

## Relative contribution of charge-transfer and electrostatic force in donor-acceptor complexes of $\pi$ - $\pi^*$ type

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The analysis of the relative contribution of charge-transfer and electrostatic forces in the formation of molecular complexes of different substituted naphthalenes with chloranil ( $\pi$ - $\pi^*$  complexes) shows that in nonpolar solvents, the charge-transfer force plays the dominant part. In polar solvents, however, the electrostatic force does have an important contribution.

The controversy about how much is the electrostatic contribution to the no-bond structure in the ground state wave function of Mulliken's<sup>1</sup> model of charge-transfer complexes still persists. According to Mulliken the ground state wave function for a donor-acceptor complex may be represented by Eq. (1)

$$\psi_G = a\phi_0(D,A) + b\phi_1(D^+ - A^-) \quad \dots (1)$$

where  $\phi_0$  represents a no-bond structure and  $\phi_1$  represents a dative structure in which an electron has been transferred from the donor to the acceptor molecule. While Dewar<sup>2</sup> for the complexes of tetracyanoethylene with different hydrocarbons and Arnaud and Bonnier<sup>3</sup> for the complexes of tetracyanoethylene with phenylthiazoles showed the predominant force to be electrostatic, Merrifield and Phillips<sup>4</sup> for complexes of tetracyanoethylene and methylbenzene showed the contrary. Dasgosh and Basu<sup>5</sup> showed that the charge-transfer force is predominant in iodine monochloride and aromatic hydrocarbon systems ( $\pi$ - $\sigma^*$  complexes) in nonpolar solvents while the contribution of electrostatic forces is not negligible if one uses the higher dielectric solvents.

In order to see what type of force is predominant in ( $\pi$ - $\pi^*$ ) complexes we have studied the interaction of chloranil with different substituted naphthalenes in *n*-heptane as well as in a few other higher dielectric solvents. Moreover, appearance of multiple charge-transfer bands are often reported for substituted benzenes<sup>6</sup> and aro-

matic hydrocarbons<sup>7</sup> as donor. In an earlier report<sup>8</sup> we have shown that some of the substituted naphthalenes also show multiple charge-transfer bands. We also wanted to investigate whether the charge-transfer nature is predominant in both these bands. Equilibrium constant measurements in different dielectric medium will definitely indicate whether the charge-transfer forces or the electrostatic forces are predominant in these systems.

### Experimental

Naphthalene, 1-methyl (Fluka), 2-methyl, 2,3-dimethyl, 1,3-dimethyl and 2,6-dimethyl naphthalenes (Koch Light Laboratories) were carefully purified by sublimation and their purities checked by their absorption spectra in alcohol. Chloranil obtained from E. Merck was recrystallised several times from chloroform and finally checked by its absorption spectrum in chloroform and m.p. The solvents (S.D. chemicals) were all purified by redistillation after drying with  $\text{CaCl}_2$ . The solvents used are *n*-heptane ( $\epsilon = 1.95$ ), chloroform ( $\epsilon = 4.80$ ), 1,2-dichloroethane ( $\epsilon = 10.65$ ) and acetonitrile ( $\epsilon = 36.5$ ).

The measurements of absorption spectra were made on a Cary 2390 spectrophotometer at  $25 \pm 1^\circ\text{C}$  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 ( $10^{-1} \text{ mol dm}^{-3}$ ) to acceptor ( $10^{-3} \text{ mol dm}^{-3}$ ) was nearly 100 : 1. But because of low solubility of chloranil in *n*-heptane, acceptor was used at a concentration of  $10^{-6} \text{ mol dm}^{-3}$ .

### Results and discussion

The equilibrium constants ( $K$ ) and molar extinction coefficient ( $\epsilon_c$ ) of complexes of different donors with chloranil were calculated by Benesi Hildebrand<sup>9</sup> method. Scott's<sup>10</sup> and Rose Drago's<sup>11</sup> methods have also been applied to calculate these constants and have been reported elsewhere. As the equilibrium constant calculated by other methods do not differ much from Benesi Hildebrand's values we have taken the Benesi Hildebrand's equilibrium constants. The equilibrium constant  $K$ , the extinction coefficient  $\epsilon_c$  and the

position of the charge-transfer band are shown in Table 1 for the complexes of different naphthalenes with chloranil in different solvents having different dielectric constants.

A downward trend in the equilibrium constant values with the increase in the dielectric constant of the solvents is observed in all cases except for

1-methyl and 2-methyl naphthalenes when the solvent is changed from chloroform ( $\epsilon = 4.81$ ) to dichloroethane ( $\epsilon = 10.4$ ).

Since charge-transfer interaction takes place on a molecular level one would expect the equilibrium constant to remain unaffected by bulk dielectric constant, whereas if electrostatic interaction

Table 1—Results for  $\lambda_{\max}$ ,  $K$  and  $\epsilon_c$  for chloranil-aromatic hydrocarbon complexes in different solvents of varying dielectric constant ( $\epsilon$ )

