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Solvent effects on charge-transfer intensities and heats of formation of chloranil complexes with aromatic hydrocarbons

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Abstract—The spectrophotometric and thermodynamic properties of the charge-transfer complexes of chloranil with aromatic hydrocarbons such as benzene, toluene, xylenes (*o*-, *m*- and *p*-) and mesitylene have been studied in *n*-heptane solvent to make a correlation between the charge-transfer intensities and the heats of formation of the complexes. The results disagree with MULLIKEN's prediction—the charge-transfer intensities decrease with increase of heats of formation. An attempt has been made to calculate the thermodynamic as well as spectrophotometric properties of these complexes free from the influence of chloranil–solvent interaction and the results thus obtained show a good correlation between the charge-transfer intensities and the heats of formation of the complexes.

INTRODUCTION

The usage of the term charge-transfer (CT) complex implies that the stability of the complex is mainly due to the mixture of ionic CT states with the neutral ground state of the donor–acceptor pair. In the CT theories [1–3], it has usually been assumed that the same pair of orbitals is involved in the bonding and the transition. However, at least in some complexes, the possibility of bonding partly or solely due to (a) the overlap of orbitals other than those involved in the observed CT transition and (b) interactions other than those of CT cannot be ruled out. For the molecular complexes where bonding is mainly due to CT interaction, it should be possible to relate, as was first done by MULLIKEN [4], the transition probability to the stability (or heat of formation) unless different sets of orbitals are involved in the two phenomena. According to MULLIKEN, the oscillator strengths (f) of CT transitions should vary directly with the heats of formation ($-\Delta H^\circ$) in a series of related complexes. This relation has been shown to be true in the case of strong complexes like iodine with *N*-heterocyclics [5], but results on weak complexes disagree with MULLIKEN's prediction. However, in the case of weak complexes like fluoranil with aromatic hydrocarbons, the expected relation between equilibrium constants (K_c) and molar extinction coefficients (ε_c) was reported [6]. The values of K_c were determined from the NMR absorption measurements, which in turn were utilized to separate ε_c values of the spectral studies. To account for the observed discrepancy in weak complexes, the modification of MULLIKEN's theory involves (a) the contribution from the nonbonded contact pairs to the CT intensity [7], and (b) the possibility of interaction between the locally excited states of the donor and the CT states as a source of CT intensity [8, 9]. In the case of weak complexes, the role of solvent is very important. The variation of both the thermodynamic as well as the spectrophotometric properties of the same CT complex in different solvents is assumed to be due to the solvent interaction with the electron acceptors [10–13]. An attempt has also been made to calculate the thermodynamics of the solvent interaction with the electron acceptors. It has been found [14] that the CT complexes of iodine with aromatic hydrocarbons free from the influence of iodine–solvent interaction agree with MULLIKEN's prediction. Recently we have studied the thermodynamic and spectrophotometric properties of chloranil complexes with benzene and mesitylene [15] in different solvents and from the results, the thermodynamic properties of the chloranil–solvent interaction have been computed. The computed results of the chloranil–solvent interaction have been justified by the study of chloranil–pyrene complex in different solvents [16]. The CT complexes of chloranil with aromatic hydrocarbons are reinvestigated in *n*-heptane with the intention of comparing the CT intensities, i.e. oscillator strengths (f) and transition dipole moments (D), with the heats of formation ($-\Delta H^\circ$) of the complexes instead of comparing formation constants, K_c, with molar extinction coefficients, ε_c, as done in most previous experimental works. The anomalies arising due to the solvent effect on these CT complexes are also investigated.

EXPERIMENTAL

Chloranil (BDH) was recrystallized from benzene and dried in a vacuum desiccator. G.R. quality aromatic hydrocarbons (BDH) were fractionally distilled just before use. Spectrograde *n*-heptane supplied by Fluka was used without further purification.

Absorption spectra were recorded on a Perkin–Elmer Model 200 spectrophotometer using a matched pair of stoppered fused silica cells of 1 cm optical path length placed in a thermostatted cell holder. All measurements were done on freshly prepared solutions.

