(5)   D. C. Mukherjee, J. W Park and B. Chakrabarti, *Arch. Biochem. Biophys.*, **191**, 393 (1978).

(6)   J. R. Dunstone, *Biochem. J.*, **85**, 336 (1962).

(7)   E. A. MacGregor and J. M. Bowness, *Can. J. Biochem.*, **49**, 417 (1971).

(8)   W. D. Comper and T. C. Laulent, *Physiol. Rev.*, **58**, 255 (1978).

(9)   E. S. Boyd and W. F. Neuman, *J. Biol. Chem.*, **193**, 243 (1951).

(10) S. Vannucchi, M. D. Rosso, C. Cella, P. Urbano and V. Chiarugi, *Biochem. J.*, **170**, 185 (1978).

(11) C. Woodward and E. A. Davidson, *Proc. Natl. Acad. Sci. U.S.A.*, **60**, 201 (1968).

(12) M. B. Mathews, "Chemistry and Molecular Biology of the Intercellular Matrix", E. A. Balazs, Ed., Vol. 2, 1121-1123, Academic Press, New York, U.S.A., 1970.

(13) J. W. Park and B. Chakrabarti, *Biochem. Biophys. Acta*, **544**, 667, (1978).

(14) A. M. Kotliar and H. Morawetz, *J. Amer. Chem. Soc.*, **77**, 3692 (1955).

(15) H. P. Gregor, L. B. Lattinger and E. M. Loebl, *J Phys. Chem.*, **59**, 34 (1955).

(16) M. B Mathews, *Biochem. Biophys. Acta*, **37**, 288 (1960).

(17) M. B. Mathews, *Arch. Biochem. Biophys.*, **104**, 394 (1964).

(18) E. Buddecke and R. Drzeniek, *Hoppe-Sevlers Z. Physiol. Chem.*, **327**, 49 (1962).

(19) J. Blackwell, K. P. Schodt and R. A. Gelman, *Fed. Proc.*, **36**, 98 (1977).

(20) T. Olivecrona, G. Bengtsson, S. E. Marklund, U. Lindahl and M. Hook, *Fed. Proc.*, **36**, 60 (1977) and references therein.

(21) G. S. Manning, "Polyelectrolytes", Proc. of the First NATO Advanced Study Institute on Charged and Reactive Polymers, Forges-les-Eaux, E. Sélégny, M. Mandel and U. P. Strauss, Eds., p.9-37, Reidel, Boston, U.S.A., 1974.

(22) C. P. Dietrich, L. O. Sampaio, O. M. S. Toledo and C. M. F. Cassaro, *Biochem. Biophys. Res. Commun.*, **75**, 329 (1977).

(23) L. O. Sampaio, C. P. Dietrich, and O. G. Filho, *Biochem. Biophys. Acta*, **498**, 123 (1977).

The Charge Transfer Complexes of Monoalkylbenzene with Iodine in Carbon Tetrachloride (II)

Oh Cheun Kwun

Department of Chemistry, Hanyang University, Seoul 133, Korea   (Received June 10, 1980)

Ultraviolet spectrophotometric investigations were carried out on monoalkylbenzene-iodine systems in carbon tetrachloride. The results reveal the formation of one-to-one molecular complexes. On the basis of the equilibrium constants for these complexes of representative monosubstituted benzenes, the following order of increasing stability is obtained: *i*-propyl-<*i*-butyl- <*t*-butyl-<*n*-butyl-benzene. The values of ΔH, ΔG and ΔS for the interaction of a number of monoalkyl substituted benzenes with iodine have been determined. In general, it can be said that as ΔH becomes increasingly negative, corresponding decreases in the ΔG and the ΔS values are observed, and these variations are linear. The thermodynamic constants become increasingly negative with increasing monoalkyl substitution of the aromatic donor nucleus. The complex bond is therefore weak, and its formation is accompanied by relatively small entropy changes. Thus, analysis of these findings is discussed.

Introduction

After Benesi and Hildebrand[1] first demonstrated the formation of one to one molecular complex between benzene and iodine in carbon tetrachloride solution, studies were extended to other system by a number of workers[2].

