Charge-transfer interaction of some aromatic hydrocarbons with chloranil

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The interaction of different substituted naphthalenes with chloranil has been studied spectrophotometrically in chloroform. Symmetrically substituted naphthalenes give one new absorption band while the unsymmetrically substituted naphthalenes show two new absorption bands. The formation constants for the charge-transfer complexes have been determined using Benesi-Hildebrand's method. Linear plots for $h\nu$ against ionization potential of the donors have been obtained.

Observation of two charge-transfer absorption bands in π-π^* complexes having substituted benzenes as the donor component was explained by Orgel[1] in terms of the possibility of the transferred electron coming from either of the two levels arising when the degeneracy of the E_1 level of benzene is removed by substitution. Orgel used a simple first order perturbation calculation to evaluate both the shift in position of the CT absorption from that found in the complex of benzene with a given acceptor and the splitting resulting from substitution of the benzenoid donor in various possible ways. Later, many other workers[2-4] studied the charge-transfer spectra of systems containing substituted benzenes. Recently, Dwivedi and Agarwal[5] studied the charge-transfer spectra of a number of hydrocarbons with chloranil and DDQ and have located multiple charge-transfer band only in the case of pyrene. In order to see whether these types of multiple charge-transfer bands appear in other higher hydrocarbons, e.g., naphthalene, we have carried out studies on a number of substituted naphthalenes.

Considering also that for stable π-π^* complexes the most stable configurations have been shown to be those where donors and acceptors lie above each other with their molecular planes more or less parallel, we have chosen chloranil as acceptor which is known to form a good π-π^* complex with its molecular plane being parallel to that of the donors.

Experimental

The hydrocarbons used were 1, 2, 4, 5-tetra methylbenzene (BDH), 2-methylnaphthalene, 2, 3-dimethylnaphthalene, 2, 6-dimethylnaphthalene, 1, 3-dimethylnaphthalene (Koch Light Laboratories), 1, 2, 3-trimethylbenzene, and 1-methylnaphthalene (Fluka). These were used as such. The solvent chloroform was procured from S.D. Chemicals (Bombay). The solvent was thoroughly dried and distilled just before use. Chloranil was an E. Merck reagent and used after several recrystallizations. Finally, its purity was checked on the basis of its melting point.

The spectral data were taken on a Cary 2390 spectrophotometer at $25 \pm 1°C$ using 1 cm matched silica cells.

In locating the position of a characteristic absorption maximum, a solution of the donor and the acceptor (chloranil) in chloroform was balanced against a solution of chloranil of the same strength, as the hydrocarbons do not absorb in the region being studied. The concentration ratio of the donor to acceptor was nearly 100:1. The donors were used at a
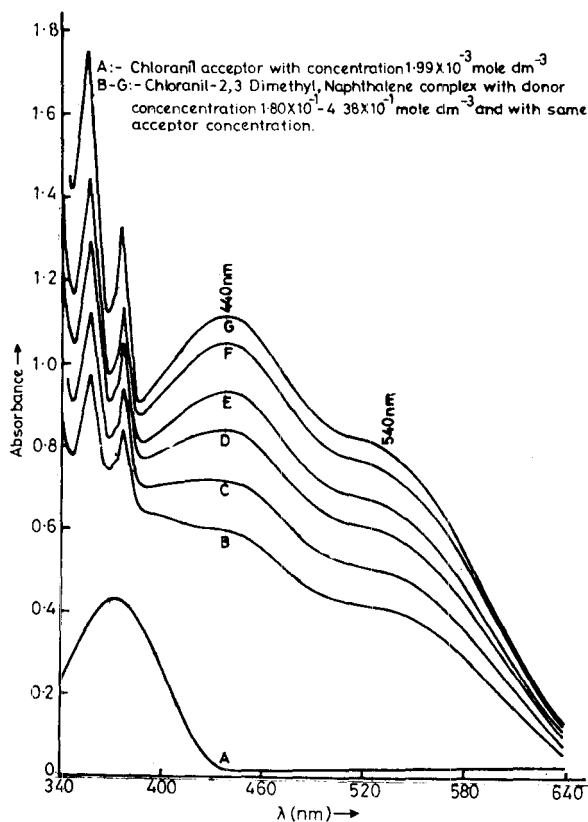

Fig. 1—Spectra of chloranil and chloranil-2, 3-dimethyl-naphthalene complex

concentration of 10^{-1} mol dm^{-3} and chloranil (acceptor) at a concentration of 10^{-3} mol dm^{-3}.

