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Spectrophotometric Studies on Electron-Donor-Acceptor Complexes of Aromatic Hydrocarbons with Tetrabromophthalic Anhydride

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Electron donor-acceptor interactions between aromatic hydrocarbons, namely acenaphthene, pyrene, hexamethylbenzene, naphthalene, mesitylene, biphenyl and benzene as electron donors and tetrabromophthalic anhydride as electron acceptor have been examined by electronic spectroscopy in carbon tetrachloride solution. The spectral and thermodynamic parameters of the complexes are reported. The hν_{CT}-ionisation potential plot is found to be linear.

Electron donor-acceptor (EDA) complexes between tetrachlorophthalic anhydride (TCPA) and tertiary amines initiate polymerization[1]. It was felt that EDA complexes of tetrabromophthalic anhydride (TBPA) with a variety of electron donors may also act as initiators. Unfortunately, reports on EDA interactions of TBPA are scanty[2,3]. The present study on the interaction of aromatic hydrocarbons with TBPA forms a part of a broad programme aimed at developing new EDA complexes as initiators in polymerisation.

All the aromatic hydrocarbons, viz, benzene, biphenyl, mesitylene, naphthalene, hexamethylbenzene, pyrene and acenaphthene, were purified by crystallisation or fractional distillation. TBPA (Aldrich Chemicals, USA) was repeatedly crystallised from benzene till identical absorption spectra were obtained in CCl_4 with samples from successive crystallisation. Carbon tetrachloride (BDH, AR) was dried and distilled before use.

Spectral measurements were made on a Beckman D U spectrophotometer fitted with variable temperature cell compartment and matched silica cells of 1 cm pathlength. Equilibrium formation constants (K) and molar extinction coefficients (ε) of the EDA complexes were calculated graphically using the modified Scott equation[4]. In evaluating K, Person's criteria[5] regarding donor concentrations were satisfied. The enthalpies of formation (ΔH) were evaluated from the equilibrium constants at different temperatures in the range of 293-313 K.

All the aromatic hydrocarbons and TBPA have appreciable absorption in the CT region. Therefore, CT bands of all the EDA complexes were obtained by difference spectra. The spectral and thermodynamic data of the EDA complexes studied presently are given in Table 1. The ν_{CT} is linearly related to the ionization potential (I_p) for most of the donors studied (Fig. 1), indicating the validity of the Mulliken's original relationship[6] $h\nu_{CT} = I_p - E + C + \sigma/(I_p - E + C)$ to all the complexes studied (ν_{CT} is the absorption frequency of CT band, I_p is the ionization potential of the donor, E is the electron affinity of the acceptor and the term $C + \sigma/(I_p - E + C)$ takes into account the stabilization energy of the ion pair). It is evident from Table 1 that CT absorption maxima of EDA complexes generally decrease with increase in I_p of the donor. While uncertainties in the determination of ΔH in systems with small K-values would be large, the ΔH values are estimated to be well within ± 10% even after accounting for all possible sources of error.

If the electron donors in Table 1 are considered in three separate groups of methyl substituted (Group I), phenyl substituted (Group II) and polynucelar hydrocarbons (Group III), the complex stability order (as measured by K and ΔH) is: hexamethylbenzene > mesitylene > benzene (Group I) biphenyl > benzene (Group II) acenaphthene > pyrene > naphthalene > benzene (Group III) The above orders satisfy the condition that lower the I_p higher is the stability of the complex.

The half-band widths ($\Delta\nu_{1/2}$) increase with increase in complex strength (as measured by ΔH) and follow the above order with the exception of pyrene in Group III. This direct relationship between $\Delta\nu_{1/2}$ and the strength of complexes was earlier[7,8,9-12] attributed to the large resonance interaction in the complexes. The values of ε and the oscillator strength (f) of

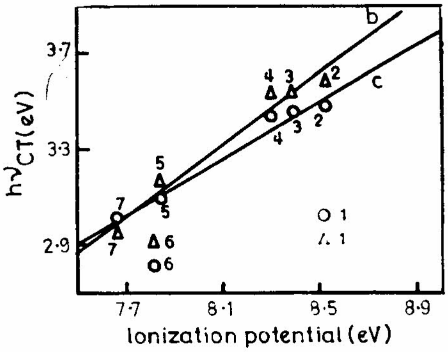

Fig. 1—hν_{CT} versus ionization potential (I_p) plots for EDA complexes of aromatic hydrocarbons with (a) TBPA and (b) TCPA (the numbers refer to donors listed in Table 1)