In a previous study[2] of this series[1], it was observed that the solutions of monoalkylbenzene (benzene, methyl-, ethyl-, *n*-propyl-benzene) with Iodine in carbon tetrachloride showed the presence of absorption maxima in the vicinity of $300 \, \text{m} \, \mu$, where none of the component materials had strong absorption. This phenomenon was attrituted to the formation of one to one molecular complexes in solution. From spec-

trophotometric data, we obtained the equilibrium constants for the complex formation and the molar absorptivities of the complexes at their absorption maxima. The equilibrium constants at 25 °C for the monoalkylbenzene complexes were found to increase in the order, benezene<methyl-<ethyl- <*n*-propyl-benzene.

The present study involved the spectrophotometric investigations at 25, 40, 60 °C on the systems of monoalkylbenzene (*i*-propyl-, *n*-butyl, *i*-butyl-, *t*-butyl-benzene) with iodine in carbon tetrachloride. Carrying out ultraviolet spectrophotometric studies to measure the temperature dependence of complex formation, Keefer and Andrews[3] determined ΔH, ΔG and ΔS for carbon tetrachloride solutions of iodine with

polyalkylbenzenes. For iodine complexes with benzene and toluene and related electron donors[4-7], heats of formation lying between -1 and -2 kcal/mole have been obtained.

In these previous studies, however, equilibrium constants and thermodynamic functions of monoalkylbenzene-iodine complexes have not been investigated so far. It therefore appeared to be interest to extend the studies to monoalkylbenzene-iodine systems in carbon tetrachloride, in order to determine the relative complexing power of iodine with monoalkylbenzenes. In the present study, spectrophotometric investigations are reported carried out to determine the temperature dependence of one-to-one complex formation in the cases of iodine and a series of monoalkylated benzenes of rather differing donor strengths in carbon tetrachloride.

Experimental

Materials. Samples of Merck & Co. iodine (superpure grade), carbon tetrachloride(uvasol grade) were used without further purification. Samples of Merck & Co. *i*-propylbenzene, *n*-butylbenzene, *i*-butylbenzene, and *t*-butylbenzene(synthesis grade) were purified by drying and distilling. Prior to use, the following boilding points and refraction indices were determined:

	Boiling point	$n^{20}D$
i-Propylbenzene	152.6 °C	1.4917
n-Butylbenzene	182-183 °C	1.4900
i-Butylbenzene	172-173 °C	1.4865
t-Butylbenzene	168.5-169 °C	1.4925

Spectrophotometric Measurements. The experimental procedures utilized for both the preparation of stock solutions and the spectrophotometric measurements of the solutions were described previously, and will not repeated in this paper. The spectra of CT-complexes is measured on a Cary model 14 spectrophotometer together with a set of 10mm quartz cell which have teflon stopper (Hellma Co. No. 110-0S). All the measurements were carried out at temperature 25, 40 and 60 °C.

Results and Discussion

Calculation of the Equilibrium Constant for the CT-Complex Formation. The equilibrium constants K for the complex formation and the molar absorptivities, $\mathcal{E}$ of the complexes at their absorption maxima were evaluated by method described previously[2].

Therefore, the following equation holds:

$$\frac{[B]_0}{A - \mathcal{E}_0 [B]_0} = \frac{1}{(\mathcal{E} - \mathcal{E}_0) K} \cdot \frac{1}{[D]_0} + \frac{1}{\mathcal{E} - \mathcal{E}_0} \quad (1)$$

In the cases studied in this paper, $[D]_0$, the initial molar concentration of the donor, is much bigger than $[B]_0$, the molar concentration of the halogen present initially. Where A denotes the absorbancy, $\mathcal{E}$ and $\mathcal{E}_0$ molar absorptivities of the complexes and the free halogens at the wave lengths corresponding to the absorption maxima of the complexes, respectively, and K the equilibrium constant. Formula (1) is obviously of the type $y = mx + b$. The values of the equilibrium constnat K and the absorption coefficient a were found with the aid of this equation.

After having determined the values for A experimentally, the corresponding y values were plotted against those of the x term. The plots reveal a good linearity between the two quantities in all the systems under investigation.

The values of the m and b terms were calculated from the slopes and the intercepts of the straight lines. The least square method was used to determine slopes and intercepts. As we know $(\mathcal{E} - \mathcal{E}_0) \cdot K$ and $\mathcal{E} - \mathcal{E}_0$, the values of K and a can easily be calculated. Thus the temperature shift (the blue shift referred to in the papers by Ewald *et al.*[8,9]) of the absorption maxima of the CT-complexes appears according to increase in temperature.

