniline-, and o-ethylaniline-complexes

obtaind experimentally can not be understood.

$$C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2 > o\text{-}C_2H_5C_6H_4NH_2.$$

Steric hindrance of o-methyl and o-ethyl groups may be considered to inhibit possible interaction between the nitrogen atoms of the aromatic amines and the iodine molecules. It can be said that the steric effect of the o-methyl and o-ethyl groups may play much more important role than the inductive effect on the formation and stability of the complexes of the o-substituted anilines with iodine molecules.

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