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

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Ultraviolet spectrophotometric investigations have been carried out the systems of monoalkylbenzene with iodine in carbon tetrachloride. The results reveal the formation of one to one molecular complexes. The equilibrium constants for these complexes of representative monosubstituted benzene reveal the following order of increasing stability: benzene < methyl- < ethyl- < *n*-propyl-benzene. The value of ΔH , ΔG , and ΔS for interaction of a number of monoalkyl substituted benzene with iodine has been determined. In general, as ΔH becomes increasingly negative, corresponding decreases in ΔG and ΔS values are observed, and these variation 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.

Introduction

Benesi and Hildebrand¹ observed that a solution of benzene and iodine in carbon tetrachloride had a maximum of absorption at 297 *mu*. They concluded that this was due to the formation of a one-to-one molecular complex, benzene-iodine, in the solution. In a similar study, Keefer and Andrews² found a different absorption maximum for the benzene-iodine complex, namely 292 *mu*. In the same publication, the authors report on the interaction of iodine monochloride with ethyl-, isopropyl-, and *t*-butylbenzenes. On the whole, it can be said that the agreement between the results the two groups of authors have obtained is not too satisfactory.

Carrying out ultraviolet spectrophotometric studies to measure the temperature dependence of complex formation, Keefer and Andrews³ determined ΔH , ΔG and ΔS for carbon tetrachloride solutions of iodine with polyalkylbenzenes. For iodine complexes with benzene and toluene and related electron donors⁴⁻⁷, 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) and benzene, toluene, carbon tetrachloride (uvasol grade) were used without further purification. Samples of Merck Co. ethylbenzene, *n*-propylbenzene (synthese grade) were dried over calcium chloride and distilled through a 100 cm distillation column packed with glass helices. The reflux ratio was kept at approximately 1:15. The middle portions of the distillates were collected. The boiling points and refraction index observed were as follows: ethylbenzene; b.p 136.3°, n_D^{20} 1.4960, *n*-propylbenzene; b.p 159.0°, n_D^{20} 1.4922.

Preparation of Stock Solutions. The solution of iodine in carbon tetrachloride was prepared by weighting an appropriate quantity of iodine into a volumetric flask, and adding carbon tetrachloride solvent to make up to volume. The solution thus prepared was diluted further to suitable concentrations. The solutions of monoalkylbenzenes (donors) in carbon tetrachloride was prepared by weighting an appropriate quantity of donors into a volumetric flask and adding carbon tetrachloride to make up to volume. Each solution was freshly prepared at room temperature, $24 \pm 1^\circ\text{C}$, before making absorption spectrum measurements and wrapped with black paper to prevent any photochemical reaction in solution. The concentration of iodine was *ca.* 10 mole·*l*⁻¹ and that of donors was 10 mole·*l*⁻¹. These were varied at least three fold for any one system. Both concentrations were adjusted so as to keep the absorbancy within suitable limits.

The Spectrophotometric Measurements. The spectra of CT-Complexes is measured on a Cary model 14 spectrophotometer together with a set of 10 mm quartz cells which have teflon stopper (Hellma Co. No. 110-QS). The absorbancies of stock solutions of iodine and donors in carbon tetrachloride were measured over the region of wave lengths from 270 to 700 m μ , using the pure solvent, carbon tetrachloride, as the blank. Then, the stock solution of donors was mixed at various ratios with the solution of the iodine. The absorbancies of the resulting solution were immediately measured. The prolonged keeping of the mixture solutions was avoided as otherwise slow chemical changes might have occurred. The blank in this case was the carbon tetrachloride solution of donors with the same concentration as those of solutions containing iodine. The optical cell was kept at constant temperature by circulating water through it supplied by a thermostat. Cell was maintained at the desired temperatures 25, 40 and 60°C, by a thermostat within $\pm 0.1^\circ\text{C}$. The absorbancies of solution, at the complex absorption maximum, were usually determined in the neighborhood of 300 m μ .

Results and Discussion

Calculation of Equilibrium Constant for the CT-Complex Formation. The absorption spectra of the individual stock solution of iodine, or donors in carbon tetrachloride did not indicate the presence of maximum absorption peaks in the vicinity of the 300 m μ . On the other hand, the absorption spectra of the solution of a mixture of donors with iodine did indicate the presence of absorption maxima in the region of wave lengths near 300 m μ . The maximum absorption observed is attributed to the formation of complexes of donors with iodine in solution.