Thus, the each value of $\mathcal{E}_0$ (value is derived through experiment; Table 1 and of A (Table 2-5) in equation (1) is equivalent to the corresponding values which are given in presence of wave length of absorption maxima of CT-complexes determined by the temperature shift. The values obtained by our experiments, put into equation (1), yield a linear relationship between y and x. They thus again confirm the original assumption of Benesi and Hildebrand that one-to-one molecular complexes are formed.

The Monoalkylbenzene-Iodine CT-Complexes Formation. To illustrate the linear relationship between y and x, one example has been choosen(*i*-propylbenzene-iodine CT-complex) and is shown in Figure 1. The values obtained with the aid of equation (1) are listed in Table 6. Values can be ordered according to the increase in the number of alkyl substituents to yield the following series: *i*-propyl- < *i*-butyl < *t*-butyl- < *n*-butyl-benzene.

Hence, the K values of the benzene- and toluene-iodine complexes given in a previous study[2] Table 6, as examples of monoalkylbenzene-iodine complexes, show that we got almost the same results as those obtained by the different authors[2,10].

When studying the alkylbenzene-iodine monochloride complex, Andrews and Keefer observed that ethyl-, isopropyl-, and *t*-butylbenzene, within close limits, yield the same K_c values as does toluene. As shown in a previous study[2] of this series, Table 6, the K values can be ordered according to the increase in the number of alkyl substituents to yield the following series: upsubstituted < methyl- < ethyl- < *n*-propyl-benzene.

As a result, the complex stability of *n*-alkylbenzene is greater than that of *i*- and *t*-alkylbenzene, probably because the steric hindrance of *n*-alkylbenzene is smaller

TABLE 1: Molar Absorptivities of Iodine in Carbon Tetrachlorides at Several Temperatures

I_2, 10^3 mole · l^{-1}	Temp (°C)								
	25			40			60		
	Wave length (mμ)	Absorbancy(A)	Molar absorptivity(a_0)	Wave length (mμ)	Absorbancy(A)	Molor absorptivity(a_0)	Wave length (mμ)	Absorbancy(A)	Molar absorptivity(a_0)
3.22	293	0.154	47.8	292	0.150	46.5	290	0.147	45.6
5.00	293	0.238	47.6	292	0.229	45.8	290	0.225	45.0
6.67	293	0.318	47.7	292	0.309	46.3	290	0.298	44.7
7.45	293	0.358	48.0	292	0.346	46.5	290	0.334	44.9
			Av. 47.8			Av. 46.3			Av. 45.1
3.22	302	0.122	37.8	301	0.122	37.8	300	0.118	36.6
5.00	302	0.192	38.4	301	0.187	37.4	300	0.182	36.4
6.67	302	0.260	39.0	301	0.253	37.9	300	0.241	36.1
7.45	302	0.290	38.9	301	0.281	37.7	300	0.273	36.7
			Av. 38.5			Av. 37.7			Av. 36.5
3.22	303	0.118	36.6	302	0.116	36.0	301	0.113	35.1
5.00	303	0.189	37.8	302	0.182	36.6	301	0.174	34.8
6.67	303	0.251	37.6	302	0.245	36.7	301	0.235	35.2
7.45	303	0.284	38.1	302	0.275	36.9	301	0.265	35.6
			Av. 37.5			Av. 36.6			Av. 35.2
3.22	304	0.114	35.4	303	0.112	34.7	302	0.110	34.1
5.00	304	0.184	36.8	303	0.178	35.6	302	0.174	34.8
6.67	304	0.245	36.7	303	0.238	35.7	302	0.228	34.2
7.45	304	0.276	37.1	303	0.267	35.9	302	0.258	34.6
			Av. 36.5			Av. 35.5 ·			Av. 34.4

TABLE 2: Formation of i-$C_6H_5C_3H_7$·I_2 in Carbon Tetrachloride at Several Temperatures

