ELECTRON DONOR-ACCEPTOR COMPLEXES OF SUBSTITUTED BENZENES WITH QUINONES

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ABSTRACT

Electron donor-acceptor complex formation between benzene, *m*-terphenyl, anisole and veratrole as electron donors and chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone as electron acceptors has been studied by electronic spectroscopy. The spectroscopic and thermodynamic parameters of the complexes are reported. Veratrole appears to be the strongest electron donor among all. The mode of interaction of both the acceptors appears to be the same in these complexes.

INTRODUCTION

CHLORANIL (CA) is known to form electron donor-acceptor (EDA) complexes with a variety of electron donors[1,2]. A structurally similar compound, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) 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 focussed towards investigating the EDA complexes of DDQ[4-12], Dwivedi and Banga[6] have reported the enthalpies of formation of a number of EDA complexes formed between aromatic hydrocarbons and DDQ. Formation constants of EDA complexes of aromatic hydrocarbons with DDQ have been determined by Srivastava and Prasad[7]. Foster and Co-workers[9] as well as Dwivedi and Co-workers[12] have shown that the EDA complexes of some aromatic hydrocarbons with DDQ undergo further irreversible reactions yielding reaction products.

Methoxy group is a more strongly interacting substituent on an aromatic nucleus compared to a methyl group. Molecular complexes of methyl-substituted aromatics have been studied extensively[2] and their energies of interaction are reported. However, no work has been done on methoxy-benzene except that of Zweig and Co-workers[8], who measured the electronic absorption spectra of the molecular complexes of methoxy benzenes with DDQ and CA. No attempt was made to evaluate the equilibrium constants of formation of these complexes. We have, therefore, examined the electron donating properties of anisole and veratrole using structurally similar electron acceptors CA and DDQ. Benzene and *m*-terphenyl have also been included in this study for the sake of comparison.

EXPERIMENTAL

Benzene (BDH, AR), anisole (BDH, AR) and veratrole (SRL) were purified by fractional distillation.

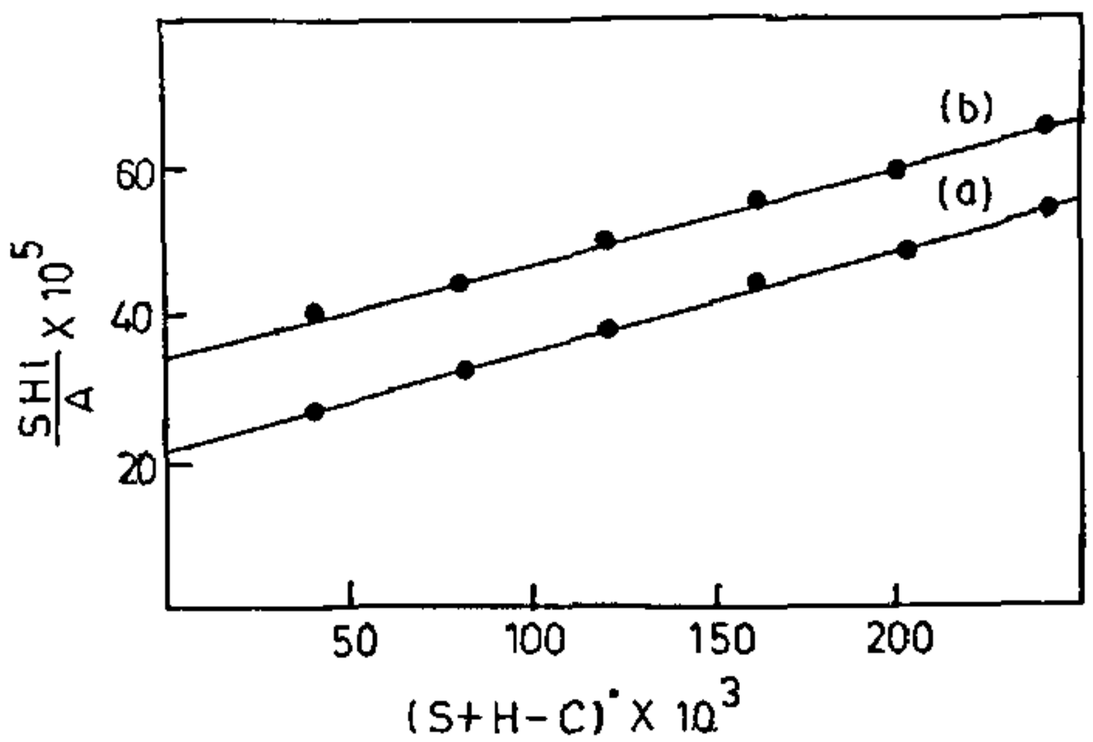

Figure 1. Modified Scott equation plot for the veratrole + DDQ complex at 32° C (Curve a) and 42° C (Curve b).

m-Terphenyl (Koch-Light) was recrystallized from absolute ethyl alcohol. Chloranil, DDQ and chloroform (E. Merck, G.R.) were purified by the methods described in our earlier publications[6,13].

