

## Spectroscopic studies of the electron donor-acceptor interactions of aromatic hydrocarbons with tetrachlorophthalic anhydride

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MS received 9 February 1983; revised 29 April 1983

**Abstract.** Electron donor-acceptor (EDA) interactions of tetrachlorophthalic anhydride (TCPA) with benzene, *p*-xylene, mesitylene, fluorene, *t*-stilbene and pyrene have been investigated by spectroscopic technique. The spectroscopic and thermodynamic parameters of the complexes formed are reported. The enthalpies of formation range between 0.2 to 5.0 kcal mole<sup>-1</sup>. Among all the donors studied, pyrene appears to be the strongest electron donor towards tetrachlorophthalic anhydride.

**Keywords.** Tetrachlorophthalic anhydride; electron donor acceptor complexes; formation constants; spectroscopic studies.

### 1. Introduction

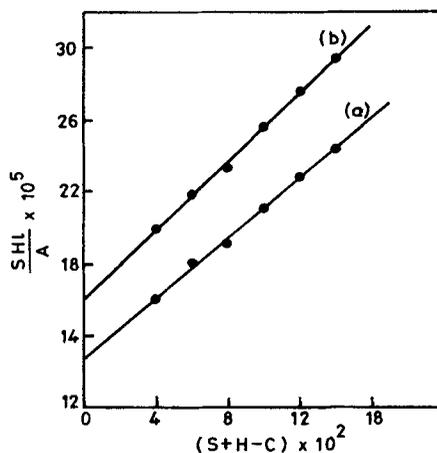
Our interest in tetrachlorophthalic anhydride (TCPA) as electron acceptor arose from the observation that the electron affinity of TCPA (1.8 eV) is comparable to that of 1,3,5-trinitrobenzene (1.86 eV), which is known to be a good electron acceptor. In spite of this, relatively little attention has been focussed towards investigating the electron donor-acceptor (EDA) complexes of TCPA (Dwivedi and Banga 1980a). Stable molecular complexes of TCPA with aromatic hydrocarbons and aza-aromatics are known (Czekalla 1956) to form. Formation constants of 1:1 EDA complexes of polynuclear aromatic hydrocarbons with TCPA have been determined by Chowdhury and Basu (1960). Dwivedi and Banga (1980a) have reported the enthalpies of formation of a number of EDA complexes formed between aromatic hydrocarbons and TCPA. The  $h\nu_{CT}$ -ionization potential plot was found to be linear. As part of an extended programme to study the EDA complexes of TCPA, we have presently investigated the interaction of TCPA with benzene, *p*-xylene, mesitylene, fluorene, *t*-stilbene and pyrene.

### 2. Experimental

Benzene, *p*-xylene (BDH, AR) and mesitylene (SRL) were purified by fractional distillation. Fluorene, *t*-stilbene and pyrene (supplied by Aldrich Chemical Co., USA) were purified by recrystallization from alcohol. TCPA was repeatedly crystallized from benzene until its absorption spectrum in CCl<sub>4</sub> showed no further change on successive crystallization. CCl<sub>4</sub> (E. Merck, G. R.) was dried and distilled before use.

Electronic absorption spectra were recorded on a Beckman DU spectrophotometer

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**Figure 1.** Modified Scott equation plot for the fluorene-TCPA complex at **a.** 21°C and **b.** 31°C. ( $S$  and  $H$  are the initial concentrations of the donor and acceptor,  $C$  is the concentration and  $A$  is the absorbance of the complex and  $l$  is the optical path length).

fitted with variable temperature cell compartment using matched silica cells of 1 cm path length. Equilibrium constant of formation,  $K$ , and molar extinction coefficient,  $\epsilon$ , of the EDA complexes were determined employing the modified Scott equation (Scott 1956) by measuring the absorbance (at the  $\lambda_{\max}$  of the charge-transfer band) of a series of solutions with varying donor concentration and a fixed TCPA concentration. In evaluating  $K$ , Person's criteria regarding donor concentration were satisfied (Person 1965). The  $K$  and  $\epsilon$  values of the complexes have an uncertainty of less than  $\pm 10\%$  as can be seen from figure 1 for the Fluorene-TCPA system. The enthalpies of formation,  $\Delta H$ , of the EDA complexes were evaluated from the equilibrium constants at different temperatures in the range 10–40°C. Freshly prepared stock solutions of the donor and acceptor were used in all the measurements.