i-$C_6H_5C_3H_7$, mole· l^{-1} [D]$_0$	I_2, 10^4 mole· l^{-1} [B]$_0$	Temp. (°C)					
		25		40		60	
		A, at 303 mμ	Y, 10^4 mole· l^{-1}	A, at 302 mμ	Y, 10^4 mole· l^{-1}	A, at 301 mμ	Y, 10^4 mole· l^{-1}
0.269	3.34	0.234	15.2	0.201	17.7	0.169	21.2
	5.02	0.349	15.2	0.304	17.6	0.258	20.9
	6.67	0.462	15.3	0.403	17.6	0.340	21.1
			Av. 15.2		Av. 17.6		Av. 21.1
0.386	3.34	0.319	10.9	0.276	12.6	0.233	15.1
	5.02	0.484	10.8	0.414	12.7	0.348	15.2
	6.67	0.638	10.9	0.557	12.5	0.468	15.0
			Av. 10.9		Av. 12.6		Av. 15.1
0.512	3.34	0.412	8.36	0.360	9.60	0.308	11.3
	5.02	0.619	8.37	0.539	9.64	0.474	11.0
	6.67	0.823	8.36	0.715	9.66	0.619	11.2
			Av. 8.36		Av. 9.63		Av. 11.2
0.637	3.34	0.501	6.84	0.436	7.87	0.367	9.39
	5.02	0.747	6.90	0.660	7.83	0.554	9.37
	6.67	0.999	6.91	0.878	7.82	0.736	9.37
			Av. 6.88		Av. 7.84		Av. 9.38

than that of i-and t-alkylbenzene. Furthermore, the stabilization of these complexes could be due to enhanced ring electron density resulting from hyperconjugation involving α-hydrogen atoms of the alkyl substituents. On the basis of the inductive effects of these groups one would rather predict the opposite order of reactivity. Lichtin and Bartlett[11]

TABLE 3: Formation of $n\text{-}C_6H_5C_4H_9\cdot I_2$ in Carbon Tetrachloride at Several Temperatures

$n\text{-}C_6H_5C_4H_9$, mole·l^{-1} $[D]_0$	I_2, 10^4 mole·l^{-1} $[B]_0$	Temp. (°C)					
		25		40		60	
		A, at 303 mμ	Y, 10^4mole·l^{-1}	A, at 302 mμ	Y, 10^4 mole·l^{-1}	A, at 302 mμ	Y, 10^4 mole·l^{-1}
0.308	3.34	0.260	13.5	0.223	15.8	0.187	19.0
	5.02	0.396	13.3	0.342	15.5	0.289	18.5
	6.67	0.528	13.3	0.455	15.5	0.382	18.6
			Av. 13.4		Av. 15.6		Av. 18.7
0.427	3.34	0.350	9.89	0.303	11.5	0.253	13.8
	5.02	0.525	9.93	0.451	11.6	0.381	13.8
	6.67	0.696	9.95	0.608	11.4	0.512	13.6
			Av. 9.92		Av. 11.5		Av. 13.7
0.549	3.34	0.424	8.11	0.370	9.33	0.317	10.9
	5.02	0.641	8.07	0.561	9.26	0.487	10.7
	6.67	0.858	8.01	0.747	9.24	0.635	10.9
			Av. 8.06		Av. 9.28		Av. 10.8
0.692	3.34	0.530	6.45	0.467	7.34	0.400	8.60
	5.02	0.802	6.41	0.701	7.36	0.602	8.59
	6.67	1.058	6.46	0.927	7.39	0.797	8.62
			Av. 6.44		Av. 7.36		Av. 8.61

TABLE 4: Formation of $i\text{-}C_6H_5C_4H_9\cdot I_2$ in Carbon Tetrachloride at Several Temperatures

