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ENERGETICS OF n-π^* AND π-π^* CHARGE-TRANSFER COMPLEXES FORMED BETWEEN AMINE DONORS AND CHLORANIL AS π-ELECTRON ACCEPTOR

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The heats of formation of n-π^* and π-π^* charge-transfer interactions have been computed from the charge-transfer spectra of molecular complexes formed in the pyridine-chloranil and aniline-chloranil systems.

Introduction

The antioxidant N-phenyl-2-naphthylamine acts as a booby trap for biochemists, because it is found as a contaminant of liquid extracts containing vitamin K, and is a result of charge-transfer (CT) complex formation between antioxidant and vitamin K derivatives [1]. Such complex formation is highly probable because phenolic and amine oxidant in general possess comparatively low ionization potentials (7–9 eV) [2] and are therefore expected to act as powerful electron donors under favourable circumstances. Since quinone-type structures are present in vitamin K as well as due to analytical utilization of the interactions between halonils as acceptors and amines [3] as electron donors, spectroscopic studies on the formation of CT complexes between quinones and amines have been reported by various workers [4–20]. However, the energetics of these complexes have not bee studied in detail and even where the experimental data on the energy parameters of these

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complexes are reported, they are not very reliable, as pointed out by Dwivedi and Rao [5]. The experimental techniques are sometimes less useful in the examination of CT complexes in relation to their heats of formation (ΔH), for ΔH may be subjected to an uncertainty of several $kJ \cdot mol^{-1}$ and where ΔH cannot be determined experimentally when the CT formation is kinetically controlled. 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 should replace the speculative guesswork often presented in the literature [21]. In view of this, as a continuation of our studies on the energetics of molecular complexes in relation to ΔH [22], we have now extended the work to n–π^* and π–π^* CT complexes formed in the pyridine-chloranil and aniline-chloranil systems.

The energy parameters were computed by employing the model of Sonnesa and Daisey [23] and the empirical relationship reported earlier [24], i.e.

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

The calculated values of the energy parameters, together with the experimental and predicted value of ΔH from the empirical relationship, are recorded in Tables 1–3. The meanings of the various symbols used in the text are explained in the Appendix. The theoretical ΔH data for n–π^* (Table 1) and π–π^* (Table 2) ground-state complexes formed in the pyridine-chloranil system could not be compared with the observed data, since these systems are kinetically controlled. The agreement between the observed and calculated values of ΔH for the aniline-chloranil systems is not very good, but the theoretical values follow the expected trend of the observed values (Table 3). This may be due to the following reasons:

i) it is likely that the equilibrium constants reported earlier [20] are in error since the method of evaluation [25] of these quantities is very sensitive to [donor], and

ii) it is difficult to measure experimentally the energetics of CT complexes because of the weak interaction between donor and acceptor and also because of the interactions of the solvent with donor and acceptor. Hence, we feel that the computed values of ΔH are more reliable than the experimental values reported earlier [20].

Table 1 Experimental and theoretical energy parameters for n–π^* CT complexes formed in aza–aromatic–chloranil systems (in eV except for a, b and F)

Aza–aromatics	$h\nu_{CT}^{\alpha}$	I.P.$^{\alpha}$	pK_a			Δ	$-R_N$	a	b	F	$-\Delta H^{\neq}$
			α	β	γ						kJ·mol^{-1}
2:4:6 sym Collidine	2.55	–	7.59	7.59	7.59	1.561	0.486	0.895	0.436	19.399	8.00
2:6 Lutidine	2.58	9.57	6.75	6.80	6.86	1.609	0.476	0.898	0.429	18.789	7.78
γ–Picoline	2.61	9.56	6.02	6.15	6.25	1.656	0.468	0.901	0.423	18.274	7.60
α–Picoline	2.64	9.66	5.97	5.50	5.65	1.702	0.460	0.904	0.417	17.765	7.42
β–Picoline	2.64	9.71	5.68	5.50	5.65	1.702	0.460	0.904	0.417	17.765	7.42
Isoquinoline	2.64	–	5.14	5.50	5.65	1.702	0.460	0.904	0.417	17.765	7.42
Quinoline	2.66	–	4.18	5.07	5.25	1.733	0.454	0.906	0.413	17.431	7.31
Pyridine	2.67	9.76	5.17	4.44	4.52	1.748	0.452	0.908	0.407	16.934	7.09

$^{\alpha}$ – Ref. [19], β – eq(iii), γ – eq (iv)

$\beta_O = -1.00$ eV; $S01 = 0.01$, $\neq$ predicted from the empirical formula

Table 2 Experimental and theoretical energy parameters for π–π^* CT complexes formed in aza–aromatic–chloranil systems (in eV except for a, b and F)