These complexes are assumed to be one to one molecular complexes, as was first proposed by Benesi and Hildebrand for the system of benzene-iodine in carbon tetrachloride¹.



Where D denotes the donor molecules, B acceptor molecules and C the one to one molecular complex $D \cdot B$. 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. Therefore, the following equation holds:

$$\frac{[B]_0}{A - \epsilon_0 [B]_0} = \frac{1}{(\epsilon - \epsilon_0)K} \cdot \frac{1}{[D]_0} + \frac{1}{\epsilon - \epsilon_0} \quad (2)$$

Where A denotes the absorbancy ϵ and ϵ_0 molar absorptivities of the complexes and the free halogens at the wave length corresponding to the absorption maxima of the complexes, respectively, and K the equilibrium constant. formula (2) is obviously of the type $y = mx + b$. The values of the equilibrium constant K and the absorption coefficient ϵ 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 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 $(\epsilon - \epsilon_0) \cdot K$ and $\epsilon - \epsilon_0$, the values of K and ϵ 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 tem-

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

$10^3 I_2$, mole $\cdot l^{-1}$	Temp ($^\circ\text{C}$)								
	25			40			60		
	Wave length (m μ)	Absor- bancy(A)	Molar absorp- tivity (ϵ)	Wave length (m μ)	Absor- bancy(A)	Molar absorp- tivity (ϵ)	Wave length (m μ)	Absor- bancy(A)	Molar absorp- tivity (ϵ)
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	0.183	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	0.328	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 $C_6H_6I_2$ in Carbon Tetrachloride at Several Temperatures

C_6H_6 , mole·l ⁻¹ [D] ₀	I_2 , mole·l ⁻¹ [B] ₀	Temp. (°C)					
		25		40		60	
		Absorbancy at 293 mμ (A)	Y, 10 ⁴ mole·l ⁻¹	Absorbancy at 292 mμ (A)	Y, 10 ⁴ mole·l ⁻¹	Absorbancy at 290 mμ (A)	Y, 10 ⁴ mole·l ⁻¹
0.250	3.34	0.211	17.1	0.187	19.5	0.165	22.3
	5.02	0.319	17.0	0.284	19.3	0.245	22.6
	6.67	0.424	17.0	0.374	19.5	0.330	22.3
			Av. 17.0		Av. 19.4		Av. 22.4
0.375	3.34	0.306	11.5	0.272	13.0	0.230	15.5
	5.02	0.457	11.6	0.407	13.1	0.345	15.6
	6.67	0.605	11.7	0.536	13.2	0.469	15.2
			Av. 11.6		Av. 13.1		Av. 15.4
0.500	3.34	0.394	8.83	0.343	10.2	0.305	11.5
	5.02	0.590	8.87	0.511	10.3	0.448	11.8
	6.67	0.786	8.85	0.688	10.2	0.600	11.7
			Av. 8.85		Av. 10.2		Av. 11.7
0.625	3.34	0.481	7.17	0.421	8.23	0.363	9.60
	5.02	0.731	7.11	0.635	8.21	0.547	9.57
	6.67	0.950	7.13	0.843	8.23	0.724	9.61
			Av. 7.14		Av. 8.22		Av. 9.59

TABLE 3: Formation of $C_6H_5CH_3I_2$ in Carbon Tetrachloride at Several Temperatures

$C_6H_5CH_3$, mole·l ⁻¹ [D] ₀	I_2 , mole·l ⁻¹ [B] ₀	Temp. (°C)					
		25		40		60	
		A, at 301 mμ	Y, 10 ⁴ mole·l ⁻¹	A, at 301 mμ	Y, 10 ⁴ mole·l ⁻¹	A, at 300 mμ	Y, 10 ⁴ mole·l ⁻¹
0.224	3.34	0.210	16.9	0.180	19.9	0.155	23.3
	5.02	0.316	16.9	0.276	19.5	0.236	23.1
	6.67	0.415	17.2	0.367	19.5	0.312	23.2
			Av. 17.0		Av. 19.6		Av. 23.2
0.366	3.34	0.295	11.8	0.255	13.8	0.221	16.0
	5.02	0.452	11.6	0.394	13.4	0.338	15.7
	6.67	0.596	11.7	0.516	13.6	0.430	16.4
			Av. 11.7		Av. 13.6		Av. 16.0
0.443	3.34	0.380	9.09	0.330	10.5	0.280	12.5
	5.02	0.573	9.08	0.502	10.4	0.423	12.4
	6.67	0.760	9.09	0.661	10.5	0.550	12.7
			Av. 9.09		Av. 10.5		Av. 12.5
0.588	3.34	0.509	6.72	0.451	7.84	0.373	9.26
	5.02	0.764	6.74	0.640	7.85	0.562	9.24
	6.67	1.018	6.73	0.879	7.82	0.746	9.26
			Av. 6.73		Av. 7.84		Av. 9.25