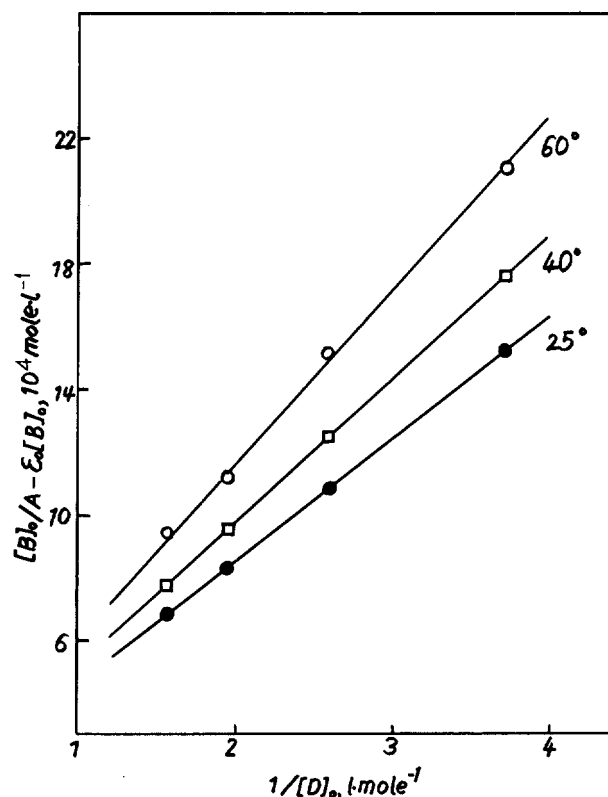| $i\text{-}C_6H_5C_4H_9$, mole·l^{-1} $[D]_0$	I_2, 10^4 mole·l^{-1} $[B]_0$	Temp. (°C)					
		25		40		60	
		A, at 304 mμ	Y, 10^4mole·l^{-1}	A, at 303 mμ	Y, 10^4 mole·l^{-1}	A, at 302 mμ	Y, 10^4 mole·l^{-1}
0.305	3.34	0.254	13.8	0.218	16.2	0.186	19.1
	5.02	0.390	13.5	0.332	16.0	0.277	19.3
	6.67	0.509	13.8	0.443	15.9	0.369	19.3
			Av. 13.7		Av. 16.0		Av. 19.2
0.424	3.34	0.338	10.2	0.292	11.9	0.248	14.1
	5.02	0.506	10.3	0.447	11.7	0.381	13.8
	6.67	0.680	10.2	0.594	11.7	0.496	14.1
			Av. 10.2		Av. 11.8		Av. 14.0
0.545	3.34	0.425	8.08	0.367	9.40	0.304	11.4
	5.02	0.639	8.09	0.554	9.36	0.466	11.2
	6.67	0.850	8.08	0.740	9.32	0.630	11.0
			Av. 8.08		Av. 9.36		Av. 11.2
0.687	3.34	0.520	6.57	0.458	7.48	0.380	9.06
	5.02	0.783	6.57	0.687	7.50	0.575	9.00
	6.67	1.038	6.58	0.912	7.51	0.769	8.95
			Av. 6.57		Av. 7.50		Av. 9.00

have given interesting coments on the problems which show up when basing theoretical work on a series of measurements reflecting the result of these effects.[12]

The above anlysis yields almost the same order of K values as found by Brown and Brady[13] w.r.t. alkylbenzene-HCl. When surveying the data given in Table 6 with respect to evidence of a steric repression of complex formation, it seemed

reasonable to adopt the viewpoint that the free energies of iodine-monoalkylbenzene interactions may serve as a comparative scale for the electronic influences of alkyl substituents on donor strengths in the absence of unfavorable steric situations. This is supported experimentally by our present study. Accordingly the $\log K_c$ values for the monoalkylbenzene-iodine complexes at 25 °C have been plotted against

TABLE 5: Formation of t-C$_6$H$_5$C$_4$H$_9$·I$_2$ in Carbon Tetrachloride at Several Temperatures

t-C$_6$H$_5$C$_4$H$_9$, mole·l^{-1} [D]$_0$	I$_2$, 10^4 mole·l^{-1} [B]$_0$	Temp. (°C) 25 A, at 304 mμ	25 Y, 10^4 mole·l^{-1}	40 A, at 303 mμ	40 Y, 10^4 mole·l^{-1}	60 A, at 302 mμ	60 Y, 10^4 mole·l^{-1}
0.310	3.34	0.270	12.9	0.232	15.2	0.193	18.4
	5.02	0.405	13.0	0.346	15.3	0.293	18.2
	6.67	0.535	13.1	0.467	15.1	0.388	18.3
			Av. 13.0		Av. 15.2		Av. 18.3
0.340	3.34	0.358	9.65	0.311	11.2	0.260	13.4
	5.02	0.540	9.63	0.462	11.3	0.389	13.5
	6.67	0.720	9.60	0.620	11.2	0.521	13.4
			Av. 9.63		Av. 11.2		Av. 13.4
0.533	3.34	0.446	7.69	0.385	8.94	0.323	10.7
	5.02	0.672	7.68	0.581	8.92	0.491	10.6
	6.67	0.895	7.67	0.781	8.81	0.650	10.6
			Av. 7.68		Av. 8.89		Av. 10.6
0.697	3.34	0.548	6.23	0.475	7.21	0.398	8.64
	5.02	0.830	6.19	0.711	7.24	0.598	8.65
	6.67	1.101	6.20	0.948	7.22	0.802	8.57
			Av. 6.21		Av. 7.22		Av. 8.62

