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The Molecular Complexes (XI). The Complexes of Toluidines and N-Methyltoluidines with Iodine in Carbon Tetrachloride*

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The interactions of iodine with toluidines (*o*-, *m*-, and *p*-) and N-methyltoluidines (*o*-, *m*-, and *p*-) in CCl$_4$ solution have been investigated through spectrophotometric measurements. The results indicate that toluidines and N-methyltoluidines form the one-to-one charge-transfer complexes with I$_2$ in solution. By comparing the values of the formation constants of the complexes, it is concluded that the relative stabilities of the I$_2$-amine complexes decrease in the following orders: *p*-toluidine>*m*-toluidine>aniline>*o*-toluidine, N-methyl-*p*-toluidine>N-methyl-*m*-toluidine>N-methylaniline >N-methyl-*o*-toluidine, N-methyltoluidines>toluidines. These results can be explained by the electron-releasing character and the steric effect of methyl group in the amine molecules.

Introduction

The formation of molecular complexes of aromatic amines with iodine in solution was studied by several investigators through spectrophotometric measurements.[1-4] In a previous paper of this series,[4] we reported that I$_2$ formed one-to-one complexes with aromatic amines such as aniline and *o*-toluidine in CCl$_4$.

$$RNH_2 + I_2 \rightleftharpoons RNH_2 \cdot I_2$$
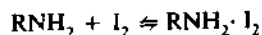
The observed values of formation constants of the complexes were as follows:

$$K_f(C_6H_5NH_2 \cdot I_2) = 12.8 \, l/mole$$
$$K_f(o\text{-}CH_3C_6H_4NH_2 \cdot I_2) = 9.31 \, l/mole$$

These complexes were considered to be formed by electron donor-acceptor interaction or charge-transfer interaction at the nitrogen atoms of the amines. If it was assumed that the electron-releasing property of methyl group was the only factor to affect relative stabilities of the complexes, iodine should be expected to form more stable complex with *o*-toluidine than with aniline. This was contrary to the experimental observations, however. It was concluded that the steric effect of the *ortho*-substituent also played important role for the formation of the charge-transfer complexes. Although the electron-releasing character of the methyl group might increase the electron density of nitrogen atoms of the amines to enhance the

basicity of the amines toward the complex formation, the steric hindrance of *o*-methyl group might be considered to inhibit possible interaction between the nitrogen atoms of the amines and the iodine molecule.

It appeared of interest to extend the studies to the corresponding systems of toluidines and N-methyltoluidines in order to compare the steric effect with the electron-releasing power of the methyl substituent towards the charge-transfer complex formation. Thus, the present study was undertaken on the complexes of *o*-, *m*- and *p*-toluidines and *o*-, *m*- and *p*-N-methyltoluidines with iodine in carbon tetrachloride.

Experimental

Material. N-Methylaninline, *o*-, *m*- and *p*-toluidines and *o*-, *m*- and *p*-N-methyltoluidines (all Reagent grades, 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 experimental studies.

Experimental Procedures. Experimental procedures for the preparation of various stock solutions and the UV spectrophotometric measurements were described in previous papers.[5-7] In each system examined, UV absorption spectra were measured in the region of 300-600 nm, and the wave lengths of the maximum absorption were observed. The absorbancy of each system at its absorption miximum was measured

at different amine concentrations. Beckman DK-2 and DU-2 Spectrophotometers were used. From the observed variations of absorbancies with initial concentration of amines and iodine, it was possible to obtain the formation constants of the complexes.

Results

The Complexes of Toluidines with Iodine. The absorption spectra of the systems of *o*-, *m*- and *p*-toluidines with iodine in carbon tetrachloride solution indicated the existence of absorption maxima in the region of 370–375 nm. This was attributed to the complex formation between toluidines molecules (*D*) and iodine molecule (*B*) in solution.[4-7] If the complexes were assumed to be one-to-one molecular complexes (*DB*), the formation constants (*K_f*) of the complexes were calculated from the observed variation of $[D]_0[B]_0/$ $\{A-a_0[B]_0\}$ versus $[D]_0$. as was explained in the previous papers.[4-7]

$$D + B \rightleftharpoons DB$$

$$\frac{[D]_0[B]_0}{A - a_0[B]_0} = \frac{[D]_0}{a - a_0} + \frac{1}{a - a_0}\cdot\frac{1}{K_f},$$

where $[D]_0$ denotes the the initial concentration of toluidines, $[B]_0$ that of iodine, A the absorbancy of the toluidines–iodine mixture solution at it absorption maximum, a the molar absorptivity of toluidines in CCl_4 and a_0 that of iodine in CCl_4. The values of a_0 obtained experimentally are listed in Table 1.