perature. Thus, the each value of ϵ_0 (value is derived through experiment; Table 1) and of A (Tables 2–5) in equation 2 is equivalent to the corresponding values which are given in the presence of wave length of absorption maxima of CT-complexes determined by the temperature shift.

Since linearities were observed between y and x experimentally, it can be concluded that the assumption of the formation of one to one complexes should be correct.

The Monoalkylbenzene-Iodine CT-Complexes Formation. To illustrate the linear relationship between y and x , one example has been chosen (benzene-iodine CT-complex) and is shown in Figure 1. The K values obtained with the aid

of equation (2) are listed in Table 6.

We shall now compare our results with those reported by Hildebrand, Tamres, Andrews and coworkers^{1,2,10}. The values they obtained of the equilibrium constants were 1.72 (K_x), 1.60 (K_x) and 0.15 (K_x) for the complex and for benzene-iodine in carbon tetrachloride, respectively.

Andrews and Keefer observed a value of 0.16 (K_x) for the toluene-iodine complex in carbon tetrachloride.

Hence, the K values of the benzene- and toluene-iodine complexes given in Table 6, as examples of monoalkylbenzene-iodine complexes, show that we got almost the same results as those obtained by the above authors.

TABLE 4: Formation of $C_6H_5C_2H_5 \cdot I_2$ in Carbon Tetrachloride at Several Temperatures

$C_6H_5C_2H_5$, 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
0.309	3.34	0.272	12.9	0.236	14.9	0.195	18.2
	5.02	0.405	13.0	0.355	14.9	0.303	17.6
	6.67	0.546	12.8	0.474	14.8	0.394	18.0
			Av. 12.9		Av. 14.9		Av. 17.9
0.455	3.34	0.378	9.12	0.330	10.5	0.275	12.7
	5.02	0.568	9.14	0.501	10.4	0.416	12.6
	6.67	0.758	9.10	0.661	10.5	0.552	12.6
			Av. 9.12		Av. 10.5		Av. 12.6
0.583	3.34	0.473	7.25	0.412	8.35	0.345	10.0
	5.02	0.713	7.23	0.625	8.28	0.515	10.1
	6.67	0.943	7.27	0.831	8.25	0.690	10.0
			Av. 7.25		Av. 8.29		Av. 10.0
0.710	3.34	0.571	5.98	0.494	6.93	0.417	8.24
	5.02	0.859	5.98	0.746	6.90	0.626	8.26
	6.67	1.137	6.00	0.992	6.90	0.831	8.26
			Av. 5.99		Av. 6.91		Av. 8.25

TABLE 5: Formation of $n-C_6H_5C_3H_7 \cdot I_2$ in Carbon Tetrachloride at Several Temperatures

$n-C_6H_5C_3H_7$, mole l [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 302 mμ	Y, 10 ⁴ mole·l ⁻¹
0.269	3.34	0.235	15.0	0.206	17.2	0.148	21.0
	5.02	0.356	14.9	0.312	17.1	0.260	20.7
	6.67	0.468	15.1	0.401	17.7	0.339	21.1
			Av. 15.0		Av. 17.3		Av. 20.9
0.386	3.34	0.322	10.8	0.284	12.3	0.235	14.9
	5.02	0.484	10.8	0.423	12.4	0.357	14.8
	6.67	0.650	10.7	0.556	12.6	0.465	15.1
			Av. 10.8		Av. 12.4		Av. 14.9
0.512	3.34	0.417	8.25	0.361	9.56	0.302	11.5
	5.02	0.622	8.32	0.520	9.52	0.458	11.4
	6.67	0.829	8.30	0.727	9.50	0.605	11.5
			Av. 8.29		Av. 9.53		Av. 11.5
0.637	3.34	0.501	6.83	0.438	7.83	0.370	9.31
	5.02	0.754	6.83	0.657	7.86	0.554	9.36
	6.67	1.011	6.77	0.874	7.86	0.736	9.36
			Av. 6.81		Av. 7.85		Av. 9.34

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 Table 6, the K values can be ordered according to the increase in the number of alkyl substituents to yield the following series: benzene- < methyl- < ethyl- < *n*-propyl-benzene.