Aromatic hydrocarbons	Solvents	$\epsilon$ of solvents	$\lambda_{\max}$ , nm	$K$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$\epsilon_c$ ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )
Naphthalene	<i>n</i> -heptane	1.95	468	1.76	66600
			388	0.52	667
	chloroform	4.80	470	0.83	715
			472	0.53	667
	dichloroethane	10.65	460	0.20	1330
			380	0.15	2000
1-Methylnaphthalene	<i>n</i> -heptane	1.95	492	2.70	167000
			388	2.19	178000
	chloroform	4.80	520	0.39	1425
			400	0.37	1666
	dichloroethane	10.65	510	0.90	766
			396	0.53	1000
Acetonitrile	36.5	488	0.45	1000	
		388	0.34	1250	
2-Methylnaphthalene	<i>n</i> -heptane	1.95	489	2.61	284000
			504	0.84	1043
	chloroform	4.80	420	0.93	1250
			494	1.27	540
	dichloroethane	10.65	416	0.39	2000
			488	0.50	1000
Acetonitrile	36.5	408	0.28	2000	
		—	—	—	
1, 3-dimethylnaphthalene	<i>n</i> -heptane	1.95	524	5.04	71525
			404	3.00	104333
	chloroform	4.80	550	4.12	430
			430	3.60	385
	dichloroethane	10.65	—	—	—
			—	—	—
Acetonitrile	36.5	—	—	—	
		—	—	—	
2, 3-dimethylnaphthalene	<i>n</i> -heptane	1.95	500	4.29	256500
			422	4.03	361750
	chloroform	4.80	540	1.26	1350
			440	2.02	1495
	dichloroethane	10.65	552	1.03	1165
			448	0.96	2034
Acetonitrile	36.5	520	0.66	1000	
		432	0.72	1310	

be predominant then the interaction will depend strongly on the dielectric constant of the medium.

The energy of formation  $\Delta E$  of a complex (D, A) holds a linear relation to  $h\nu$ , when  $\nu$  is the frequency of the first charge-transfer band as given in Eq. (2)

$$\Delta E = \frac{C}{\nu} + D = C'\lambda + D \quad \dots (2)$$

where, C, C' and D are constants and  $\lambda$  is the wave length of the first charge-transfer band. The above relation follows directly from a perturbation treatment of the energy of formation  $\Delta E$  of a complex (D, A) from its components and can be represented by Eq. (3)

$$\Delta E = [(D+A), (D+A)] + \sum_i \frac{[(D+A), (D+A)_i]^*]^2}{E_0 - F_i} + \sum_j \frac{[(D+A), (D+A)_j^\pm]^2}{E_0 - G_j} \quad \dots (3)$$

All the terms have the usual significance. The theory underlying has been discussed earlier<sup>5</sup>. Dewar<sup>2</sup> and Arnaud and Bonnier<sup>3</sup> carried out a similar type of work with tetracyanoethylene as the acceptor.

We have chosen here the aromatic hydrocarbons for which we can safely neglect the polarizability contribution (the first term). Variation of the conventional van der Waals' force not being very much (the second term thus may be neglected), change in  $\Delta E$  should be mainly due to change in the charge-transfer contributions. Moreover the numerator of the third term in Eq. 3 should vary little along the series, because of the similarity between the donor components, thus difference in the denominator should be approximately equal to the excitation energy of the first charge-transfer transition giving Eq. (2) above.

If we now make the usual assumption that in a series of this kind, the variations in the equilibrium constant  $K$  are due to changes in the energy rather than the entropy of reaction, then Eq. (2) becomes Eq. (4).

$$\log K/K_0 = C''(\lambda - \lambda_0) \quad \dots (4)$$

where  $K_0$ ,  $\lambda_0$  are values of  $K$ ,  $\lambda$  for one standard molecule (we have taken naphthalene molecule as reference in the present series of studies). Figure 1 shows such a plot for the systems in *n*-heptane. As is evident, the curve is fairly linear in *n*-heptane. This is in accord with the previous liter-

ature values<sup>4,5</sup>, but differ from those of Dewar<sup>2</sup>, and Arnaud and Bonnier<sup>3</sup>. Thus the variations in  $K$  for these systems in non-polar solvents at least are due mainly to variations in charge-transfer forces.

However the contribution of electrostatic force plays a dominant role when the media is changed from nonpolar to polar solvents.

Table 1 shows that the equilibrium constants for these series decreases with increase in the dielectric constants of the medium thus indicating that electrostatic force has also some contribution. Again, if we plot the equilibrium constant versus  $(\lambda - \lambda_0)$  in solvents with higher dielectric constant (chloroform, dichloroethane or acetonitrile) the curves are no longer linear.

Lastly it appears from Table 1 that the second charge-transfer bands always show a blue shift with respect to the naphthalene band and most of the time this band can be located when the complex was balanced against the same concentration of the acceptor but not against the solvent itself. Moreover, if this shift is plotted against  $\log K/K_0$  in the same way as for the first charge-transfer band the curve is not at all linear indicating that in this band perhaps the electrostatic force is predominant.

Onsager's<sup>12</sup> continuum model for dielectrics ignores the solvent structure and the solvent was represented by a single parameter  $\epsilon$  and the solute as a point dipole. Dielectric permittivity being an average property reflects an average of solvent arrangements over macroscopic distances and thus cannot describe adequately the solvent structure in the immediate neighbourhood of the solute molecule. Hence it becomes too crude an approximation for polar solvents. Kirkwood<sup>13</sup> developed Onsager's reaction field idea to correlate the mutual interaction between the solute mole-

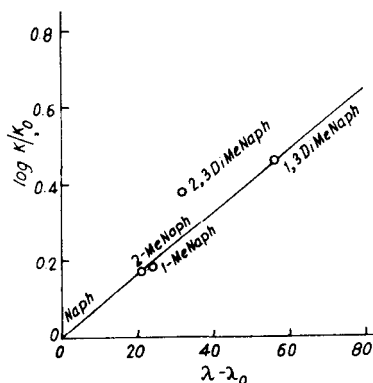


Fig. 1—Plot of  $\log(K/K_0)$  versus  $(\lambda - \lambda_0)$

cule and its nearest neighbours. However this mutual action is not thus far known even in the case of simple molecules. So it becomes necessary to introduce undetermined parameters whose presence excludes the possibility of quantitative comparison with experiment.

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