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Ground state dipole moment of the charge transfer complexes of some aromatic hydrocarbons with chloranil from solvent shift data

Nupur Aditya & Rama Basu*
Department of Chemistry, University College of Science,
92 A P C Road, Calcutta 700 009

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The ground state dipole moment of charge transfer complexes of chloranil with aromatic hydrocarbons has been calculated as a linear function of solvent shift. Very close values of μ_1 and μ_2 for multiple charge transfer bands indicate that orientation is not playing a major role. The weak nature of the complexes is manifested by the oscillator strength values. Nevertheless lower energy transition shows a greater overlap.

The appearance of multiple charge transfer bands in substituted benzenes might be due to the removal of the degeneracy of the $^2E_{1g}$ ground state of the benzene positive ion by suitably arranged substituents[1], so that two ionization potentials I_1 and I_2 exist in place of one giving rise to two charge-transfer bands or due to the presence of different orientational isomers[2]. If the appearance of multiple charge transfer bands were due to different orientational isomers the dipole moments as derived from solvent effect on different charge transfer bands would also be different. In order to find the effect of solvents on the multiple charge-transfer bands we have carried out spectrophotometric experiments on charge transfer complexes of some substituted naphthalenes and benzenes with chloranil in a number of solvents of different dielectric constants. In a previous communication[3] we have already shown that only the unsymmetrically substituted naphthalenes show two charge transfer bands in chloroform solvent.

Experimental

The hydrocarbons, namely, 1-methylnaphthalene, 1,2,3-trimethylbenzene (Fluka), 2-methylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1,3-dimethylnaphthalene, hexamethylbenzene (Koch Light) and 1,2,4,5-tetramethylbenzene (BDH) were used as such. The solvents *n*-heptane ($\varepsilon = 1.95$), chloroform ($\varepsilon = 4.8$), dichloroethane ($\varepsilon = 10.3$) and acetonitrile ($\varepsilon = 37.6$) (S.D. Chemicals) were thoroughly dried and distilled just before use. Chloranil (E. Merck) was used after several recrystallisations from chloroform and finally checking its melting point.

Cary 2390 spectrophotometer with 1 cm matched silica cells was used at 25 ± 1°C, for spectral data.

Two charge transfer bands could be isolated only when the position of the characteristic absorption maximum was located by balancing a solution of the donor and the acceptor in the particular solvent against a solution of the acceptor (chloranil) of the same strength in the same solvent. The concentration ratio of the donor to acceptor was usually 100:1. The donors were used at a concentration of 10^{-1} mol dm^{-3} and chloranil at a concentration of 10^{-3} mol dm^{-3} except in *n*-heptane (10^{-6} mol dm^{-3}), because of low solubility of chloranil in such solvent.

Results and discussion

Following Onsager[4] model and utilising the reaction field idea, the ground state dipole moment of a charge-transfer complex can be expressed according to Basu[5] as a linear function of solvent shift of the particular charge-transfer absorption maxima as

$$h\nu_{(\mathrm{gas})} - h\nu_{(\mathrm{soln})} = \frac{1}{a^3}\left(\frac{2n_0^2+1}{n_0^2+2}\right)^2\left[2\mu_g(\mu_g-\mu_e)\times\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n_0^2-1}{n_0^2+2}\right)+\left(\frac{n_0^2-1}{n_0^2+2}\right)\left(\mu_g^2-\mu_e^2\right)\right]$$

where ε and n_0 are the dielectric constant and refractive index of the respective solvent and a is Onsager cavity radius equal to 3.2 Å. From this relationship we can estimate μ_g and μ_e (ground and excited state dipole moments) of the particular charge transfer complex. The respective data are shown in Table 1. As is evident from the data in Table 1 μ_1 and μ_2 calculated for two charge-transfer bands (where these can be isolated) do not differ very much from each other. We have shown earlier[6] that although electrostatic contribution is greater in highly polar solvents, charge-transfer force is the predominating one in nonpolar solvents. The close values of two dipole moments calculated for two charge transfer bands also indicate the complexes to be of more charge-transfer type. Again, μ_1 and μ_2 being very close we may consider that orientation is not playing a major role here. Although the concept of reaction field is possibly free from any objection, the continuum model for the dielectric is open to criticism simply because it does not take into account the solvent structure and describes the solvent by a single parameter ε. Considering these the data may not be fully quantitative.

The intensity of a charge-transfer band is determined by the stability of the complex and the extent of the overlap between the donor and acceptor orbitals. Since resonance energy of charge-transfer complex is directly proportional to its oscillator strength, the oscillator strength calculation would give us some idea about the stability of the complex. The absolute value of the oscillator strength is determined primarily by the extent of overlap[7]. In the quantum theory, the oscillator strength[8] of an absorption band depends upon the absorption frequency ν and the electronic transition moment length Q. The transition moment length is a measure of the mean displacement of the promoted electron during transition. The molar absorptivity or extinction co-efficient ε_ν of any

Table 1—Ground and excited state dipole moment of charge-transfer complexes of chloranil (acceptor)