As a result, 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 Bartlett¹¹ have given interesting

comments on the problems which show up when basing theoretical work on a series of measurements reflecting the result of these effects¹².

The above analysis yields almost the same order of K values as found by Brown and Brady¹³ 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

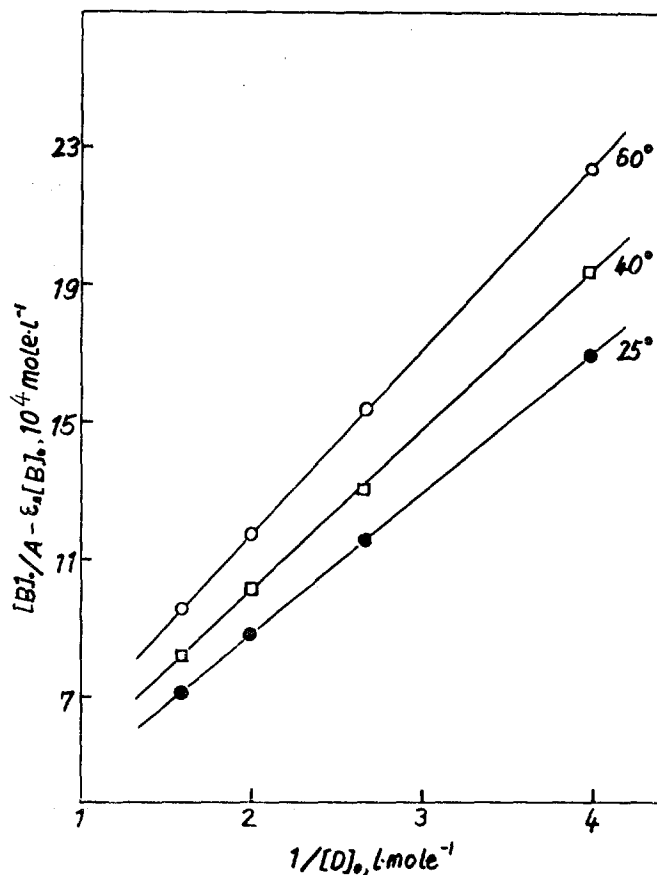


Figure 1. Plot of $[B]_0/A - \epsilon_0[B]_0$ versus $1/[D]_0$ of the benzene-iodine system at several temperatures.

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

Alkylbenzene	λ_{\max} m μ	$\epsilon \times 10^{-3}$	K_c l·mole ⁻¹
Benzene	293	16.2	0.151
Toluene	302	16.4	0.165
Ethylbenzene	303	13.6	0.196
n-Propylbenzene	303	11.6	0.226

monoalkylbenzene-iodine complexes at 25°C have been plotted against the number of alkyl donor substituents (see Figure 2). Most of the data, when so plotted, conform reasonably well to a straight line. Marked deviations from linearity, which may be associated with the structures, are not observed generally.

Heat of CT-Complex Formation

Heat of CT-Complex Formation. The heats of formation for complexes were calculated from spectrophotometric data taken at three different temperatures as described in the Experimental section. The ratios of equilibrium constants at two different temperatures which were required to calculate ΔH values were obtained from the ratios of slopes of plots of the data according to equation 2 at the temperatures T_1 and T_2 by using equation 3.

$$2.303 \log \frac{(\text{slope}) T_1}{(\text{slope}) T_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