TABLE 1: Molar Absorptivity of Iodine in Carbon Tetrachloride

Wave length, nm	Molar absorptivity (a_0)
370	13.7
375	13.2
385	205

TABLE 2: Data Obtained for the Systems of Toluidines with Iodine in Carbon Tetrachloride at Room Temperatures

Amine	Amine conc., mole/l $[D]_0$	I_2 Conc., 10^{-5} mole/l $[B]_0$	Absorbancy at absorp. max A	$\dfrac{[D]_0[B]_0}{A - a_0[B]_0}$ 10^{-5} mole/l	Absorp. max., nm	K_f l/mole
o-Toluidine	0.186	4.00	0.230	3.24	370	8.63
		6.00	0.345	3.25 3.24		
		8.00	0.461	3.24		
	0.373	4.00	0.286	5.21		
		6.00	0.428	5.24 5.22		
		8.00	0.573	5.21		
	0.559	4.00	0.311	7.19		
		6.00	0.464	7.24 7.20		
		8.00	0.624	7.18		
	0.745	4.00	0.323	9.23		
		6.00	0.485	9.23 9.22		
		8.00	0.648	9.21		
m-Toluidine	0.0927	4.00	0.272	1.36	375	13.2
		6.00	0.409	1.36 1.36		
		8.00	0.545	1.36		
	0.185	4.00	0.345	2.15		
		6.00	0.519	2.15 2.15		
		8.00	0.691	2.15		
	0.371	4.00	0.381	3.89		
		6.00	0.573	3.89 3.89		
		8.00	0.761	3.90		
	0.556	4.00	0.415	5.36		
		6.00	0.624	5.36 5.36		
		8.00	0.833	5.35		
p-Toluidine	0.0451	4.00	0.200	0.901	370	27.8
		6.00	0.303	0.896 0.899		
		8.00	0.402	0.899		
	0.0901	4.00	0.252	1.43		
		6.00	0.378	1.44 1.43		
		8.00	0.507	1.43		
	0.180	4.00	0.290	2.49		
		6.00	0.438	2.48 2.48		
		8.00	0.579	2.47		
	0.361	4.00	0.313	4.61		
		6.00	0.470	4.61 4.61		
		8.00	0.627	4.61		

TABLE 3: Data Obtained for the Systems of N-Methylaniline and N-Methyltoluidines with Iodine in Carbon Tetrachloride at Room Temperatures

Amine	Amine conc., mole/l $[D]_0$	I_2 conc., 10^{-4} mole/l $[B]_0$	Absorbancy at absorp. max A	$\dfrac{[D]_0\,[B]_0}{A - a_0\,[B]_0}$ 10^{-4} mole/l		Absorp. max., nm	K_f l/mole
N-Methylaniline	0.185	2.00	0.289	1.48		385	13.2
		3.00	0.431	1.49	1.48		
		4.00	0.580	1.48			
	0.370	2.00	0.335	2.51			
		3.00	0.499	2.52	2.51		
		4.00	0.673	2.49			
	0.554	2.00	0.352	3.55			
		3.00	0.528	3.55	3.56		
		4.00	0.699	3.58			
	0.739	2.00	0.359	4.64			
		3.00	0.533	4.69	4.65		
		4.00	0.719	4.63			
N-Methyl-o-toluidine	0.161	2.00	0.276	1.37		385	10.4
		3.00	0.432	1.30	1.30		
		4.00	0.603	1.23			
	0.242	2.00	0.293	1.91			
		3.00	0.486	1.70	1.76		
		4.00	0.661	1.67			
	0.322	2.00	0.315	2.35			
		3.00	0.527	2.07	2.15		
		4.00	0.720	2.02			
	0.484	2.00	0.335	3.28			
		3.00	0.550	2.96	2.99		
		4.00	0.790	2.73			
N-Methyl-m-toluidine	0.161	2.00	0.325	1.13		385	19.6
		3.00	0.517	1.05	1.06		
		4.00	0.722	1.00			
	2.241	2.00	0.346	1.57			
		3.00	0.546	1.46	1.48		
		4.00	0.762	1.41			
	0.321	2.00	0.364	1.98			
		3.00	0.588	1.82	1.86		
		4.00	0.807	1.77			
	0.482	2.00	0.376	2.87			
		3.00	0.615	2.60	2.69		
		4.00	0.821	2.60			
N-Methyl-p-toluidine	0.0772	2.00	0.304	0.585		385	35.5
		3.00	0.482	0.549	0.563		
		4.00	0.635	0.556			
	0.154	2.00	0.338	1.04			
		3.00	0.572	0.905	0.905		
		4.00	0.795	0.864			
	0.309	2.00	0.376	1.84			
		3.00	0.593	1.74	1.72		
		4.00	0.859	1.59			
	0.463	2.00	0.394	2.62			
		3.00	0.614	2.51	2.50		
		4.00	0.859	2.38			

The experimental data obtained for the systems of o-, m- and p-toluidines with iodine are summarized in Table 2. The data indicated good linearities between $[D]_0[B]_0/\{A-a_0[B]_0\}$ and $[D]_0$ in each case examined. To illustrate the linearity, an example of the plots is shown in Figure 1.

