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Charge Transfer Interaction between 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone and Substituted Benzenes

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Charge transfer complexes between 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and various methyl and phenyl substituted benzenes have been studied. The spectral characteristics and equilibrium constants of *o*-, *m*-, and *p*-xylenes and those of *o*-, *m*-, and *p*- terphenyls are reported. The results have been interpreted in terms of Mulliken's charge transfer theory. From the spectral data, the electron affinity of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone has been estimated to be 1.974 eV. The energy of the first CT band has been found to be related to the ionization potential of the donors by the expression $h\vartheta_{CT}=0.7I_D-3.86$.

In a previous communication[1] we have reported some of the studies on the charge transfer complexes of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) with aromatic hydrocarbons. The studies have now been extended to substituted benzenes with a view to get a more clear picture of the interactions and to test the characteristic regularities of the charge transfer complexes. The reported results have been used in estimating the electron affinity of DDQ.

Experimental

Pure 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was obtained from Light & Co. It was further purified by crystallizing from chloroform. Xylenes (B.D.H.) were distilled before use while terphenyls (Light & Co.) were crystallized from carbon tetrachloride or chloroform.

Spectrophotometric studies were carried out on a Unicam SP-500 spectrophotometer using 1.00 cm matched silica cells. The measurements were made at room temperature 25°C±2.0. Stock solutions for each of the donors were prepared separately which were mixed and diluted to required concentrations just before use. Optical density measurements have a maximum error of 1 percent. Equilibrium constants K_c (l mol^{-1}) and extinction coefficient, ε (l mol$^{-1}\cdot$cm^{-1}) were calculated graphically, using the appropriate forms of the Ketelaar's equation.[2] The following two equations served the purpose:

$$\frac{q}{A-A_q}=\frac{1}{(\varepsilon-\varepsilon_q)K_c}\cdot\frac{1}{D}+\frac{1}{\varepsilon-\varepsilon_q} \tag{1}$$

$$\frac{q}{A}=\frac{1}{\varepsilon K_c}\cdot\frac{1}{D}+\frac{1}{\varepsilon} \tag{2}$$

Equation (1) was used in cases where the absorption due to the acceptor molecules could not be neglected, while Eq. (2) was used when the acceptor and donor molecules did not have appreciable absorption at the λ_{max}. In the above equations, q represents the acceptor concentration, D the concentration of the donor, both in mol/l. A is the optical density, ε is the extinction coefficient at the maximum of the charge transfer band λ_{max}, and the subscript q represents the contribution in the property due to the presence of the acceptor in the system. In cases where the optical density of the quinone could not be neglected, its appropriate concentration was taken in the reference cell.

Results and Discussion

The yellow colour of DDQ turned to deep red on addition of xylenes and to amethyst or apple green on addition of terphenyls. Spectroscopic investigations in the region 400 to 700 mμ revealed in each case band characteristics of charge transfer complexes of the stoichiometric ratio of 1 : 1. In the case of xylenes one charge transfer band was obtained, but in the case of terphenyls two charge transfer bands were noted. It may be pointed out that xylenes are expected to show two bands but these could not be resolved in our experiments. Hammond[3] using 10 cm silica cells isolated the second CT band of *o*- and *m*-xylenses in dichloromethane, which are found to occur at 452 mμ and 451 mμ respectively. From the shape of the curves it is apparent that second CT and of *p*-xylene should appear somewhere around 460 and 470 mμ.

Ionization Potential and Energy of CT Band. The energy of the CT band is approximately related to the parameters of the components by the equation

$$h\vartheta_{CT}=I_D-E_A-W \tag{3}$$

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[1] R. D. Srivastava and G. Prasad, *Spectrochim. Acta*, **22**, 1969 (1966).

[2] J. A. A. Ketelaar, C. van De Stolpe, A. Goudsmit and W. Dzcubass, *Rec. Trav. Chim. Pays-Bas*, **71**, 1104 (1952).

[3] P. Hammond, *J. Chem. Soc.*, **1963**, 3113.

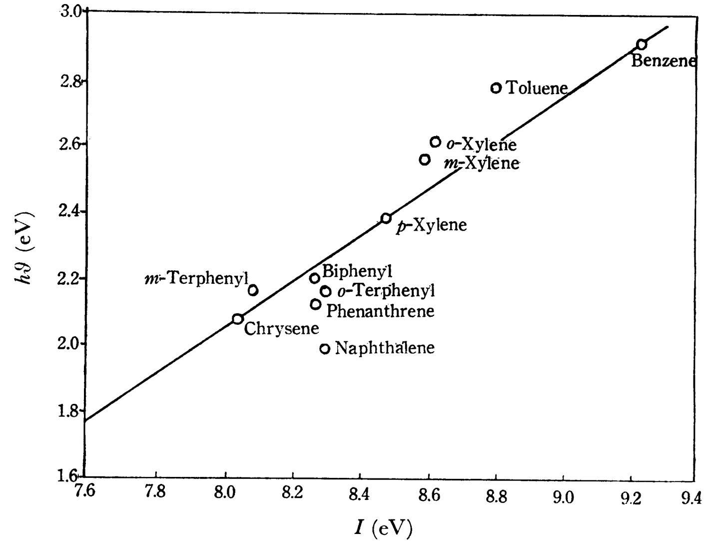

Fig. 1. Relationship between ionization potential (I) and energy of the charge-transfer band ($h\vartheta_{CT}$)