### 3. Results and discussion

The charge-transfer bands of all the EDA complexes appear in the region of the donor absorption and therefore the charge-transfer band maxima ( $\lambda_{CT}$  values) were obtained by difference spectra (figure 2). The results of the present investigation are summarised in table 1. The  $\lambda_{CT}$  values for the EDA complexes of TCPA with *t*-stilbene and pyrene agree well with those reported by Chowdhury and Basu (1960). However, the  $K$  and  $\epsilon$  values in these systems differ from our data. We believe that the present values are more reliable since the donor concentration employed was sufficiently high and satisfied Person's (1965) criteria. Mulliken (1952) pointed out that the lower the ionization potential, higher will be the stability (as measured by  $K$  and  $\Delta H$ ) of the EDA complex. This is found to be true from our data in table 1. While uncertainties in the determination of  $\Delta H$  in systems with small  $K$  values would be large, the  $\Delta H$  values are estimated to be well within  $\pm 10\%$  even after accounting for all possible sources of error. These  $\Delta H$  and  $K$  values for the complexes studied are comparable to other  $\pi$ -donor- $\pi$ -acceptor systems (Rao *et al* 1971), indicating that TCPA acts as a  $\pi$ -acceptor in these systems. The  $\Delta H$  values with compounds 1, 2 and 3 (table 1) as electron donors are very small and reminiscent of contact pairs (Dwivedi and Rao 1970). The half band

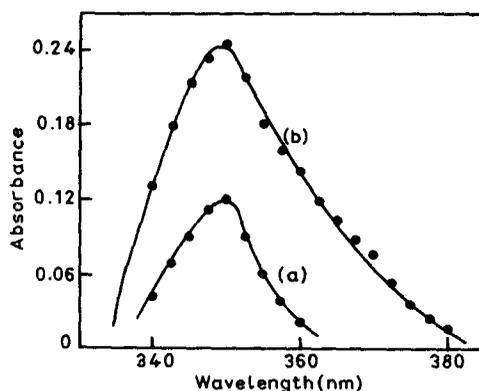


Figure 2. Electronic absorption spectra of a. benzene (0.4 M) + TCPA ( $4.0 \times 10^{-4}$  M) and b. *p*-xylene (0.4 M) + TCPA ( $4.0 \times 10^{-4}$  M) in  $\text{CCl}_4$  solution.

Table 1. Spectroscopic and thermodynamic data for EDA complexes of aromatic hydrocarbons with TCPA in  $\text{CCl}_4$  solution.

Electron donor	$I_p$ (eV)	$\lambda_{\text{CT}}$ (nm)	$K^*$ ( $\text{l mol}^{-1}$ )	$\epsilon$ ( $\text{l mol}^{-1} \text{cm}^{-1}$ )	$-\Delta H$ ( $\text{k cal mol}^{-1}$ )	$\Delta v_{1/2}$ ( $\text{cm}^{-1}$ )	$f$
Benzene	9.24	350	$1.5 \pm 0.1$	$666 \pm 40$	$0.24 \pm 0.02$	1243	0.003
<i>p</i> -xylene	8.44	350	$2.2 \pm 0.2$	$1363 \pm 40$	$0.46 \pm 0.03$	1787	0.011
Mesitylene	8.39	350	$3.5 \pm 0.2$	$1500 \pm 50$	$1.6 \pm 0.1$	2152	0.014
Fluorene	—	350	$6.7 \pm 0.2$	$1177 \pm 50$	$2.6 \pm 0.2$	812	0.004
<i>t</i> -stilbene	7.99	350	$7.7 \pm 0.1$	$1077 \pm 40$	$3.6 \pm 0.2$	1124	0.005
Pyrene	7.82	425	$10.4 \pm 0.1$	$1300 \pm 50$	$5.0 \pm 0.2$	3323	0.043

\*at 21°C; data are given at one temperature only for the sake of brevity.

width ( $\Delta v_{1/2}$ ),  $\epsilon$  and oscillator strength ( $f$ ) data can be analysed if one carefully chooses electron donors which are similar in structure. Thus, if the donors in table 1 are considered in three separate groups of methyl substituted (group 1), phenyl substituted (group 2) and polynuclear hydrocarbons (group 3), the  $\Delta v_{1/2}$  order is:

mesitylene > *p*-xylene > benzene  
*t*-stilbene < benzene  
 pyrene > fluorene < benzene

The  $\Delta v_{1/2}$  values increase with increasing complex strength (as measured by  $-\Delta H$ ) with the exception of benzene. This direct relationship between  $\Delta v_{1/2}$  and the strength of the complexes was observed earlier (Dwivedi and Banga 1980b; Dwivedi *et al* 1982) and was attributed to the large resonance interaction in the complexes.

The  $\epsilon$  and  $f$  values of the EDA complexes provide a measure of the intensity of the charge-transfer (CT) band. Based on these data in table 1, the CT band intensity order is:

mesitylene > *p*-xylene > benzene  
*t*-stilbene > benzene  
 pyrene > fluorene > benzene

It is, thus, seen that the intensity of the CT band increases as the strength of interaction increases in electron donors of all the three groups. This observation is similar to that reported by Daisey and Sonnessa (1972) and Dwivedi and Banga (1980b,c) for a number of EDA complexes.

### Acknowledgement

The award of a Junior Research Fellowship (to AG) by the CSIR, New Delhi, is gratefully acknowledged.

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