Figure 1. Plot of $[B]_0/A$-$\mathcal{E}_0[B]_0$ versus $1/[D]_0$ of the i-propyl-benzene-iodine system at several temperatures.
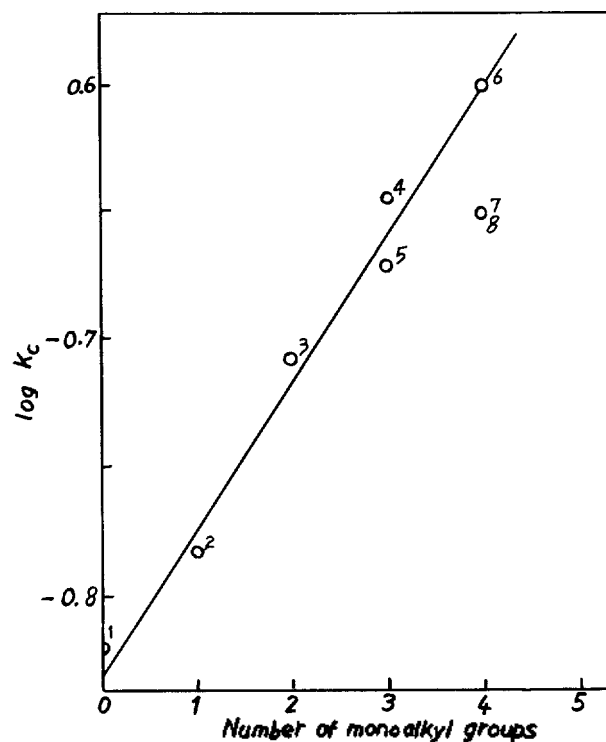
Figure 2. Plot of log K_0 versus the number of monoalkyl substituents on the donor ring for monoalkylbenzene-iodine complexes at 25 °C. Donors: 1; benzene[2], 2; touluene[2], 3; ethylbenzene[2], 4' n-propylbenzene[2] 5; i-propylbenzene, 6; n-butylbenzene, 7; i-buytlbenzene, 8; t-butylbenzene.

the number of alkyl donor substituents (see Figure 2). Most of the data, when so plotted, conform reasonably well to a straight line. Marketed deviations from linearity, which may be associated with the structures, are not observed generally.

Heat of CT-Complex Formation. The heats of complex formation were calculated from spectrophotometric data taken at

three different temperatures (25, 40 and 60 °C). The ratios of equilibrium constants at two different temperatures which were required to calculate the ΔH values were obtained using the ratios of the slope coefficients obtained when plotting the data, according to equation (1), at temperatures T_1 and T_2 using equation (2):

TABLE 6: Absorption Maxima, Molar absorptivities and Equilibrium constants for Monoalkylbenzene-Iodine CT-Complexes at 25° in Carbon Tetrachloride

Alkylbenzene	λ_{max} $m\mu$	$a \times 10^{-3}$	K_c $l \cdot mole^{-1}$
i-Propylbenzene	303	12.2	0.213
n-Butylbenzene	303	10.5	0.250
i-Butylbenzene	304	11.5	0.223
t-Butylbenzene	304	11.9	0.223

TABLE 7: Thermodynamic Functions[a] for Monoalkylbenzene-Iodine CT-Complexes in Carbon Tetrachloride

Alkylbenzene	$-\Delta H$ 25, 40 °C	$-\Delta H$ 40, 60 °C	$-\Delta H$ av.	$-\Delta G$ 25 °C	$-\Delta S$ 25 °C
i-Propylbenzene	1.95	2.02	1.99	0.470	5.09
n-Butylbenzene	2.08	2.16	2.12	0.564	5.21
i-Butylbenzene	2.00	2.00	2.00	0.496	5.05
t-Butylbenzene	2.02	2.01	2.02	0.496	5.11

[a] ΔH, ΔG in kcal·mole^{-1}, ΔS in cal·mole^{-1}·deg^{-1}.

$$2.303 \log \frac{(slope)_{T_1}}{(slope)_{T_2}} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

