

Electron Donor-Acceptor Complexes of Some Aromatic Hydrocarbons with Chlorosubstituted Quinones

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Electron donor-acceptor interactions between fluorene, 2-bromofluorene, *t*-stilbene and pyrene as electron donors and chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone as electron acceptors have been examined by electronic spectroscopy. The spectroscopic and thermodynamic parameters of the complexes are reported. Among all the donors studied, pyrene appears to be the strongest electron donor towards both the electron acceptors.

Electron donor-acceptor (EDA) complexes of chloranil (CA as electron acceptor) have been studied extensively^{1,2}. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), which is structurally similar to CA, is reported to be a strong electron acceptor^{3,4} having greater electron affinity than that of CA. As yet, relatively little attention has been paid to the EDA complexes of DDQ. Dwivedi and coworkers^{5,6} have reported the enthalpies of formation of a number of EDA complexes formed between aromatic hydrocarbons and DDQ. In some instances, the EDA complexes of DDQ with aromatic hydrocarbons undergo further irreversible reactions^{7,8}. Srivastava and Prasad⁹ have determined the formation constants of the DDQ complexes with fluorene and pyrene as electron donors. However, no attempt was made to evaluate the energies of interaction in these systems. We have presently investigated the interaction of DDQ with fluorene, 2-bromofluorene, *t*-stilbene and pyrene. These studies have also been extended to structurally similar electron acceptor CA.

Materials and Methods

Chloroform (BDH, AR) was dried over anhydrous calcium chloride and distilled before use. DDQ was purified by recrystallisation from chloroform. Chloranil was recrystallised four times from benzene to give yellow platelets (sealed tube m.p. 289°C). Fluorene, 2-bromofluorene, *t*-stilbene and pyrene were purified by recrystallisation from ethanol.

Electronic absorption spectra were recorded on a Beckman DU spectrophotometer fitted with a variable temperature cell compartment using matched pair of 1 cm fused silica cells. Equilibrium formation constant, K , and molar extinction coefficient, ϵ , of the EDA complexes were evaluated by employing the modified Scott equation¹⁰. The absorbances of a series of solutions with varying donor concentration and a fixed

acceptor concentration were measured at the charge-transfer band maximum (λ_{CT}). Person's criteria regarding donor concentration were always satisfied in evaluating the equilibrium constants¹¹. The enthalpies of formation, ΔH , of the EDA complexes were determined from the K values at several temperatures between 10° and 40°C. The K as well as the ΔH values of the complexes have an uncertainty of less than $\pm 10\%$ as can be seen from a typical plot shown in Fig. 1 for the fluorene + DDQ system.

Results and Discussion

All the aromatics on mixing with DDQ in chloroform solution exhibit well-defined charge-transfer (CT) bands characteristic of EDA complexes (see Fig. 2 for some typical spectra). The spectra were well separated from the transition of either of the components. Absorbance measurements at λ_{CT} yielded linear modified Scott equation plots indicating the formation of 1:1 EDA complexes in these systems. The results of the present investigation are summarised in Table 1. The λ_{CT} , K and ϵ values found by us for the

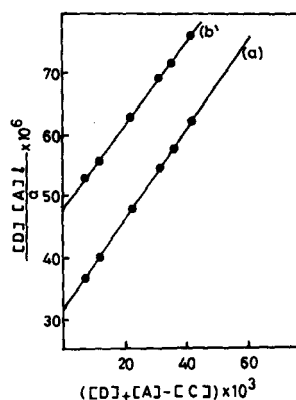


Fig. 1—Modified Scott equation plot for the fluorene + DDQ complex at (a) 21°C and (b) 31°C.

Table 1—Spectroscopic and Thermodynamic Data for EDA Complexes of Aromatics with CA and DDQ in CHCl_3 Solution

Electron donor	Ionization potential (eV)	Electron acceptor	λ_{CT} (nm)	$K^{(a)}$ (l mol^{-1})	ϵ ($\text{l mol}^{-1}\text{cm}^{-1}$)	$-\Delta H$ (kcal mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f
Benzene ^(b)	9.24	DDQ	425	0.59	2174	1.7	5481	0.052
<i>t</i> -stilbene	7.99	CA	525	4.5	240	5.8	5128	0.004
		DDQ	680	5.1	1785	7.7	3531	0.024
Fluorene	—	CA	530	10.2	183	6.9	3546	0.003
		DDQ	630	14.0	1500	8.0	1455	0.015
2-Bromofluorene	—	CA	520	2.1	500	1.4	2914	0.006
		DDQ	650	2.7	1933	2.7	4787	0.040
Pyrene ^(c)	7.82	CA	440	15.9	140	8.6	4096	0.002
		DDQ	545	20.0	1429	9.6	1926	0.010

^a At 31°C, data are given at one temperature only for the sake of brevity.