Donor	Solvent	ε	n_c	$(h\nu_{soln})_1$ eV	$(h\nu_{soln})_2$ eV	$(\mu_g)_1$ (D)	$(\mu_g)_2$ (D)	$(\mu_e)_1$ (D)	$(\mu_e)_2$ (D)	$(h\nu_{gas})_1$ eV	$(h\nu_{gas})_2$ eV
1,2,4,5-Tetramethylbenzene	*n*-Heptane	1.95	1.3870	2.60	—	0.20	—	5.06	—	2.88	—
	Chloroform	4.80	1.4445	2.58	—						
	Dichloroethane	10.65	1.4438	2.60	—						
1,2,3-Trimethylbenzene	*n*-Heptane	1.95	1.3870	2.88	—		—				
	Chloroform	4.80	1.4445	2.95	—	1.13	—	13.49	—	4.86	—
	Dichloroethane	10.65	1.4438	3.26	—						
Hexamethylbenzene	*n*-Heptane	1.95	1.3870	2.38	—						
	Chloroform	4.80	1.4445	2.40	—	0.003	—	3.41	—	2.26	—
	Dichloroethane	10.65	1.4438	2.40	—						
1-Methylnaphthalene	*n*-Heptane	1.95	1.3870	2.52	3.19						
	Chloroform	4.80	1.4445	2.38	3.10	0.22	0.18	9.93	8.28	3.60	3.94
	Dichloroethane	10.65	1.4438	2.43	3.13						
2-Methylnaphthalene	*n*-Heptane	1.95	1.3870	2.54	—						
	Chloroform	4.80	1.4445	2.46	—	0.28	—	8.44	—	3.32	—
	Dichloroethane	10.65	1.4438	2.51	—						
2,3-Dimethylnaphthalene	*n*-Heptane	1.95	1.3870	2.48	2.93						
	Chloroform	4.80	1.4445	2.29	2.82	0.36	0.58	7.46	4.94	3.09	3.20
	Dichloroethane	10.65	1.4438	2.24	2.76						
1,3-Dimethylnaphthalene	*n*-Heptane	1.95	1.3870	2.36	3.07						
	Chloroform	4.80	1.4445	2.25	2.88	0.06	0.01	7.04	5.76	2.91	2.70
	Acetonitrile	36.5	1.3393	2.42	3.01						

Table 2—The oscillator strength (f) and transition dipole (D) of the charge-transfer band of chloranil (acceptor)

Donor	*n*-Heptane			Chloroform			Dichloroethane			Acetonitrile		
	λ_{max} (nm)	f	D	λ_{max} (nm)	f	D	λ_{max} (nm)	f	D	λ_{max} (nm)	f	D
1,2,4,5-Tetramethylbenzene	476	1.8782	13.3214	480	0.0473	2.1848	476	0.0163	1.2873	460	0.0098	0.9796
Hexamethylbenzene	520	2.2291	14.9238	515	0.0103	1.0560	515	0.0138	1.1457	496	0.0048	0.7098
1,2,3-Trimethylbenzene	430	0.1793	4.0245	420	0.0183	1.2752	380	0.0034	0.5569	410	0.0085	0.8578
1-Methylnaphthalene	492	0.7376	8.7889	520	0.0102	1.0590	510	0.0027	0.5344	488	0.0042	0.6640
	388	0.0729	2.4209	400	0.0017	0.3844	396	0.0009	0.2743	388	0.0004	0.1914
2-Methylnaphthalene	489	2.2146	15.1426	504	0.0047	0.7043	494	0.0032	0.5554	488	0.0032	0.5725
				420	0.0004	0.1957	416	0.0003	0.1729	408	0.0003	0.1499
1,3-Dimethylnaphthalene	524	0.2352	5.0568	550	0.0023	0.5136	—	—	—	512	0.0018	0.4409
	404	0.0679	2.3740	430	0.0009	0.294				412	0.0008	0.2594
2,3-Dimethylnaphthalene	500	3.0823	18.0372	540	0.0084	0.9643	552	0.0099	1.0460	520	0.0032	0.5734
	422	0.5648	7.0859	440	0.0024	0.4775	448	0.0019	0.4206	432	0.0007	0.2445
2,6-Dimethylnaphthalene	—	—	—	536	0.0023	0.5092	—	—	—	—	—	—

molecular species is defined by Beer's law

$$I_\nu = I_\nu^0\, 10^{-\varepsilon_\nu Cl}$$

where C is the concentration in moles per litre, 1 is the path length in centimeters and I_ν and I°_ν are the intensities of the transmitted and incident light of frequency ν. The oscillator strength is related to the magnitude of the theoretical electronic transition dipole D in e.s.u. cm by

$$f = \left(\frac{8\pi^2 mc}{3h}\right) \nu \frac{D}{e^2}$$

$$D = 0.0958 \left[\frac{\varepsilon_{\max}\ \nu_{1/2}}{\bar{\nu}}\right]^{1/2}$$

where $\bar{\nu}$ is the average wave number in cm^{-1}.

The oscillator strength and the transition dipoles are calculated for each peak position and the results are given in Table 2.

The oscillator strengths of all the complexes are very low except in *n*-heptane solvent (Table 2) meaning that the complexes are weak in other solvents. However, whenever two charge-transfer bands arise, the band with lower energy shows higher oscillator strength and higher transition dipole indicating a greater overlap at the lower energy region.

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