Table 1. Equilibrium constants of the complexes with DDQ

Donor	$q \times 10^3$ mol/l	D range mol/l	λ_{max} mμ	(1 mol^{-1} cm^{-1}) ε_c	K_c (1 mol^{-1})
o-Xylene	0.348	0.248 to 2.08	480	3480	2.60
m-Xylene	0.351	0.245 to 1.75	480	3636	2.50
p-Xylene	3.810	0.245 to 1.65	520	3540	3.00
o-Terphenyl	1.960	0.213 to 0.48	580	1000	0.83
m-Terphenyl	1.870	0.068 to 0.18	574	900	2.70
p-Terphenyl	6.000	0.019 to 0.05	635	1000	5.00

where ϑ_{CT} is the frequency of the CT band, I_D is the ionization potential of the donor, E_A is the electron affinity of the acceptor and W is the difference in the stablization energy of the ground and excited state. From the data given in Tables 1 and 2 we find that a plot of $h\vartheta_{CT}$ *versus* I_D gives a straight line of the form (see Fig. 1)

$$h\vartheta_{CT} = 0.7I_D - 3.86 \tag{4}$$

Orgel[4] explains the appearance of more than one CT band in the substituted benzenes on the basis that degeneracy of $^2E_{1g}$ ground state of benzene positive ion is removed by suitably arranged substitution. The two orbitals now split to an extent depending on the number of substituents, their nature and relative positions on the ring. The resultant two electronic states have two different ionization energies. The following are the expressions for the energy difference between the ionisation potential, I_B of benzene itself and the two ionisation potentials, I_1 and I_{11} of the substituted molecules.

$$I_1 = I_B - n\vartheta_S - p_1\varepsilon_S \tag{5}$$
$$I_{11} = I_B - n\vartheta_S - p_{11}\varepsilon_S \tag{6}$$

Here n is the number of the substituents S in the benzene ring; ε_S and ϑ_S are parameters arising from perturbation by S and depend on the nature of the substituent. ε_S relates to the total interaction of S with the π-electron system of the ring, while ϑ_S describes the interaction of S with the σ-system of the ring. p_1 and p_{11} are constants depending on both n and the relative position of the substituents; these values were calculated by Orgel,[4] which are shown below for 0, 1, 1-2, 1-3, and 1-4, substituents.

Position substituent	0	1	1-2	1-3	1-4
p_1	0	1	3/2	3/2	2
p_{11}	0	0	1/2	1/2	0

If $p_1 \neq p_{11}$, two charge transfer bands will result for all substitutions; for $p_1 = p_{11}$ only one band will be observed. When $p_1 = p_{11} = 0$, the charge-transfer energy will be fairly close to that of the benzene complex, since ϑ_S turns out to be rather small compared to ε_S. The band separation $h\vartheta_{11,1} \simeq I_{11} - I_1 = \Delta p_{11,1}\varepsilon_S$ will be very significant in the case of *p*-disubstituted and symmetrically tetra substituted benzenes. Therefore for *o*- and *m*-substituents of benzene, the two ionization potentials would be

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[4] L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).

Table 2. Spectral characteristics of DDQ complexes

Donor	λ_{max} in mμ	$h\vartheta_{CT}$ in eV	I_d in eV	f	K_c (1 mol^{-1})
Benzene	427	2.906	9.24	0.0995	0.47
Toluene	450	2.760	8.82	0.1076	0.92
o-Xylene	480	2.585	8.58	0.1520	2.60
m-Xylene	480	2.585	8.60	0.1528	2.50
p-Xylene	520	2.385	8.48	0.1240	3.00
Biphenyl	564	2.200	8.27	0.0653	0.95
	440	2.816	—	—	—
o-Terphenyl	580	2.140	8.25	—	0.83
	458	2.710	—	—	—
m-Terphenyl	574	2.160	8.09	—	2.70
	444	2.794	—	—	—
p-Terphenyl	635	1.954	8.30	—	5.00
	425	2.920	—	—	—

Table 3. Separation of the first CT band of methyl derivatives with respect to benzene