For each complex, values of ΔH were calculated in this way from data taken at each wave length at 25 and 40 °C and also from data taken at 40 and 60 °C. The average values of ΔH calculated from data at two temperatures, $\Delta H_{25, 40 °C}$ and $\Delta H_{40, 60 °C}$ are listed in Table 7. The heats of formation are expressed in mole fractions. The values for ΔG and ΔS given in Table 7 have been calculated using the reported values of ΔH and the equilibrium constants, $K_{25°C}$. The values of ΔG, ΔH, ΔS, which may be regarded as the values of complex formation at 25 °C, are given in Table 7. Our value for the benzene-iodine complex in a previous study[1] of this series, Table 1 is almost equal to that obtained by the previous authors[3] The ΔH values listed in the Table should differ by approximately 200 cal from those derived from equilibrium constants which are based on molar concentrations of the donors[14]. As can also been seen from the Table, decreases in ΔH with the formation of iodine-monosubstituted benzene complexes, when changing the donor substituents, are accompanied by parallel decrease in ΔG and ΔS of the interactions. The thermodynamic data of our present paper do indeed conform well to the linear plots of ΔH versus ΔG and ΔH versus ΔS for iodine-substituted polyalkylbenzene complexes[3] (see Figure 3 and 4).

The observed variations in ΔH with ΔG for iodine-monoalkyl-benzene complexes are linear. This can only hold true either if ΔS also varies linearly with ΔH. In
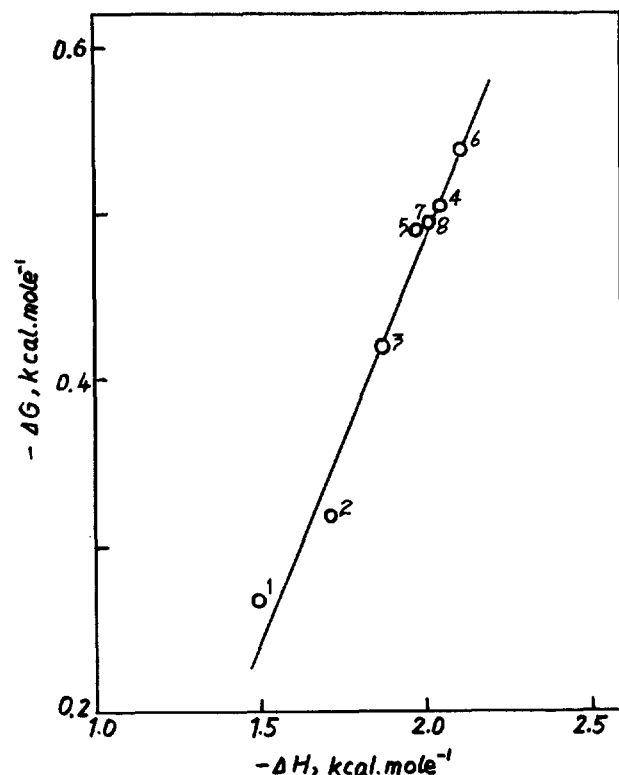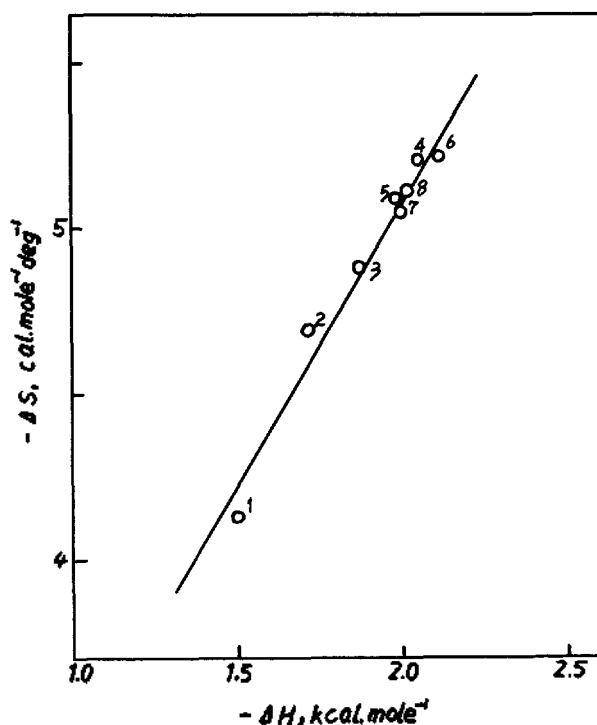

Figure 3. Plot of -ΔG versus -ΔH for monoalkylbenzene-iodine complexes at 25 °C. Donors: 1; benzene[2], 2; toluene[2], 3; ethylbenzene[2], 4; *n*-propylbenzene[2], 5' *i*-propylbenzene, 6; *n*-butylbenzene, 7; *i*-butylbenzene, 8; *t*-butylbenzene.