The formation constants (K) and molar extinction coefficients (ε) of complexes of different donors with chloranil were calculated by the Benesi-Hildebrand[6], Scott[7] and Rose-Drago[8] methods. The Benesi-Hildebrand plots for methylbenzene-chloranil mixture and of the other donor-chloranil mixtures in chloroform were linear indicating the formation of 1:1 molecular complexes. Moreover, the absorbance

Table 1—The formation constant and molar extinction coefficient data for charge-transfer complexes

Donor	$v-$ (cm^{-1}) $\times 10^{-4}$	hv (eV)	[Acceptor] (mol dm^{-3}) $\times 10^3$	K (dm^3 mol^{-1}) $\times 10\ddagger$			I.P. (eV)
				[6]B.H. method	[7]Scott method	[8]Rose & Drago method	
1,2,3-Trimethylbenzene	2.38	2.95	2.85	3.95	5.26	11.8±0.3	8.49[a]
			1.42	(1.81)	(1.53)	(1.13)	
				3.96	4.20		
				(3.03)	(2.93)		
1,2,4,5-Tetramethylbenzene	2.08	2.58	0.46	8.66	6.22	7.4±0.2	8.53[b]
			0.93	(3.33)	(4.19)	(3.2)	
			1.39	8.81	7.40		
				(2.85)	(3.13)		
				7.25	6.70		
				(3.33)	(3.52)		
1-Methylnaphthalene	1.92	2.38	2.30	3.94	4.97	5±0.1	8.41[a]
				(1.19)	(1.06)	(1.02)	
			0.87	4.0	4.12		
				(1.66)	(1.62)		
2-Methylnaphthalene	1.98	2.46	0.94	8.16	9.6	8.7±0.3	8.48[a]
			1.41	(1.0)	(0.87)	(0.95)	
			2.08	10.66	—		
				(0.8)	—		
				6.66	5.66		
				(1.33)	(1.40)		
2,3-Dimethylnaphthalene	1.85	2.29	1.33	13.5	10.89	10.7±0.7	8.11[c]
	2.27	2.81	1.99	(1.53)	(1.70)	(1.65)	
				11.12	7.89		
				(1.66)	(1.53)	6.60±0.05	
				11.65	11.30	(2.02)	
				(1.17)	(1.73)		
				9.29	10.95		
				(1.33)	(1.22)		
2,6-Dimethylnaphthalene	1.86	2.31	1.65	18.39	16.65	—	—
				(0.85)	(0.94)		
1,3-Dimethylnaphthalene	1.81	2.25	3.31	46.7	35.65	—	—
	2.32	2.88	2.25	(0.39)	(0.48)		
				32.30	32.30		
				(0.42)	(0.46)		
				35.7	28.61		
				(0.47)	(0.53)		
				39.7	21.64		
				(0.35)	(0.59)		

[a] Streitwieser Andrew, *J Am chem Soc*, 82 (1960) 4123.
[b] Franklin J L, *J chem Phys*, 22 (1954) 1304.
[c] Slifkin M A & Allison A C, *Nature*, 215 (1967) 949.
‡ Values in parentheses are ε values in dm^{3}mol^{-1}cm^{-1} $\times 10^{-3}$

versus mole fraction plot for the systems gave a further proof of the 1:1 nature of the molecular complex.

Fig. 1 shows the absorption spectra of chloranil and chloranil plus 2,3-dimethylnaphthalene in chloroform. While chloranil has the absorption maximum at 375 nm, the chloranil-hydrocarbon mixture shows two peaks at 540 and 440 nm. As the hydrocarbon concentration is increased at a fixed chloranil concentration, the absorbance at both the bands increases. Evidently, the red shifted bands at 540 and 440 nm arise from a molecular complex formed between chloranil and the hydrocarbon. Table 1 shows the wave number of charge-transfer band (v, cm^{-1}), the formation constant (K, dm^{3}mol^{-1}) and the molar extinction coefficients (ε, dm^3 mol^{-1}cm^{-1}) of the complexes of the different donors with chloranil in chloroform as obtained by the three methods. Linear regression was carried out in the final stage of the computation. The points ([A]/absorbance) which were off by $\pm 0.1 \times 10^{-4}$ from the perfect linear curve were omitted in the linear regression calculations.

As is evident from Table 1, all the substituted benzenes and naphthalenes show a red-shifted band with respect to the donors and acceptors which is present neither in the donors nor in the acceptors. The hv values of the red shifted bands when plotted against the ionization potentials of the respective donors gave a straight line. Accordingly, we may conclude that the complexes produced are of charge-transfer type. Moreover, among the donors, 2,3-dimethylnaphthalene and 1,3-dimethyl-naphthalene show two charge-transfer bands. Orgel's idea of all substituted benzenes showing two charge-transfer bands is not corroborated in the case of naphthalene. According to Orgel, visible bands of chloranil complexes with alkylbenzenes are generally composite consisting of two overlapping charge-transfer bands. We, however, could not distinguish two overlapping bands (Table 1) with the resolution available with Cary 2390 instrument. The appearance of two charge-transfer bands in the cases of 2,3-dimethyl- and 1,3-dimethylnaphthalenes may be due to the loss of symmetry of the π-electronic structure of the naphthalene molecule by unsymmetrical substitution. The formation constants, and extinction coefficients calculated by three different methods as shown in Table 1 are more or less same. The high values of the extinction coefficients indicate that the complexes formed are quite stable in nature.

Acknowledgement

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