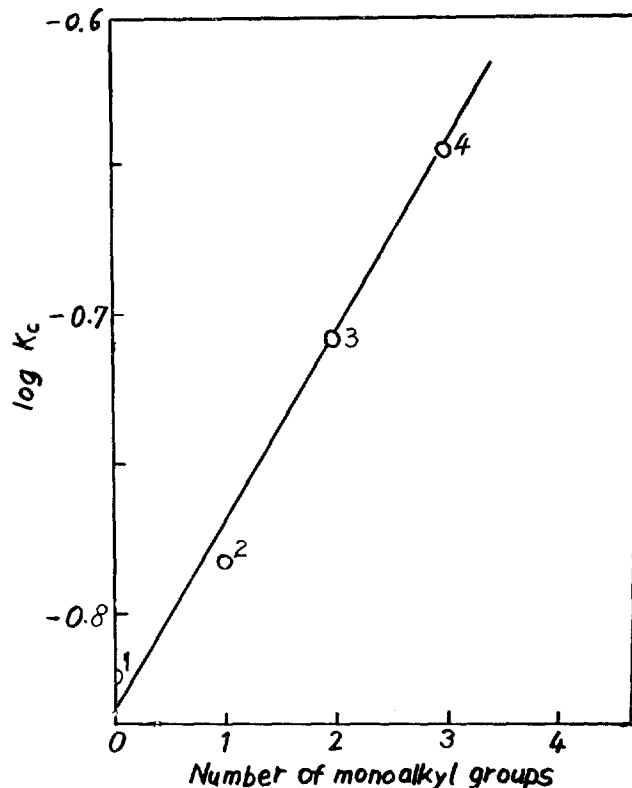


Figure 2. Plot of $\log K_c$ versus the number of monoalkyl substituents on the donor ring for monoalkylbenzene-iodine complexes at 25°C. Donors: 1; benzene, 2; toluene, 3; ethylbenzene, 4; n-propylbenzene.

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

Alkylbenzene	$-\Delta H$ 25, 40°	$-\Delta H$ 40, 60°	$-\Delta H$ av.	$-\Delta G$ 25°	$-\Delta S$ 25°
Benzene	1.52	1.48	1.50	0.267	4.13
Toluene	1.69	1.74	1.72	0.318	4.69
Ethylbenzene	1.82	1.93	1.87	0.420	4.88
n-Propylbenzene	2.06	2.05	2.06	0.504	5.20

^a ΔH ΔG in kcal·mole⁻¹ ΔS in cal·mole⁻¹ deg⁻¹.

For each complex values of ΔH were evaluated by this analysis 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 the two temperatures, $\Delta H_{25,40^\circ}$ and $\Delta H_{40,60^\circ}$ are summarized in Table 7. The heat of formation is expressed in mole fractions.

The values for ΔG and ΔS which are given in Table 7 have been evaluated from the reported values of ΔH and from the equilibrium constants, K_{25° . The values of ΔG , ΔH , ΔS which could be regarded as values of complex formation at 25°C, are given in Table 7. The value of benzene-iodine complex in Table 7 is almost similar to the results of previous authors³.

The ΔH values of Table 7 should differ by approximately 200 cal from those derived from equilibrium constants which are based on molar concentrations of the donors¹⁴. As shown in Table 7, decreases in ΔH of formation of iodine-monoalkylbenzene complexes with changes in donor substituents are accompanied by parallel decreases in ΔG