It was concluded from the observed linearities that o-, m- and p-toluidines formed the one-to-one complexes with iodine in carbon tetrachloride. From the values of slopes and

intercepts of the linear plots, the formation constants of the complexes were obtained. The results are included in Table 2.

The Complexes of N-Methylaniline and N-Methyltoluidines with Iodine. Similar studies were carried out on the systems of N-methylaniline and N-methyltoluidines with iodine in carbon tetrachloride. The results are summarized in Table 3. Since the results indicated good linearties between $[D]_0[B]_0/\{A-a_0[B]_0\}$ and $[D]_0$, it was concluded that
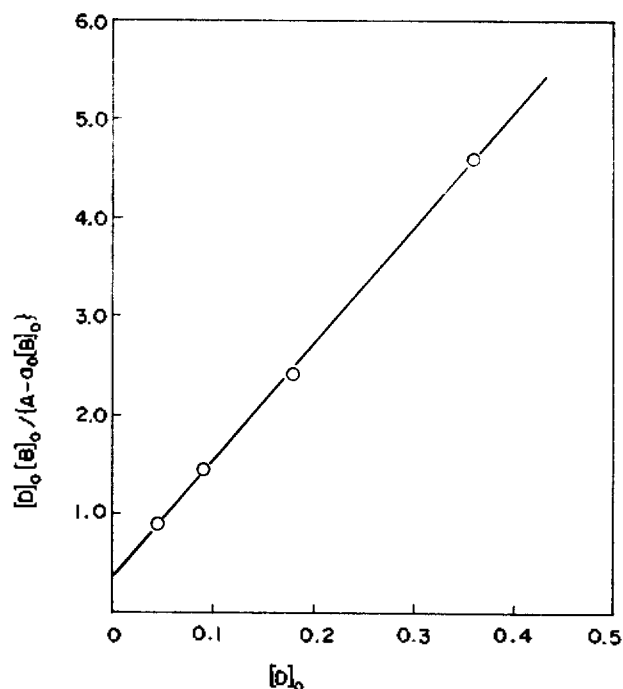
Figure 1. Plots of $[D]_0[B]_0/\{A-a_0[B]_0\}$ versus $[D]_0$ of the p-toluidine-iodine systems.

TABLE 4: Formation Constants of Toluidines and N-Methyltoluidines with Iodine in Carbon Tetrachloride

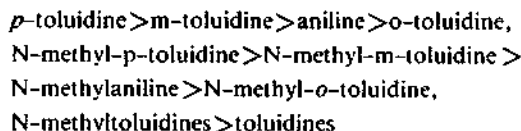| X	Formation const., //mole	
	X·C₆H₄NH₂·I₂	X·C₆H₄NH(CH₃)·I₂
H	12.8*	13.2
-CH₃	8.63 (9.31*)	10.4
m-CH₃	13.2	19.6
p-CH₃	28.7	35.5

* Ref. 4

N-methylaniline and o-, m- and p-N-methyltoluidines also formed the one-to-one complexes with iodine in carbon tetrachloride. The formation constants of the complexes were obtained by the method mentioned above. The results are listed in Table 3.

Discussion

The results of the present study indicate that o-, m-, and p-toluidines and o-, m-, and p-N-methyltoluidines form the one-to-one molecular complexes with I_2 in CCl_4 solution. By comparing the values of the formation constants of the complexes (Table 4), it is concluded that the relative stabilities of the complexes decrease in the following orders:

p-toluidine>m-toluidine>aniline>o-toluidine,
N-methyl-p-toluidine>N-methyl-m-toluidine>
N-methylaniline>N-methyl-o-toluidine,
N-methyltoluidines>toluidines

These complexes are assumed to be formed by the eletron donor-acceptor interaction or the charge-transfer interaction at the nitrogen atoms of amine molecules. Thus, it is expected that the electron-releasing property of the CH_3 group may increase the electron density of the nitrogen atoms of the amine molecules to enhance the stabilities of the complexes. It can be said therefore that the p-CH_3 substituent leads to the formation of more stable complexes than the m-CH_3 substituent, which in turn results in greater stability of the complexes than the unsubstituted molecules.

The experimental observations that N-methyltoluidines form more stable complexes than toluidines may be explained also by the electron-releasing power of CH_3 substituent.

If it is assumed that the electron-releasing character of the methyl group is the only major factor to affect the relative stabilities of the charge-transfer complexes, it is expected that the o-substituted amines must form the complexes of about same stability as p-substituted amines. This is not true, however. In order to explain the experimental results, the steric effect of o-CH_3 group may be considered. Steric hindrance of o-CH_3 group may inhibit the possible interaction between I_2 and N atoms of the amine molecules.

Hence, it could be said that both the electron-releasing charactor and the steric effect of CH_3 substituent play important role of the formation of the charge-transfer complexes of toluidines and N-methyltoluidines with I_2 in solution.

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