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Note

ON THE HEAT OF FORMATION OF n—π OR π—n TYPES OF CHARGE TRANSFER COMPLEXES

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Sometimes it is difficult to study experimentally the energetics of the electron donor—acceptor complexes, especially charge transfer (CT) complexes, because of weak interaction between the donor and the acceptor and also due to the interaction of the solvent with donor and acceptor. In such cases scientists have to rely on the values predicted from the empirical relationships.

Recently [1], we have proposed an empirical relationship among the energy parameters for the prediction of heat of formation (ΔH) of n—π or π—n types of CT complexes. The empirical formula is

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

where h is Planck's constant, ν_{CT} is the frequency of the CT band, a and b are the weighting factors for no-bond and dative structures of CT complexes. The agreement between the observed and calculated values of ΔH is good and the average uncertainty is of the order of ±0.018 eV.

In the present communication, we have computed the energy parameters for the π—n type CT complexes formed between aromatic hydrocarbons and olefins donor and thiopyrylium cation acceptor employing the method of Sonnessa and Daisey [2] in order to predict ΔH of these complexes. The calculated values of energy parameters along with the predicted value of ΔH from the empirical relationship are tabulated in Table 1.

Table 1 reveals that the value of interaction energy G_0 depicted from the equation

$$G_0 = \Delta H - X_0$$

where X_0 is the resonance interaction energy of the ground state of the CT complex, follows the expected trend [1—3], which indirectly lends support to the empirical relationship and hence also the authenticity of the depicted values of ΔH. The calculated values of ΔH could not be compared with

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TABLE 1

Experimental and theoretical energy parameters for the CT complexes of thiopyrylium cation with aromatic hydrocarbons and olefins (in eV except for *a*, *b* and *F*)

		$h\nu_{CT}$ *	Δ	$-X_0$	X_1	$-\beta_1$	$b^*/a^{\neq}$	G_0	$-\Delta H^{\neq}$	a	b	F
Group A donors												
I	Anthracene	2.655	0.86	0.82	0.98	1.34	0.68	0.62	0.19	0.77	0.56	36.1
II	Pyrene	2.683	0.92	0.80	0.96	1.35	0.66	0.61	0.18	0.78	0.55	34.9
Group B donors												
III	Ethyl vinyl ether(i)	2.857	1.28	0.69	0.89	1.40	0.60	0.55	0.14	0.81	0.50	29.1
IV	*n*-Butyl vinyl ether(i)	2.857	1.28	0.69	0.89	1.40	0.60	0.55	0.14	0.81	0.50	29.1
V	Cyclohexene(i)	2.938	1.42	0.66	0.86	1.41	0.57	0.52	0.13	0.83	0.48	27.0
VI	1-Methyl cyclohexene(i)	2.938	1.42	0.66	0.86	1.41	0.57	0.52	0.13	0.83	0.48	27.0
VII	3-Methyl cyclohexene(i)	2.938	1.42	0.66	0.86	1.41	0.57	0.52	0.13	0.83	0.48	27.0
VIII	Isobutene(i)	2.952	1.44	0.65	0.86	1.42	0.57	0.52	0.13	0.83	0.48	26.7
IX	1-Pentene(i)	3.054	1.61	0.61	0.83	1.44	0.54	0.49	0.12	0.85	0.46	24.5
X	1-Methyl naphthalene	3.061	1.63	0.61	0.83	1.44	0.54	0.49	0.12	0.85	0.45	24.4
XI	2-Methyl naphthalene	3.131	1.74	0.59	0.81	1.46	0.53	0.47	0.11	0.86	0.44	23.1
XII	Naphthalene	3.237	1.90	0.56	0.78	1.48	0.50	0.45	0.10	0.87	0.42	21.3
Group C donors												
XIII	Mesitylene	3.594	2.40	0.48	0.72	1.55	0.44	0.39	0.08	0.89	0.37	16.9
XIV	*m*-Xylene	3.887	2.78	0.43	0.68	1.60	0.41	0.36	0.07	0.91	0.37	14.3
XV	Ethyl vinyl ether(ii)	3.937	2.84	0.42	0.68	1.61	0.40	0.35	0.07	0.91	0.33	13.9
XVI	*n*-Butyl Vinyl Ether(ii)	3.937	2.84	0.42	0.68	1.61	0.40	0.35	0.07	0.91	0.33	13.9
XVII	Cyclohexene(ii)	3.987	2.90	0.41	0.67	1.62	0.39	0.34	0.06	0.91	0.33	13.6
XVIII	1-Methyl cyclohexene(ii)	3.987	2.90	0.41	0.67	1.62	0.39	0.34	0.06	0.91	0.33	13.6
XIX	3-Methyl cyclohexene(ii)	3.987	2.90	0.41	0.67	1.62	0.39	0.34	0.06	0.91	0.33	13.6
XX	4-Methyl cyclohexene(ii)	3.987	2.90	0.41	0.67	1.62	0.39	0.34	0.06	0.91	0.33	13.6
XXI	Isobutene(ii)	4.000	2.92	0.41	0.67	1.63	0.39	0.34	0.06	0.91	0.33	13.5

* Ref. 6; $\beta_0 = -1.20$; $S_{01} = 0.1$, ≠ predicted from the empirical formulae; (i) and (ii) correspond to first and second CT band,

experimental ones since the latter are not reported in the literature.

It is interesting to note (Table 1) that little variation is found for any set of energy parameters. This may be due to the small variations of the values of $h\nu_{CT}$ and ΔH among these complexes. On the basis of these variations the complexes are classified into three groups: A, the strong complexes; B, the medium complexes; and C, the weak complexes formed from the respective donors (Table 1).

If we compare the energy terms of the A, B and C type complexes (Table 1), some trends in the calculated values of the energy parameters become apparent, like those of n—σ type complexes [3,4].

Table 1 reveals that the value of Δ is inversely proportional to the strength of the complexes and is in agreement with the findings of earlier workers [1—4]. This supports the theoretical predictions that the closer proximity of D and A is responsible for greater repulsion for stronger complexes in the ground state. The large positive value of G_0 gives rise to smaller values of Δ. Since in weak complexes the electrostatic forces of attraction predominate, the value of G_0, i.e. the interaction energy obtained when the donor and acceptor are brought together in the no-bond state, becomes negative. The positive value of G_0 for the systems considered here supports the earlier prediction that in stronger complexes with a short D—A distance the repulsive forces will predominate over the attractive forces. The increase in the negative values of resonance energy X_0 in the ground state follows the trend of ΔH, that is, X_0 is directly proportional to ΔH. This could perhaps best be explained by the increase in the contribution of resonance interaction, and hence charge transfer is responsible for the stabilization of the ground state in these complexes. The value of the charge transfer, i.e. F, also increases with the strength of the complexes. These findings are in agreement with theory.

The electrostatic terms in the case of weak complexes make significant contributions and in most cases the electrostatic terms outweigh the charge transfer resonance contributions [5]. Since in stronger complexes the electrostatic terms are operative, the values of X_0 as well as the trend of these values for these charge transfer complexes (Table 1) led us to conclude that the charge transfer interaction makes significant contribution to the stability of the ground state, like those of n—σ and n—π types of complexes [1—4]. The conclusions concerning the properties of the excited state dative structure of these complexes could not be drawn since it is difficult to compute the interaction energy G_1 (due to the non-availability of the verticle electron affinity of thiopyrylium cation), a term arising from the formation of the dative form D^+A^- from the free ions in the excited state.

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