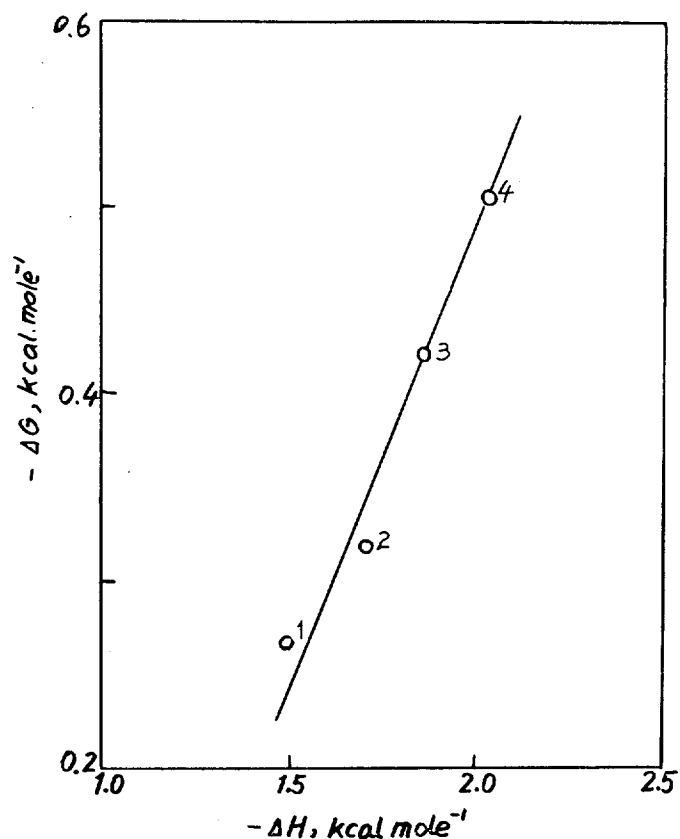


Figure 3. Plot of $-\Delta G$ versus $-\Delta H$ for monoalkylbenzene-iodine complexes at 25°C. Donors: 1; benzene, 2; toluene, 3; ethylbenzene, 4; *n*-propylbenzene.

and ΔS of the interactions. Indeed the thermodynamic data in this study conform well to the linear plots of ΔH versus ΔG and ΔH versus ΔS for iodine-substituted polyalkylbenzene complexes³ (see Figure 3 and 4).

The observed variations in ΔH with ΔG for iodine-monoalkylbenzene complexes are linear. This can only be true either if ΔS is invariant with changes in donor structure or, as is actually the case, ΔS also varies in linear fashion with ΔH . In other words, barring unusual steric effects in donor molecules, one can in the present instance measure the effects of alkyl substitution on the tendency for complex formation equally well in terms of variations in ΔG , ΔH or ΔS .

It is particularly interesting that as ΔH values become more negative, corresponding decreases in ΔS are observed. The simultaneous decrease in these terms may serve as an indication of the physical restraints imposed upon the complex components as the strength of the bond between them increases.

C. van de Stolpe⁶ reports values for ΔS_{25° of formation of a number of such iodine complexes which are all of the order of magnitude of 4 to 5 e.u. It is apparent from the data of Table 7 that the ΔS values for iodine complex formation of monoalkylbenzenes show a definite downward trend with an increase in the number of alkyl substituents on the aromatic nucleus. In all cases both ΔH and ΔS terms have appreciable influence on the magnitude of ΔG for complex formation. The changes in ΔG with increasing alkyl group of the benzene ring are consistent with anticipated electronic influences^{15,16} of alkyl substituents on the π -electron density of the donor nucleus.

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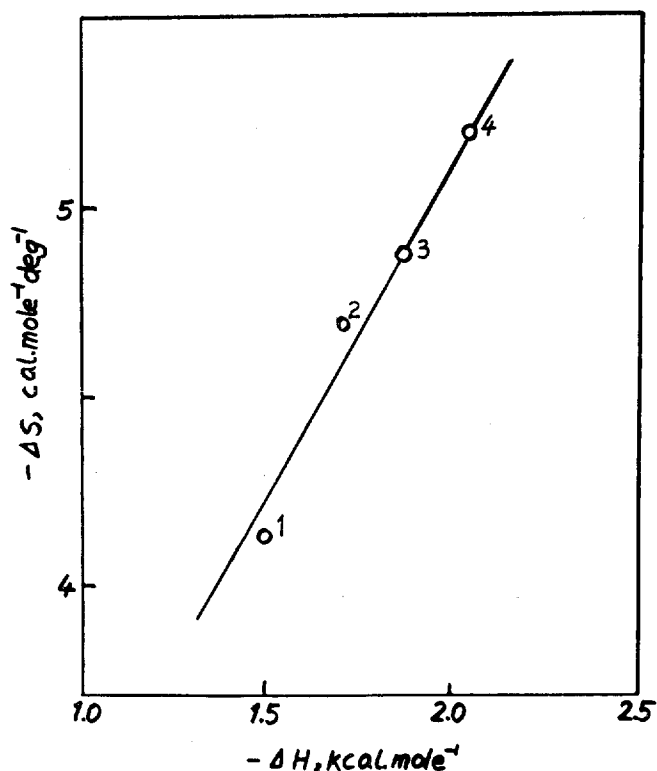


Figure 4. Plot of $-\Delta S$ versus $-\Delta H$ for monoalkylbenzene-iodine complexes at 25°C. Donors: 1; benzene, 2; toluene, 3; ethylbenzene, 4; *n*-propylbenzene.