^b Data from reference (5).

^c Same K and ΔH data were obtained at two other CT bands.

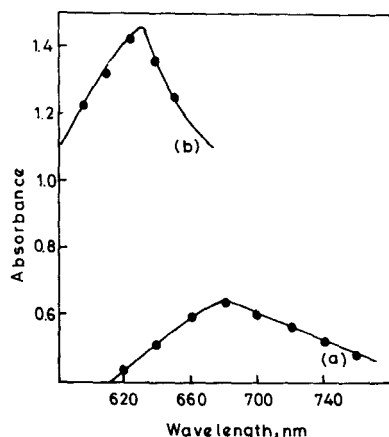


Fig. 2—Electronic absorption spectra of (a) *t*-stilbene + DDQ and (b) fluorene + DDQ in CHCl_3 solution (D and A concentrations are 0.04 M and 2.0×10^{-3} M respectively in both the cases)

fluorene + DDQ and pyrene + DDQ systems are in good agreement with the data reported by Srivastava and Prasad⁹. However, it is noteworthy to mention that three charge-transfer bands are observed by us for the pyrene + CA (380, 440, 640 nm) and pyrene + DDQ (390, 545, 880 nm) systems in these studies. Schenk and Fryer¹² have indicated the existence of multiple CT bands in the case of π -complexes of DDQ with aromatic hydrocarbons by utilizing the Dewar Molecular Orbital theory of CT spectra. They have experimentally measured the absorption spectra of pyrene + DDQ system in dichloromethane medium upto 400 nm and observed two CT bands at 530 ± 8 nm and 850 ± 12 nm.

Mulliken¹³ pointed out that the main stabilisation energy for an EDA complex formed between an electron donor (D) and an electron acceptor (A) arises

from the resonance energy between the no- bond ($\text{D}-\text{A}$) and the ionic ($\text{D}^+ - \text{A}^-$) configuration of the complex. Thus, the lower the ionization potential, the higher should be the stability of the EDA complex (as measured by K and ΔH). This is found to be true for structurally similar electron donors^{5,6}. Thus, if the donors in Table 1 are considered in two separate groups of phenyl substituted (group 1) and polynuclear hydrocarbons (group 2), the complex stability order is:

t-stilbene > benzene (group 1) and pyrene > fluorene > 2-bromofluorene > benzene (group 2)

The above order satisfies the condition for group 1 that the lower the ionization potential, the greater is the stability of the complex, as pointed out by Mulliken¹³. However, we cannot comment on this statement for donors of group 2 because of the non-availability of the ionization potentials of fluorene and 2-bromofluorene. The half band widths, $\Delta\nu_{1/2}$, decrease with increasing complex strength for both the groups of donors with the exception of fluorene + DDQ system. This is contrary to our earlier observations^{5,6,14,15} and the reason for this is not clear to us. The values of the molar extinction coefficient, ϵ , and the oscillator strength, f , of the EDA complexes provide a measure of the intensity of the CT band. Based on these data in Table 1 the CT band intensity order is:

t-stilbene < benzene and pyrene < fluorene < 2-bromofluorene < benzene

It is, thus, seen that the CT band intensity decreases as the strength of interaction (as measured by ΔH) increases in the case of electron donors of both the

Table 2—Composition of CT Bands of CA and DDQ

Donor	$\nu_{CT} \times 10^{-2}, \text{cm}^{-1}$		$\Delta\nu \times 10^{-2}, \text{cm}^{-1}$
	CA	DDQ	
Benzene ^(a)	290	234	56
2-Bromofluorene	192	154	38
<i>t</i> -Stilbene	190	147	43
Fluorene	189	159	30
Pyrene	227	184	43

^a Data from reference (6).

groups. This observation is similar to our earlier reports^{5,6} on a number of EDA complexes.

For a series of acceptors with similar structure, the CT band of a particular donor should be separated with an energy interval proportional to the corresponding difference in the electron affinity if, ω in the Mulliken's¹³ relationship ($h\nu_{CT} = I_p - E_a - \omega$, where ν_{CT} is the absorption frequency of the CT band, I_p is the ionization potential of the donor, E_a is the electron affinity of the acceptor and ω takes into account the stabilisation energy of the ion pair) is assumed to remain constant. Also, for a series of donors of like structures, the shift should be constant. Structurally, DDQ is similar to CA but has a greater electron affinity than that of CA. The CT bands of DDQ should shift towards longer wavelengths in

comparison to similar bands for the CA complexes. A comparison of the CT bands of DDQ and CA has been made in Table 2. It is seen that both CA and DDQ respond similarly to Mulliken's relationship¹³. The shifts, $\Delta\nu$, are nearly constant indicating that the mode of interaction of both the acceptors in these complexes is the same, as expected from the similarity in their structures.

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