Separation in	Calculated	Observed $\Delta\vartheta_{max}$
Benzene and toluene	$\vartheta_s+\varepsilon_s$	1200cm^{-1}
Benzene and *o*-xylene	$2\vartheta_s+3/2\ \varepsilon_s$	2600cm^{-1}
Benzene and *m*-xylene	$2\vartheta_s+3/2\ \varepsilon_s$	2600cm^{-1}
Benzene and *p*-xylene	$2\vartheta_s+2\ \varepsilon_s$	4200cm^{-1}

Table 4. Separation of the first CT band of phenyl derivatives with respect to benzene

Separation in	Calculated	Observed $\Delta\vartheta_{max}$
Benzene and biphenyl	$\vartheta_s+\varepsilon_s$	5700cm^{-1}
Benzene and *o*-terphenyl	$2\vartheta_s+3/2\ \varepsilon_s$	6100cm^{-1}
Benzene and *m*-terphenyl	$2\vartheta_s+3/2\ \varepsilon_s$	6000cm^{-1}
Benzene and *p*-terphenyl	$2\vartheta_s+2\ \varepsilon_s$	7700cm^{-1}

equal to each other. This would mean that corresponding CT bands should occur with equal energy and in fact this has been found to be the case in the present investigations. (Tables 3 and 4).

The band separations, $\Delta\vartheta_{max}$ (11-1) observed on varying the number and positions of donor substitutent are *p*-disubstituted$>$*o*- and *m*-disubstituted donors$>$mono substituted donor. Again this agreed with what is predicted from the difference Δp (11-1): *p*-disubstituted$>$*o*- and *m*-disubstituted$=$ mono substituted donor.

In fact, numerically, the charge-transfer band for a *p*-(1-4) substituted isomer corresponding to a fixed arbitrary value of ϑ_S and ε_S has to be separated from the bands of benzene with an energy interval twice that of corresponding separation between the second CT bands of mono substituted benzenes. This has not been found to be true. The reported separations as given in Tables 3—5 do not support the above prediction.

Table 5. Separation of the second CT band of phenyl derivatives with respect to benzene

Separation in	Calculated	Observed $\Delta\vartheta_{max}$
Benzene and biphenyl	ϑ_s	600cm^{-1}
Benzene and *p*-terphenyl	$2\vartheta_s$	$\approx$000cm^{-1}

Electron Affinity of DDQ. Another consequence of Eq. (3) is that the CT spectra of a single donor with various closely related acceptors should be displaced with an energy interval corresponding to the difference in the electron affinities of the two acceptors. Also if the electron affinity of one of the acceptors is known and the spectra shift is studied, the electron affinity of an acceptor can be estimated from this shift. As pointed out in Ref. 1, the CT band of DDQ complexes with various hydrocarbons shifts to the red region with respect to the corresponding CT band of chloranil. This shift is 4870 cm^{-1} or equivalent to 0.604 eV.

The electron affinity of chloranil is 1.37 eV.[5] Hence the electron affinity of DDQ should be

$$h\vartheta_{CT}(\text{chloranil}) - h\vartheta_{CT}(\text{DDQ})$$

$$= E_A(\text{DDQ}) - E_A(\text{chloranil}) = 0.604\text{ eV}$$

$$\therefore\quad E_A(\text{DDQ}) = 1.37 + 0.604 = 1.974\text{ eV}$$

Stability of the Complex and the Ionization Potential. The main stablization energy[6] for the charge transfer complex arises from the resonance energy between the no bond state (A–D) and the ionic stage (A^-D^+) of the complex configurations. Thus, the lower the ionization potential, the higher should be the stability of the complex. This preposition has been found to be true. If the K_c values of Ref. 1 and of the present investigations are considered, it is seen that in general the complexes of donors of comparatively lower ionisation potentials have greater values of equilibrium constants than the complexes of donors of comparatively higher ionization potentials. One must however be careful to choose donors which are similar. For instance, the three separate groups of methyl substituted, the phenyl substituted and the polynuclear hydrocarbon donors should be considered separately. When this is done regularity in regard to complex stability is observed.

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5) G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960); G. Briegleb, *ibid.*, **76**, 617 (1964).

6) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

Benzene $<$ toluene $<$ xylene
Benzene $<$ biphenyl $<$ terphenyl
Benzene $<$ naphthalene $<$ phenanthrene
$<$ chrysene $<$ pyrene

Intensity and Stability. According to Mulliken[6] the intensity of the charge transfer band μ_{In} should be directly proportional to the stability or the equilibrium constant of the complex. The intensity is related to oscillator strength by the equation

$$f = 4.704 \times 10^{-7} \vartheta_{\mathrm{mesc}} \times \mu_{\mathrm{In}} \tag{7}$$

The oscillator strength has been calculated using the equation of Briegleb[7] and is recorded in Table 2. The present investigations do not conform to the predicted relationship.

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[7] G. Briegleb and J. Czekalla, *Z. Phys. Chem.* (Frankfurt), **24**, 37 (1960).