RESULTS

The absorption spectra of mixed solutions with a fixed concentration of chloranil and varying concentrations of benzene in *n*-heptane solvent at 24°C are shown in Fig. 1. The absorption spectra of other aromatic hydrocarbon–chloranil complexes in *n*-heptane solvent are of similar nature except the extent of overlapping with the spectra of aromatic hydrocarbon and chloranil in the shorter wavelength region and the position of the absorption maximum of the complex. These spectrophotometric data were employed to calculate the equilibrium constant, K_c, and molar extinction coefficient, ε_c, of the chloranil–aromatic hydrocarbon complexes in *n*-heptane using the Scott equation [17]. For a 1 : 1 complex, this equation can be written as

$$\frac{[A][D]l}{d} = \frac{[D]}{\varepsilon_c} + \frac{1}{K_c \varepsilon_c} \qquad (1)$$

where [A] and [D] are the initial molar concentrations of the electron acceptor (chloranil) and the electron donor (aromatic hydrocarbon) respectively; l is the optical path length of the cell; d is the absorbance of the complex. Equation (1) is applicable when $[D] \gg [A]$ and the complex absorbs at a wavelength where both electron acceptor and donor have no appreciable absorption. The little absorption due to chloranil in *n*-heptane at the absorption maxima of the CT complexes is considered in measuring the absorbance, d. The plots of $[A][D]l/d$ against [D] were found to be linear in all cases showing 1 : 1 complexing. K_c and ε_c were calculated from the slope and intercept of the curve. The absorption spectra due solely to the CT complex of chloranil–aromatic hydrocarbon were obtained by a similar method as mentioned earlier [5]. These spectra are presented in Fig. 2. Thus ε_c obtained from these absorption spectra due solely to the CT complexes was always compared with the value calculated from the slope of the curve obtained from the plots of $[A][D]l/d$ vs [D]. The identical value of ε_c in both cases helped us to justify the reliability of the results. The thermodynamic quantities of these complexes were obtained from K_c values at three different temperatures (38, 24 and 14°C) by the usual method, and the values are presented in Table 1. Almost identical values of K_c and thermodynamic quantities of these complexes were obtained by using both Benesi–Hildebrand [18] and Scatchard [19] equations and the results were reported elsewhere [20].

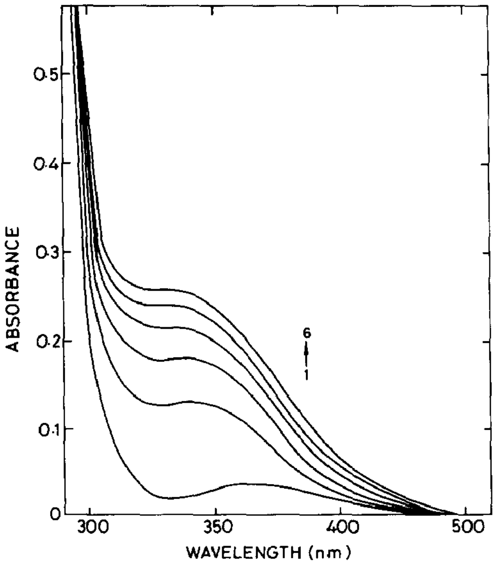

Fig. 1. The absorption spectra of chloranil–benzene in *n*-heptane at 24°C (1 cm cell). Concentration of chloranil: 1.285 × 10^{-4} mol dm^{-3}; concentration of benzene (mol dm^{-3}): (1) 0.0, (2) 1.124, (3) 2.248, (4) 3.372, (5) 4.496 and (6) 5.620.