Table 1—Spectral and Thermodynamic Data for EDA Complexes of Aromatic Hydrocarbons with TBPA and TCPA[(a)] in CCl_4 Solution

Electron Donor	Ionisation potential	Electron acceptor[(b)]	λ_{CT} (nm)	$K^{(c)}$ (dm^3, mol^{-1})	ε ($dm^3\ mol^{-1}cm^{-1}$)	$-\Delta H$ (kcal mol^{-1})	$\Delta\nu_{1/2}$	f	$\Delta\nu^{(d)} \times 10^{-2}$ (cm^{-1})
Benzene	9.24	(i)	350	1.48	666	0.24	1243	0.003	8
		(ii)	340	0.42	704	0.36	1115	0.003	
Biphenyl	8.53	(i)	345	1.40	1071	1.4	1741	0.006	10
		(ii)	357	0.63	1666	2.9	2032	0.015	
Mesitylene	8.39	(i)	350	3.3	1500	1.6	2152	0.014	8
		(ii)	360	5.2	978	3.9	2164	0.019	
Naphthalene	8.30	(i)	350	3.8	1000	3.0	2003	0.009	10
		(ii)	362	2.3	1667	2.0	3409	0.026	
Hexamethylbenzene	7.85	(i)	390	13.4	1409	7.0	4536	0.028	6
		(ii)	400	12.1	1833	5.9	4845	0.038	
Pyrene	7.82	(i)	425	9.0	1300	5.0	3323	0.013	8
		(ii)	440	5.6	1333	2.8	6945	0.023	
Acenaphthene	7.66	(i)	420	9.3	778	5.8	3652	0.012	6
		(ii)	410	8.4	821	3.5	5403	0.019	

[(a)] Data from references (7) and (8)

[(b)] (i) TCPA, (ii) TBPA

[(c)] At 26°C; data are given at one temperature only for the sake of brevity.

[(d)] The difference in the ν_{CT} values of TCPA and TBPA.

EDA complexes, which provide a measure of the intensity of CT band, follow the above order in the case of donors of Groups I and II. However, in the case of the donors of Group III these values are in the order: benzene < acenaphthene < pyrene < naphthalene.

It is, thus, seen that the intensity of CT band increases for donors of Groups I and II as the strength of interaction (as measured by ΔH) increases. However, intensity of CT band decreases as the strength of interaction increases in the case of donors of Group III (with the exception of benzene). Similar observations have been made earlier in some instances[8,10]. This exceptional behaviour may possibly be due to the difference in the overlap parameter (σ) of the Mulliken's original relationship for the three groups of donors.

It is known that for a series of EDA complexes of donors of like structure with acceptors of, also of like structures, the shift ($\Delta\nu$) should be constant. In Table 1, the $\Delta\nu$ values of corresponding CT bands of TCPA and TBPA complexes ($\Delta\nu$ represents the difference in ν_{CT} values of TCPA and TBPA) are nearly constant indicating that the mode of interaction of both the acceptors in these complexes is the same. Similar observations have been made on structurally identical chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone as acceptors[10,13].

Nagy and coworkers[14] have estimated the electron affinity (E) of TBPA to be 0.7 eV in a series of EDA complexes with a common electron donor and closely related electron acceptors. This value, being higher than that for TCPA (0.58 eV) seems to suggest that TBPA should be a better electron acceptor than TCPA. Accordingly, the stability of the naphthalene + TBPA complex has been reported[3] to be higher than that of naphthalene + TCPA complex. The values of λ_{CT}, $\Delta\nu_{1/2}$, ε and f in Table 1 are generally higher for the TBPA complexes than those for TCPA complexes. The slope of the $h\nu_{CT}$ versus I_p plot, a, is smaller for TBPA (0.6) than that for TCPA (0.75) (see Fig. 1). It may be mentioned here that the values of $\Delta\nu_{1/2}$, ε and f are known to increase with increase in the strength of interaction for a number of EDA complexes[7,8,9-12,15,16]. Also, the smaller the a and the ν_{CT} values the stronger is the resonance interaction[17]. Based on these observations, TBPA appears to be a better electron acceptor than TCPA. However, the K and ΔH values (which are measure of the stability of the EDA complexes) are generally higher for the TCPA complexes. This may be due to larger uncertainty in the measurement of K and ΔH values in these systems.

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