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THERMOCHEMISTRY OF SOME π–π^* CHARGE TRANSFER COMPLEXES FORMED BETWEEN METHYLBENZENE DONORS AND π-ELECTRON ACCEPTORS

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The heats of formation for π–π^* charge transfer interactions have been computed from the charge transfer spectra of molecular complexes formed between methylbenzene donors and π-electron acceptors.

The techniques of ultraviolet/visible spectroscopy have led to great success in the measurement of charge transfer (CT) transition energies of CT complexes formed between various types of donors and acceptors. These data constitute the raw material needed for the theoretical prediction of energy functions of CT complexes. The experimental techniques are sometimes less successful in the examination of CT complexes in relation to their heats of formation (ΔH_f), for ΔH_f may be subject to uncertainties of several kJ/mol. Here theoretical relations, though empirical in nature, should be competitive and may frequently provide better results. For those complexes for which there are no experimental data, theoretical ΔH_f should replace the speculative guesswork often presented in the literature, especially for π–π^* CT complexes, where the magnitude of ΔH_f is of the order of 4–17 kJ/mol [1] and hence the uncertainty in the experimental data is higher. Therefore, as a continuation of our studies on the thermochemistry of molecular complexes [2–10] in relation to ΔH_f, we have examined the π–π^* CT complexes formed between methylbenzene donors and three acceptors, viz. pyromellitic dianhydride (PMDA), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 2,3-dicyano-*p*-benzoquinone (DCNQ). The experimental values of the transition energies, $h\nu_{CT}$, [11, 12] are used to evaluate some of the energy parameters, employing the model of Sonnesa and Daisey [13], and use is then made of these parameters to estimate the

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values of ΔH_f for the π–π^* ground state complexes formed in the above systems via the empirical relation reported earlier from our laboratory:

$$\frac{b^2}{7.30a^2} = \frac{-\Delta H_f}{h\nu_{\mathrm{CT}}}$$

The average uncertainty between the observed and calculated values of ΔH_f is of the order of ±0.018 eV [4]. The experimental and calculated values of the energy parameters and the values of ΔH_f predicted from the formula are given in Tables 1–3. The meanings of the various symbols used are explained in the Appendix.

Table 1 Experimental and theoretical energy parameters (in eV except *a*, *b* and *F* otherwise mentioned) for CT complexes of PMDA with some donors

Donors	Energy parameters						
	$h\nu^*_{\mathrm{CT}}$	Δ	$-X_0$	a	b	F	$-\Delta H_f^{\neq}$ (kJ/mol)
Benzene	4.164	3.585	0.259	0.965	0.250	6.491	3.686
Toluene	3.755	3.114	0.292	0.957	0.280	8.107	4.246
o-Xylene	3.582	2.908	0.309	0.952	0.294	8.919	4.493
m-Xylene	3.545	2.863	0.313	0.951	0.299	9.222	4.627
p-Xylene	3.483	2.789	0.320	0.949	0.304	9.538	4.723
1,2,4-Trimethyl benzene	3.346	2.620	0.337	0.944	0.319	10.471	5.041
Mesitylene	3.383	2.666	0.332	0.946	0.315	10.217	4.958
Durene	3.173	2.402	0.360	0.938	0.339	11.807	5.481
Pentamethyl benzene	3.024	2.207	0.384	0.929	0.358	13.152	5.924
Hexamethyl benzene	2.851	1.971	0.417	0.919	0.385	15.173	6.606

* Ref. [11]; $\beta_0 = -1.00$ eV; $S_{01} = 0.01$, ≠ predicted from the empirical formula.

Table 2 Experimental and theoretical parameters (in eV except *a*, *b* and *F* otherwise mentioned) for CT complexes of DDQ with some donors

Donors	Energy parameters						
	$h\nu^*_{\mathrm{CT}}$	Δ	$-X_0$	a	b	F	$-\Delta H_f^{\neq}$ (kJ/mol)
Benzene	3.049	2.240	0.379	0.932	0.355	12.900	5.836
Toluene	2.814	1.918	0.425	0.916	0.391	15.628	6.761
o-Xylene	2.615	1.624	0.474	0.899	0.428	18.694	7.824
m-Xylene	2.615	1.624	0.474	0.899	0.428	18.694	7.824
p-Xylene	2.429	1.315	0.537	0.876	0.473	22.744	9.334
Mesitylene	2.429	1.315	0.537	0.876	0.473	22.744	9.334
Durene	2.132	0.857	0.621	0.834	0.543	29.982	11.962
Pentamethyl benzene	2.082	0.731	0.673	0.803	0.567	32.605	13.627
Hexamethyl benzene	1.983	0.390	0.783	0.768	0.632	40.425	17.719

* Ref. [12]; $\beta_0 = -1.00$ except for Durene and pentamethyl benzene $\beta_0 = -0.96$ eV, $S_{01} = 0.01$, ≠ predicted from the empirical formula.

Table 3 Experimental and theoretical energy parameters (in eV except *a*, *b* and *F* otherwise mentioned) for CT complexes of DCNQ with some donors

Donors	Energy parameters						
	$h\nu^*_{CT}$	Δ	$-X_0$	a	b	F	$-\Delta H^{\neq}_f$ (kJ/mol)
Benzene	3.185	2.418	0.358	0.938	0.337	11.676	5.435
Toluene	2.949	2.106	0.397	0.926	0.369	13.951	6.188
o-Xylene	2.752	1.829	0.439	0.912	0.402	16.526	7.070
m-Xylene	2.752	1.829	0.439	0.912	0.402	16.526	7.070
p-Xylene	2.566	1.546	0.489	0.890	0.437	19.508	8.112
Mesitylene	2.603	1.604	0.478	0.898	0.431	18.987	7.937
Durene	2.293	1.054	0.601	0.852	0.515	26.963	11.075
Pentamethyl benzene	2.255	0.972	0.624	0.843	0.529	28.435	11.736
Hexamethyl benzene	2.132	0.857	0.621	0.834	0.543	29.982	11.962

* Ref. [12]; $\beta_0 = -1.00$ eV except for hexamethyl benzene where $\beta_0 = -0.96$ eV; $S_{01} = 0.01$; $\neq$ predicted from the empirical formula.

It is quite evident from Tables 1–3 that the whole set of theoretical data on ΔH_f fall well within the experimental range of 4–17 kJ/mole for π–π^* interactions reported in the literature [1]. However, the reliability of the theoretical ΔH_f data could not be tested due to the non-availability of experimental data on these systems in the literature. Further, a comparison of the various types of energy parameters (Tables 1–3) reveals that the electron affinities of the acceptors should follow the trend:

$$\mathrm{DDQ} > \mathrm{DCNQ} > \mathrm{PMDA}$$

Appendix

ν_{CT} — frequency of the CT band
a and b — weighting factors for the no-bond and dative structures of the CT complexes
F — charge transferred in the CT complex formation
X_0 — resonance interaction energy of the ground state of the CT complexes
h — Planck's constant
β_0 — resonance integral in the ground state of the CT complexes
S_{01} — overlap integral in the ground state of the CT complexes
Δ — energy difference between the dative and no-bond structures.

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