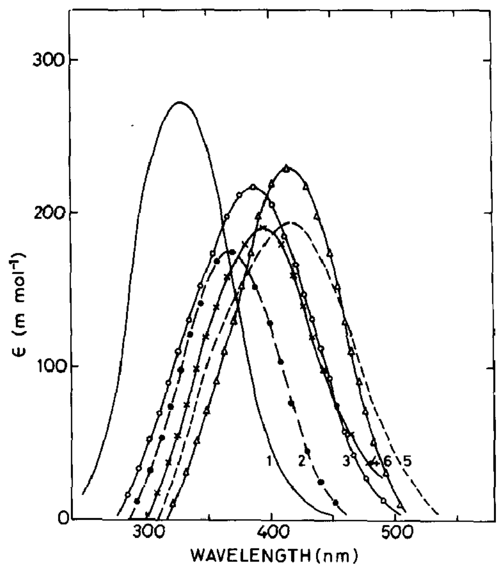

Fig. 2. The charge-transfer absorption spectra of chloranil–aromatic hydrocarbon complexes in *n*-heptane. The aromatic hydrocarbons are: (1) benzene, (2) toluene, (3) *m*-xylene, (4) *o*-xylene, (5) *p*-xylene and (6) mesitylene.

The experimental oscillator strength (f) and the transition dipole moment (D) were calculated using the following approximate formulae [3] after making appropriate correction for the medium effect:

$$f = 4.319 \times 10^{-9} n^{-2} [\varepsilon_{max} \Delta\bar{\nu}_{1/2}] \qquad (2)$$

and

$$D = 0.0958\, n^{-1/2} \left[\frac{\varepsilon_{max} \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max}} \right]^{1/2} \qquad (3)$$

where $\Delta\bar{\nu}_{1/2}$ is the band width at half intensity; n is the refractive index of the medium; ε_{max} and $\bar{\nu}_{max}$ are the molar extinction coefficient and wave number respectively at the absorption maximum of the complex. The spectrophotometric properties of these complexes are also reported in Table 1.

DISCUSSION

There are reports [21] of both 1:1 and 2:1 CT complexes between aromatic hydrocarbons and different electron acceptors when the concentration of aromatic hydrocarbon is many times larger than that of the electron acceptors. Our earlier results [15, 16] on chloranil complexes with benzene, mesitylene and

Table 1. Thermodynamic and spectrophotometric results of chloranil complexes with aromatic hydrocarbons in *n*-heptane at 24°C

					Charge-transfer band				
Donor*	K_c ($dm^3\,mol^{-1}$)	$-\Delta G^\circ$ ($kJ\,mol^{-1}$)	$-\Delta H^\circ$ ($kJ\,mol^{-1}$)	$-\Delta S^\circ$ ($J\,mol^{-1}\,deg^{-1}$)	λ_{max} (nm)	ε_c ($m^2\,mol^{-1}$)	$\Delta\bar{\nu}_{1/2}$ (cm^{-1})	f ($m\,mol^{-1}$)	D (10^{-20} C)
Benzene	0.39 ± 0.03	-2.32 ± 0.13	15.21 ± 0.89	59.00 ± 3.43	330	269 ± 20	9697	0.584	7.94
Toluene	1.03 ± 0.04	0.08 ± 0.05	17.62 ± 0.45	59.05 ± 1.35	366	226 ± 25	9416	0.476	7.56
m-Xylene	1.59 ± 0.16	1.15 ± 0.17	19.28 ± 1.46	61.03 ± 4.35	388	213 ± 19	8931	0.426	7.36
o-Xylene	1.82 ± 0.19	1.49 ± 0.18	19.93 ± 1.58	62.11 ± 4.70	397	213 ± 23	8654	0.413	7.33
p-Xylene	1.98 ± 0.21	1.70 ± 0.18	20.95 ± 1.79	64.82 ± 5.43	413	196 ± 21	8622	0.379	7.17
Mesitylene	2.24 ± 0.21	2.00 ± 0.16	22.44 ± 1.78	68.79 ± 5.45	415	238 ± 16	6756	0.361	7.00

*The concentration of chloranil used in all cases is 1.285×10^{-4} mol dm^{-3}. Concentration ranges of aromatic hydrocarbons used are (mol dm^{-3}): benzene, 1.124–5.620; toluene, 0.938–4.69; *m*-xylene, 0.818–4.09; *o*-xylene, 0.829–4.145; *p*-xylene, 0.811–4.055 and mesitylene, 0.72–3.60.

pyrene as well as the present experimental data show the evidence of 1:1 complex formation only. As the saturation fraction [22] of the dilute component, [AD]/[A] here, lies between 0.31 and 0.84, reasonably accurate values in K_c and ε_c can be expected from our experimental data.