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Photocyclization of 1,2-Bispyrazylethylene and 2-Styrylpyrazine

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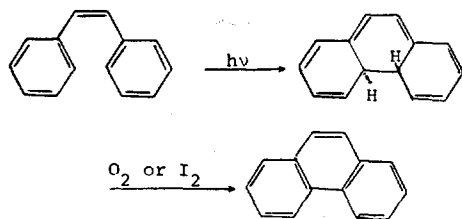
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1,4,5,8-Tetraazaphenanthrene, a new tetraazaheteroaromatic compound, has been synthesized photochemically in 90% yield and quantum yield of 5.1×10^{-2} from dilute benzene solutions of 1,2-bispyrazyl ethylene (BPE) in the presence of oxygen as an oxidant. Iodine was not appropriate oxidant because of strong complexing with BPE and also enhanced intersystem crossing of BPE and thereby decreasing the photocyclization of BPE. Salt effect, solvent effect, and quenching and sensitization studies on the photocyclization of BPE have shown that $^1(n, \pi^*)$ is the reactive state for the cyclization in comparison to $^1(\pi, \pi^*)$ state for the ordinary stilbene derivatives.

Introduction

The oxidative photodehydrocyclization of stilbenes, substituted stilbenes, other 1,2-diaryl-substituted ethylenes generally proceeds by the partial steps of conrotatory ring closure as predicted by the Woodward-Hoffmann rule for a concerted photocyclization of 1,3,5-hexatrienes in the S_1 state followed by oxidation of thus formed dihydrophenanthrenes. For the cyclization to occur, the sum of the free valence indices ($\sum F^*$) for the first excited state at atoms between which the new bond is formed must be greater than unity. This elegant method has proved to be the efficient method to synthesize phenanthrenes and over 100 phenanthrenes have been synthesized by this method¹⁻⁹.



This type of photodehydrocyclization reaction has also been extensively used for the synthesis of chrysene derivatives and has proved to be the best method for the synthesis of helicenes¹⁰. The synthesis of azaphenanthrenes by classical methods is very difficult and most of the time failed⁷. The synthesis of 1,4,5,8-tetraazaphenanthrene, a new tetraazaheteroaromatic compound, is attempted by the oxidative photocyclization of 1,2-bispyrazylethylene (BPE), one of the nitrogen containing stilbene analogues.

In BPE, $^1(n, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state and consequently extensive mixing between these two states results obscuring $n-\pi^*$ band¹¹. Because of the (n, π^*) excited states, BPE shows quite different photoche-

mical behavior from the ordinary stilbenes such as photoreduction¹² and photoaddition to tetramethylethylene¹³ through the $^1(n, \pi^*)$ states. Thus, the mechanism of the photocyclization reaction is also expected to be different from that of the stilbenes and the subject will be investigated along with the photocyclization of 2-styrylpyrazine.

Experimental

Materials. All the solvents such as benzene, cyclohexane, ethanol, *t*-butanol, and acetonitrile were purified immediately prior to use by the known standard methods¹⁴. Benzophenone (Merck) was recrystallized three times from cyclohexane (m.p. 46°C). Azulene (Aldrich) was sublimed under vacuum immediately prior to use. Naphthalene (Aldrich) was recrystallized and sublimed under vacuum. Sodium acetate (Wako E.P. Grade) was recrystallized twice from water-ethanol (1:4 v/v) mixed solvent. *Trans*-BPE and *cis*-BPE were synthesized by the method reported¹¹. *Trans*-styrylpyrazine (STP)¹⁵ and *cis*-STP⁸ were synthesized as reported.

Spectra. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane internal standard in deuteriochloroform (BPE) and carbon tetrachloride (STP). Chemical shifts are reported as δ values. Infrared spectra were obtained on a Perkin-Elmer Model 267 spectrophotometer in KBr pellets. UV-VIS spectra were recorded on a Cary 17 spectrophotometer. The mass spectra were obtained at 30 eV on a Hitachi RMU-7M mass spectrometer. Elemental analysis was carried out at the Korea Institute of Science and Technology, Seoul, Korea. Gas chromatograms were obtained on a Varian 2800 series gas chromatograph using FID detector and 6% OV-17 on Chromosorb W packing material in a 6 ft \times 1/8 in copper column.