Figure 4. Plot of -ΔS versus -ΔH for monoalkylbenzene-iodine complexes at 25 °C. Donors: 1, benzene[2], 2; toluene[2], 3' ethylbenzene[2], 4; *n*-propylbenzene[2], 5; *i*-propylbenzene, 6' *n*-butylbenzene, 7; *i*-butylbenzene, 8; *t*-butylbenzene.

other words, barring unusual steric effects in donor molecules, one can in the present instance measure the effects of alkyl substitution on the tendency of complex formation equally well in terms of variations in ΔG, ΔH or ΔS.

It is particularly intersting that as ΔH values become more negative, corresponding decreases in ΔS are observed. The simultaneous decrease of these terms may serve as an indication of physical restraints imposed upon the complex components as the strength of the bond between them increases. van de Stolpe[6], studying the formation of a number of such iodine complexes, reports values of $\Delta S_{25^\circ C}$ which are all of the order of magnitude of 4 to 5 e.u. It is apparent from Table 7 that the ΔS values for iodine complex formation with monoalkylbenzenes show a definite downward trend as the number of alkyl substituents at the aromatic uncleus increases. In all cases, both ΔH and $T \cdot \Delta S$ terms have an appreciable influence on the magnitude of ΔG for complex formation. The changes in ΔG with increasing alkyl groups at the benzene ring are consistent with the anticipated electronic influences[15,16] of alkyl substituents on the π-electron density of the donor nucleus.

References

(1)   H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.,* 71, 2703 (1949).

(2)   O. C. Kwun, *J. Korean Chem. Soc.,* (In Process)

(3)   R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.,* 77, 2164 (1955).

(4)   T. M. Cromwell and R. L. Scott, *ibid.,* 72, 3825 (1950).

(5)   K. Hartley and H. A. Skinner, *Trans. Faraday Soc.,* 45, 621, (1950).

(6)   C. van de Stolpe, Thesis, "Solvatie van Jodium in Organische Oplosmiddelen", University of Amsterdam, 1953.

(7)   L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry", Holden-Day, Inc., London, 1964.

(8)   A. H. Ewald, *Trans. Faraday Soc.,* 64, 733 (1968).

(9)   A. H. Ewald and J. A. Scudder, *J. Phys. Chem.,* 76, 249 (1972).

(10)   L. J. Andrews, *Chem. Revs.,* 54, 713 (1954).

(11)   N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.,* 73, 5530 (1951).

(12)   R. Foster, "Organic Charge-Transfer Complexes,", Academic Press, London, 1969.

(13)   H. C. Brown and J. D. Brady, *ibid.,* 74, 3570 (1952).

(14)   J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. Trav. Chem.,* 71, 1104 (1952).

(15)   J. P. Wibaut, E. L. J. Sixma, L. W. F. Kampschmidt and H. Borer, *Re. Trav. Chem.,* 69, 1355 (1950).

(16)   R. Foster, C. A. Fyfe and M. I. Foreman, *Chem. Commun.,* 913 (1967).

Fluorescence of Phototautomeric Lumichrome in Pyridine-Dioxane

Pill-Soon Song* and Jung Do Choi**

Department of Chemistry, Seoul National University, Seoul 151, Korea (Received May 29, 1980)

Lumichrome (7,8-dimethylalloxazine) exhibits two fluorescence emission maxima at 440 and 540 nm in pyridine-dioxane. These emission band maxima are attributable to radiative decays from the excited states of lumichrome and its flavin tautomer, 7,8-dimethylisoalloxazine, respectively. The growth of the latter can be followed upon excitation of the former with a 2-nanosecond light pulse generated from the nitrogen plasma discharge lamp. The excited state tautomerism results from proton transfer from N-1 to N-10 position during the lifetime of the lumichrome singlet excited state. The rate depends on the concentration of general base, pyridine, and it is an order of magnitude slower than diffusion-controlled processes.

Introduction

In our previous reports[1,2], we described the phototautomerism of lumichrome (7,8-dimethylalloxazine, **1**, Scheme 1) in pyridine-dioxane and acetic acid-ethanol mixtures, as studied by fluorescence intensity and nanosecond time-resolved methods. Lumichrome exhibits two fluorescence emission maxima in these mixtures; for example, 440 and 540 nm, in pyridine-dioxane. The latter is due to the isoalloxazine tautomer (**2**, a flavin) formed in the excited state from the alloxazine **1** singlet during its lifetime as the result of pyridinecatalyzed transfer of proton from N-1 to N-10.[2-4]