The experimental results of chloranil complexes with aromatic hydrocarbons in *n*-heptane (Table 1) show that the stabilities of the complexes ($-\Delta H^\circ$) increase with the decrease of the CT intensities, i.e. the oscillator strengths (f) and the transition dipole moments (D), and the relation does not support MULLIKEN's theory [4] in the case of weak CT complexes. Change of solvent can have a rather larger change on the measured equilibrium constant, so solvent competition must be taken into account. Considering a second equilibrium between chloranil and the solvent *n*-heptane [15, 16], in addition to the normal chloranil–aromatic hydrocarbon interaction, an equation can be developed. Suppose the reactions

$$D + A \rightleftharpoons DA \quad K_1 = \frac{[C_1]}{[D]\{[A]-[C_1]-[C_2]\}} \tag{4}$$

$$S + A \rightleftharpoons SA \quad K_2 = \frac{[C_2]}{[S]\{[A]-[C_1]-[C_2]\}} \tag{5}$$

where $[C_1]$ and $[C_2]$ are the molar concentrations of chloranil complexes of aromatic hydrocarbons and *n*-heptane respectively. For the experimental conditions employed, $[D] \gg [C_1]$ and $[S] \gg [C_2]$. Then analysis similar to the derivation of equation (1) yields the relation

$$\frac{[A][D]l}{d} = \frac{[D]}{\varepsilon_1 + \varepsilon_2 \dfrac{K_2[S]}{K_1[D]}} + \frac{1 + K_2[S]}{K_1\left\{\varepsilon_1 + \varepsilon_2 \dfrac{K_2[S]}{K_1[D]}\right\}} \tag{6}$$

where ε_1 and ε_2 are the molar extinction coefficients of the chloranil complexes of aromatic hydrocarbons and *n*-heptane respectively at the wavelength region of the chloranil–aromatic hydrocarbons CT transitions. Comparing equation (6) with equation (1) one obtains the relations

$$K_c = \frac{K_1}{1 + K_2[S]} \tag{7}$$

$$\varepsilon_c = \varepsilon_1 + \varepsilon_2 \frac{K_2[S]}{K_1[D]}. \tag{8}$$

The equations (7) and (8) show that K_c and ε_c calculated from equation (1) are markedly affected when a solvent like *n*-heptane interacts with chloranil, i.e. we underestimate K_c and overestimate ε_c. Further, these equations also show that K_c calculated from equation (1) is a function of K_2, the *n*-heptane–chloranil interaction equilibrium and ε_c is dependent on the term $\varepsilon_2 K_2[S]/K_1[D]$ which appears when absorbance due to the contact CT interaction of chloranil with *n*-heptane is considered. The equilibrium constants of chloranil complexes with aromatic hydrocarbons free from the solvent interaction are calculated at different temperatures from equation (7) using the earlier reported equilibrium constant of chloranil–*n*-heptane interaction free from other interactions [15]. The results are reported in Table 2 along with the thermodynamic quantities. With the help of these equilibrium constant values, the absorption spectra due solely to CT complexes of chloranil–aromatic hydrocarbons free from solvent interaction are calculated from the recorded absorption spectra of chloranil in pure aromatic hydrocarbons. The molar extinction coefficients of these complexes thus obtained are compared with the values calculated from equation (8) using experimental results in *n*-heptane and the values in both cases are almost identical. All the spectrophotometric properties of the chloranil–aromatic hydrocarbons CT complexes free from solvent interaction are also mentioned in Table 2. The results show that the thermodynamic as well as spectrophotometric properties of chloranil complexes with aromatic hydrocarbons free from the solvent–chloranil interaction are markedly changed and the relation between the stabilities of the complexes vs CT intensities has much improved. Figure 3 shows the plot of transition dipole moment (*D*) of the CT absorption bands against the stability of the CT complex ($-\Delta H°$) of the chloranil–aromatic hydrocarbons before and after solvent correction.