Aza–aromatics	$h\nu_{CT}$	I.P.			Δ	$-R_N$	a	b	F	$-\Delta H^{\neq}$ / kJ·mol^{-1}
		α	β	γ						
Isoquinoline	3.043	8.346	8.345	8.345	2.273	0.375	0.932	0.350	12.576	5.67
Quinoline	3.073	8.394	8.449	8.452	2.312	0.370	0.934	0.346	12.294	5.57
2:4:6 sym Collidine	3.277	8.944	9.052	9.027	2.575	0.341	0.943	0.322	10.671	5.05
2:6 Lutidine	3.294	8.944	9.100	9.066	2.594	0.339	0.943	0.320	10.541	5.01
β–Picoline	3.303	9.111	9.122	9.098	2.608	0.337	0.944	0.319	10.482	4.99
γ–Picoline	3.339	9.180	9.219	9.188	2.653	0.333	0.945	0.315	10.219	4.90
α–Picoline	3.357	9.108	9.243	9.204	2.675	0.331	0.946	0.314	10.156	4.89
Pyridine	3.375	9.271	9.299	9.289	2.698	0.328	0.947	0.311	10.003	4.81

α – Ref. [19], β – eq(i), γ – eq (ii)

$\beta_O = -1.00$ eV; $S_{01} = 0.01$, $\neq$ predicted from the empirical formula

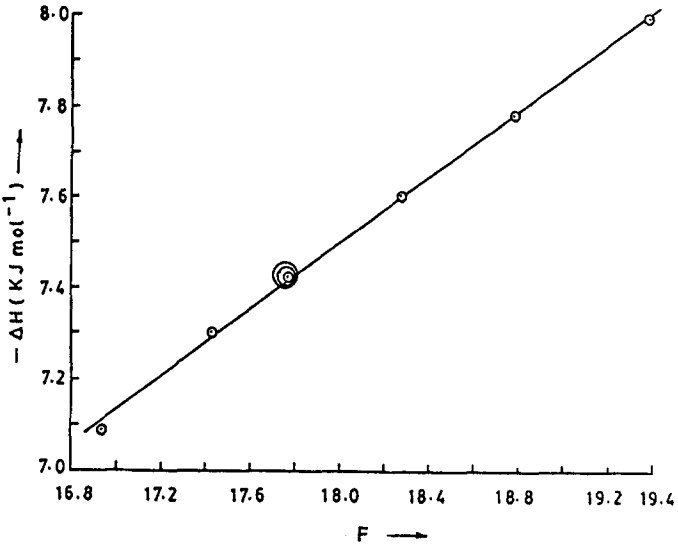

Fig 1 The behaviour of enthalpy of formation ($-\Delta H$) of n–π^* charge transfer complexes with charge transferred (%F) in pyridine–chloranil system

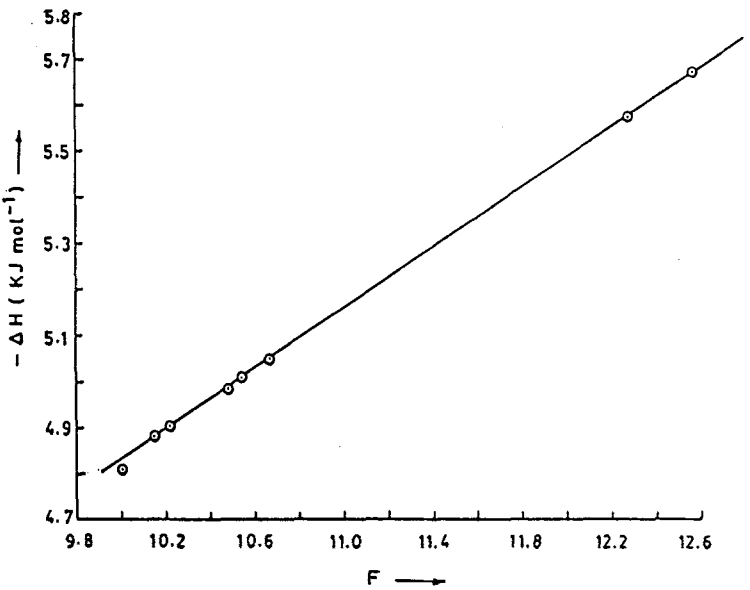

Fig. 2 The behaviour of enthalpy of formation ($-\Delta H$)of π–π^* charge transfer complexes with charge transferred (%F) in pyridine–chloranil system