Spectral measurements were made on a Beckman DU spectrophotometer using matched silica cells of 1 cm path length and fitted with ground glass stoppers. The equilibrium constants of formation, K, of the EDA complexes were determined using the modified Scott equation[14]. 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}). In evaluating K, Person's criteria[15] regarding donor concentration were satisfied. The enthalpies of formation, ΔH, were determined by evaluating the equilibrium constants at various temperatures in the range 20 to 45° 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 the typical plot shown in figure 1 for the veratrole + DDQ system.

TABLE 1

Spectroscopic and thermodynamic data for EDA complexes of aromatic hydrocarbons with CA and DDQ in chloroform solution

Electron donor	I_p (eV)	Electron acceptor	λ_{CT} (nm)	K_c[a] (litre mole^{-1})	ϵ (litre mole^{-1} cm^{-1})	$-\Delta H$ (kcal/(mole^{-1}))	$\Delta\bar{\nu}\ 1/2$ (cm^{-1})	Oscillator/ strength f
Benzene	9.24	CA	345	0.27	1875	0.6	9322	0.075
		DDQ	425	0.45	2174	1.7	5481	0.051
m-terphenyl	8.09	CA	450	1.07	536	1.1	9445	0.022
		DDQ	570	2.21	875	2.3	7716	0.029
Anisole	8.22	CA	460	0.31	833	2.3	6823	0.025
		DDQ	560	1.35	1040	4.1	6683	0.030
Veratrole	—	CA	510	0.65	640	9.2	7081	0.019
		DDQ	640	6.20	769	11.0	6868	0.023

[a] At 32° C; data are given at one temperature for the sake of brevity.

RESULTS AND DISCUSSION

All the systems studied exhibit charge-transfer (CT) bands characteristic of EDA complexes in the electronic absorption spectra. These bands are quite sharp and well-separated from the transition of either of the components. Absorbance measurements at λ_{CT} of the EDA complexes yielded linear modified Scott equation plots[14] indicating formation of 1:1 complexes in these systems.

The results of the present investigation are summarised in table 1. The λ_{CT} values found by us are in good agreement with the reported data[7,8].

Mulliken[16] has pointed out that the main stabilization 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 (D—A) and the ionic (D^+-A^-) configuration of the complex. Thus, the lower the ionization potential, the higher should be the stability of the complex. This is found to be true if one carefully chooses electron donors which are similar in structure. Thus, if the donors in table 1 are considered in two separate groups of phenyl-substituted (Group 1) and methoxy-substituted (Group 2) hydrocarbons, the complex stability order (as measured by K and ΔH) is:

m-terphenyl > benzene

Veratrole > anisole > benzene

The above order satisfies the condition that the lower the ionization potential, the greater is the stability of the complex as pointed out by Mulliken[16]. The half band widths, $\Delta\bar{\nu}^{1/2}$ increase with an increase in the complex strength and follow the above order with the exception of benzene + CA system in Group 2. This direct relationship between $\Delta\bar{\nu}^{1/2}$ and the strength of complexes (as measured by ΔH) has been observed earlier[6,17,18] and was attributed to the large resonance interaction in the complexes.

The exceptionally high ΔH values of methoxy benzene seem to suggest that these compounds possess greater electron donating properties compared to those of methyl and phenyl-substituted benzenes[6].

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:

m-terphenyl < benzene

Veratrole < anisole < benzene

It is seen that the intensity of the CT band decreases as the strength of interaction (as measured by ΔH) increases in the case of electron donors of both the groups. This observation is similar to that reported by Dwivedi and Co-workers[6] for other phenyl-substituted hydrocarbon + DDQ systems.

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, W in the Mulliken's relationship[16] ($h\bar{\nu}_{CT} = I_p - E_a - W$, where $\bar{\nu}_{CT}$ 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 W takes into account the stabilization energy of the ion-pair) is assumed to remain constant. Also, for a series of donors of like structure, 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 CA for similar donors. A comparison of the CT bands of

TABLE 2

Comparison of CT bands of DDQ and CA

Donors	$-\triangle H$, kcal/mole		$\bar{\nu}_{CT} \times 10^{-2}$, cm^{-1}		$\triangle \nu \times 10^{-2}$, cm^{-1}
	CA	DDQ	CA	DDQ	
Benzene[a]	0.6	1.7	290	234	56
Toulene[b]	—	—	270	222	48
m-xylene[b]	—	—	247	208	39
Biphenyl[a]	—	2.8[c]	287	227	60
			230	177	53
m-terphenyl[a]	1.1	2.3	222	175	47
Naphthalene[b]	—	3.9[c]	256	212	44
			208	160	48
Phenanthrene[b]	—	5.7[c]	216	171	45
Fluorene[b]	—	—	200	160	40
Pyrene[b]	—	—	231	185	46
Anisole[a]	2.3	4.1	217	178	39
Veratrole[a]	9.2	11.0	196	156	40

[a]Our data; [b]Data from Ref. 7; [c]Data from Ref. 6.

DDQ and CA has been given in table 2. It is seen that both respond similarly to Mulliken's relationship[16]. The shifts, $\triangle \nu$ are nearly constant indicating that the mode of interaction of both the acceptors in these complexes is the same, as expected from their similarity in structure.

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