Without solvent correction (curve a), an inverse correlation exists between *D* and $-\Delta H°$. After solvent correction (curve b), an appropriate relationship between *D* and $-\Delta H°$ does exist but the straight line does not go through the origin. According to classical theory [23], *f* is related to the square of *D*, so a

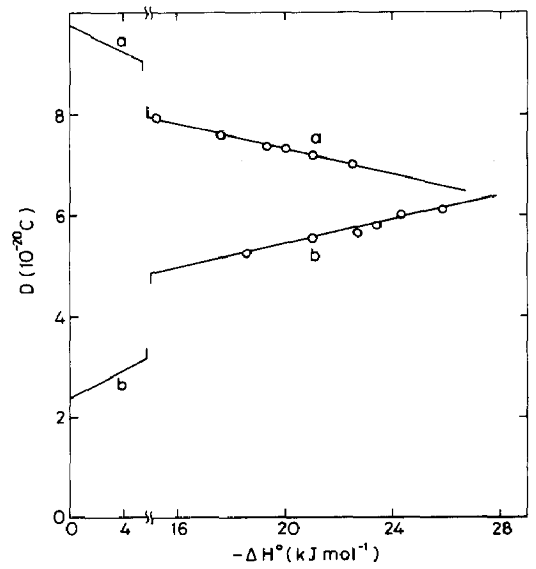

Fig. 3. Plot of transition dipole moment (*D*) of the CT absorption bands against the stabilities of the chloranil–aromatic hydrocarbon complexes ($-\Delta H°$). Curves (a) and (b) refer to the values with and without solvent–chloranil interaction respectively.

Table 2. Thermodynamic and spectrophotometric results of chloranil complexes with aromatic hydrocarbons free from other interactions at 24°C

Donors	K_1 (dm^3 mol^{-1})	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$-\Delta S°$ (J mol^{-1} deg^{-1})	Charge-transfer absorption spectra* λ_{max} (nm)	ε_1 (m^2 mol^{-1})	$\Delta\bar{\nu}_{1/2}$ (cm^{-1})	*f* (m mol^{-1})	*D* (10^{-20}C)
Benzene	0.673	−0.98	18.55	65.76	336	223	5392	0.230	5.239
Toluene	1.766	1.41	20.97	65.83	362	171	7310	0.241	5.547
m-Xylene	2.723	2.49	22.64	67.84	385	160	7547	0.233	5.633
o-Xylene	3.112	2.82	23.34	69.10	390	163	7799	0.242	5.796
p-Xylene	3.389	3.03	24.33	71.69	408	163	7994	0.252	6.029
Mesitylene	3.837	3.34	25.79	75.59	416	159	8246	0.252	6.097

*Values are obtained from the absorption spectra of chloranil in pure aromatic hydrocarbons with the help of equilibrium constants mentioned in this table.

nonlinear relationship between f and $-\Delta H^\circ$ is expected and it is supported by our experimental results. A linear relationship has been found between f and the square of $-\Delta H^\circ$ and the nature of the curves before and after solvent correction is similar to that of D vs $-\Delta H^\circ$ plots.

Thus, in the case of weak CT complexes like chloranil–aromatic hydrocarbons, the solvent plays an important role by complexing with chloranil and changes both the thermodynamic and spectrophotometric properties of the CT complexes due to solvent–chloranil interaction. MULLIKEN's theory also holds good to some extent in these weak complexes if solvent interaction is considered and corrected. However, we cannot ignore the other important factors involved such as thermodynamic nonideality of the solution, solvation of the CT complexes, variation of the geometry of these weak complexes in solution etc. which are also responsible for the observed discrepancy of the CT theory. The number of these factors, together with the fact that they combine to produce small overall changes in an already small ΔH value which is difficult to measure precisely experimentally, severely complicates the design of experiments to elucidate their respective roles.

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