Table 3 Experimental and theoretical energy parameters for n–π^* CT complexes formed inaniline–chloranil systems (in eV except a, b and F)

Electron donor	$h\nu_{CT}^{\alpha}$	I.P.		Δ	$-R_N$	a	b	F	$-\Delta H$ / kJ·mol–1	
		α	β						α (obs)	calc$^{\neq}$
Aniline	2.33	7.70	7.70	1.258	0.454	0.850	0.447	23.780	23.43	7.71
m–Toluidine	2.25	7.66	7.66	1.127	0.482	0.836	0.469	25.916	25.52	8.68
o–Toluidine	2.20	7.62	7.64	1.041	0.503	0.826	0.484	27.423	28.45	9.63
p–Toluidine	2.15	7.48	7.61	0.950	0.526	0.815	0.502	29.291	29.29	10.60
Diphenylamine	1.90	–	7.37	0.356	0.728	0.718	0.626	43.682	30.12	18.31
N,N–Dimethylaniline	1.83	7.20	7.19	0.001	0.900	0.640	0.705	54.214	32.66	28.89

α – Ref. [20], β – eq (vii)

$\beta_o = -0.9058$ eV; $S_{01} = 0.1$, $\neq$ predicted from the empirical formula

In the pyridine-chloranil systems, the values of F and $-\Delta H$ for n–π^* complexes follow the expected trend of the values of pK_a (except for pyridine) and ionization potential (I.P.) (except for γ–picoline) of n–donors. A similar behaviour of F and $-\Delta H$ with the I.P. of π–donors (except for α–picoline) has also been noted. The descending sequence of the strength of the complexes, based on the values of F and $-\Delta H$, is: isoquinoline >quinoline > collidine> lutidine > β– picoline > γ–picoline > α–picoline for π–π^* complexes; and collidine > lutidine > γ–picoline > α–picoline > β–picoline > isoquinoline > quinoline > pyridine for n–π^* complexes. Similar trends have been observed between F and $-\Delta H$ and the I.P. of n-donors of n–π^* complexes formed in the aniline-chloranil systems. The sequence of donicity in the aniline-chloranil systems on the basis of F and $-\Delta H$ is: N,N–dimethylaniline > diphenylamine > p–toluidine> o–toluidine > m–toluidine > aniline.

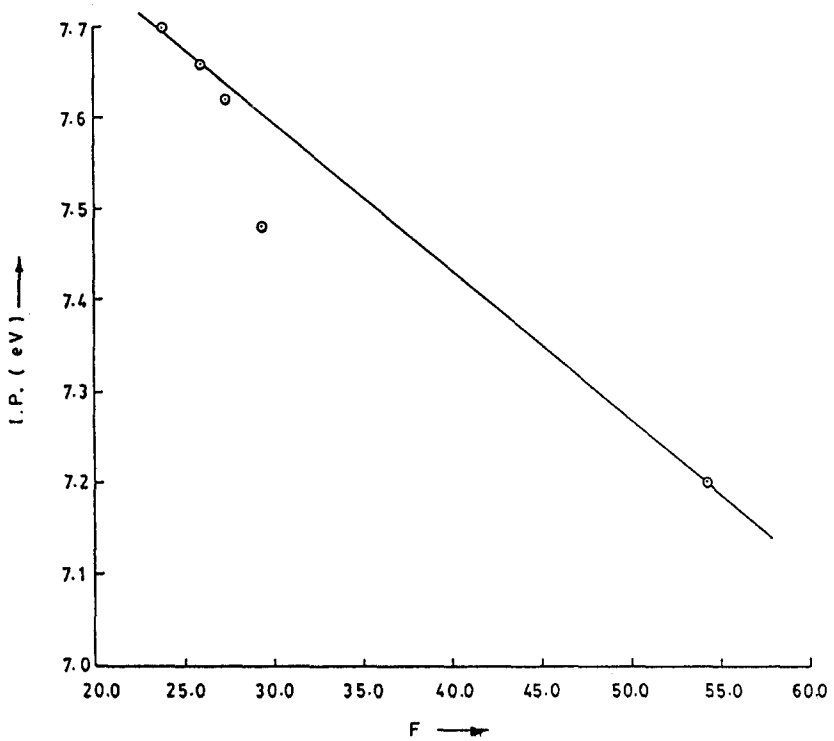

Fig. 3 The behaviour of ionization potential (I. P.) of n–π^* charge transfer complexes with charge transferred (%F) in aniline–chloranil system

The plots between various parameters in Figs 1–3 reveal that there are linear correlations between different parameters. The linear correlations between the various quantities are:

pyridine–chloranil systems:

I.P.(π)	$= 13.011 - 0.371\,F$	($r = 0.9877$)	(i)
I.P.(π)	$= 14.562 + 1.096\,\Delta H$	($r = 0.9899$)	(ii)
pK_a	$= -17.240 + 1.28\,F$	($r = 0.8823$)	(iii)
pK_a	$= -19.443 - 3.380\,\Delta H$	($r = 0.8689$)	(iv)
$\Delta H(\pi)$	$= -1.584 - 0.325\,F$	($r = 0.9996$)	(v)
$\Delta H(n)$	$= -0.956 - 0.363\,F$	($r = 0.9989$)	(vi)

aniline–chloranil systems:

I.P.(n)	$= 8.095 - 0.0166\,F$	($r = 0.9630$)	(vii)

The values of various parameters predicted from the linear correlations for n–π^* and π–π^* complexes are also given in Tables 1–3. The agreement between the literature values and the values of the various parameters computed from the correlations seems to be good. The maximum uncertainty in the case of I.P. (π) has been found to be of the order of ± 0.15 eV and is ± 1.07 in the case of the pK_a values of n-donors for the pyridine-chloranil systems. The I.P. of diphenylamine predicted from the linear correlation between I.P. and F (eqn. vii) fits well with the expected trend of I.P. of donors (Table 3, col.2).

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

R_N – Resonance interaction energy of the ground state of the CT complexes

h – Planck's constant

β_o – 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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References

1 B. S. Brown, Chem. Br., 3 (1967) 524.
2 G. Scott, Atmospheric Oxidation and Antioxidants, Elsevier, London, 1965.
3 U. Muralikrishna, J. Indian Chem. Soc., 62 (1985) 1052.
4 A. Ledwilli and D. H. Iles, Chem. Br., 4 (1968) 266.
5 P. C. Dwivedi and K. G. Rao, Indian J. Chem., 10 (9) (1972) 944.
6 B. K. Das and B. Majee, J. Indian Chem. Soc., 45 (11) (1968) 1054.
7 P. C. Dwivedi, N. Sharma and A. Srivastava, Indian J. Chem., 27A (1988) 994.
8 U. Muralikrishna and M. Krishnamurthy, Indian J. Chem., 21A (1982) 1018.
9 U. Muralikrishna and M. Krishnamurthy, Proc. Indian Natn. Sci. Acad., 55A (3) (1989) 496.
10 P. C. Dwivedi, A. Bansal, A. Srivastava and A. K. Banga, Indian J. Chem., 26A (1987) 389.
11 P. C. Dwivedi and A. K. Banga, J. Phys. Chem., 85 (1981) 1768.
12 U. Muralikrishna, Y. V. S. Seshasayi and M. Krishnamurthy, J. Indian Chem. Soc., 60 (1983) 1048.
13 P. C. Dwivedi and R. Agarwal, Indian J. Chem., 24A (1985) 100.
14 M. Krishnamurthy, K. S. Babu and U. Muralikrishna, Indian J. Chem., 27A (1988) 669.
15 S. B. Shah and A. S. N. Murthy, J. Phys. Chem., 79 (1975) 322.
16 P. C. Dwivedi, A. Bansal and A. Srivastava, Indian J. Chem., 27A (1988) 753.
17 U. Muralikrishna and M. Krishnamurthy, Indian J. Chem., 25A (1986) 949.
18 U. Muralikrishna, Y. V. S. K. Seshasayi and M. Krishnamurthy, J. Indian Chem. Soc., 60 (1983) 447.
19 D. C. Mukherjee and A. K. Chandra, Spectrochim. Acta., 19 (1963) 731.
20 P. C. Dwivedi, A. Gupta and A. K. Banga, Current Science, 51 (1982) 1152.
21 S. P. Mcglynn, Chem. Rev., 58 (1958) 1113.
22 H. S. Randhawa, R. Sachdeva and A. Singla, J. Thermal Anal., 31 (1986) 675 and the references cited therein.
23 A. J. Sonnesa and J. M. Daisey, Spectrochim. Acta. Part A, 32 (1976) 465.
24 H. S. Randhawa, H. Tung and G. S. Grewal, Indian Chem., Manuf., 18 (1980) 8.
25 W. B. Person, J. Am. Chem. Soc., 87 (1965) 167.

Zusammenfassung — Anhand der Charge-Transfer-Spektren von Molekülkomplexen aus Pyridin-Chloranil und Anilin-Chloranil wurde die Wärme für die Bildung von $n-\pi^*$ und $\pi - \pi^*$ Charge-Transfer-Wechselwirkungen berechnet.