Charge-transfer Contributions to the Stabilisation of the Ground State of Organic Electron Donor–Acceptor Complexes

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A recent argument, based on published experimental results, claims to support the hypothesis that there is a significant charge-transfer contribution to the ground-state stabilisation of typical π-donor–π^*-acceptor complexes. The argument is based on a fortuitous linear relationship. Other experimental results show that this conclusion is unjustified.

RECENTLY a relationship between the enthalpy of complex formation ($\Delta H^\ominus$) of organic electron donor–acceptor complexes and the ionisation potential of the donor component (D) for series of complexes involving a common electron-acceptor species (A) has been derived.[1] This has been applied to published experimental values of $\Delta H^\ominus$ for various series of complexes in order to argue that there is a significant dative (charge-transfer) contribution to the stabilisation of the ground state of these complexes.

In Mulliken's [2] valence-bond description of such complexes, the wave function of the ground state (ψ_N) is given by equation (1) where ψ_0(D, A) is wave function

$$\psi_N = a\psi_0(\text{D, A}) + b\psi_1(\text{D}^+\text{–A}^-) \qquad (1)$$

of the no-bond structure and $\psi_1(\text{D}^+\text{–A}^-)$ is the wave function of the dative structure. The ground-state energy (E_N) can be written as (2) where R_N is the

$$E_N = R_N + E_0 = \Delta H^\ominus = \frac{\beta_0^2}{E_1 - E_0} - E_0 \qquad (2)$$

resonance energy due to interaction between the no-bond and the dative structures; this is extra to the energy of interaction (E_0) between A and D through other forms such as polarisation and London forces encompassed by the term 'no-bond'; E_1 is the corresponding energy for the dative state; β_0 is the resonance integral.

For such complexes an excited state (ψ_E) exists such that equation (3) holds where $a \approx a^*$ and $b \approx b^*$.

$$\psi_E = a^*\psi_1(\text{D}^+\text{–A}^-) - b^*\psi_0(\text{D, A}) \qquad (3)$$

In so-called 'weak' charge-transfer complexes, $a \gg b$. The charge-transfer band characteristic of such complexes corresponds to the transition $\psi_N \rightarrow \psi_E$, and has an energy ($E_{CT}$) which for a series of complexes of structurally related donors with a given acceptor may be written as (4) where I is the ionisation potential

$$E_{CT} = I - c_1 - c_2/(I - c_1) \qquad (4)$$

of the donor and c_1, c_2 are effectively constant. These constants have been evaluated for several sets of complexes from the empirical relationships derived from the experimental values of E_{CT} and I.

From the classical treatment of the energetics of complex formation first described by Mulliken, Sambhi [1] has related the difference in $\Delta H^\ominus$ between two complexes (S and N) of a given acceptor with structurally related donors in terms of the ionisation potentials of the two donors (I_S and I_N), constant c_1 in equation (4) and the energy terms defined in equation (2) namely equation (5).

$$\Delta H_S^\ominus - \Delta H_N^\ominus = \frac{\beta_0^2(I_S - I_N)}{(I_S - c_1)(I_N - c_1)} - (E_{ON} - E_{OS}) \qquad (5)$$

As a consequence of equation (5) it was argued that, if for a series of complexes of a given donor with related acceptors the term ($E_{ON} - E_{OS}$) was effectively constant, the plot of ($\Delta H_S^\ominus - \Delta H_N^\ominus$) against $(I_S - I_N)/(I_N - c_1)$ should be linear, and that this might be taken as evidence for a significant contribution of charge transfer to the ground-state stability of the complex and further would provide a measure of this contribution.

Two such series of complexes, namely 1,3,5-trinitrobenzene with a series of methylbenzenes and iodine with a series of methylbenzenes, were shown to behave in this way. (Not unexpectedly, complexes involving a variety of structural types of donor showed little correlation.)

There is one other set of complexes which fulfils well the above conditions and for which experimental values of $\Delta H^\ominus$ are available. This is the group of fluoranil–methylbenzene complexes in carbon tetrachloride solution.[3,4] In many ways the stabilities of these complexes are closely related to those of 1,3,5-trinitrobenzene with the same donors also in carbon tetrachloride. For example there is a very good correlation between the free energies of formation for the two series of complexes.[5] Although a value of c_1 for the fluoranil complexes has not been published, there is sufficient information available to provide an accurate estimate of c_1, namely 5·7 eV (E_{CT}, I measured in eV). From these data, a plot of ($\Delta H_S^\ominus - \Delta H_N$) against $(I_S - I_N)/(I_N - c_1)$ has been obtained (Figure). Unlike the plot presented for the 1,3,5-trinitrobenzene complexes, this is very curved. It is difficult to argue that there is any fundamental difference between these two sets of complexes

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[1] M. S. Sambhi, *J. Phys. Chem.*, 1973, **77**, 2290.

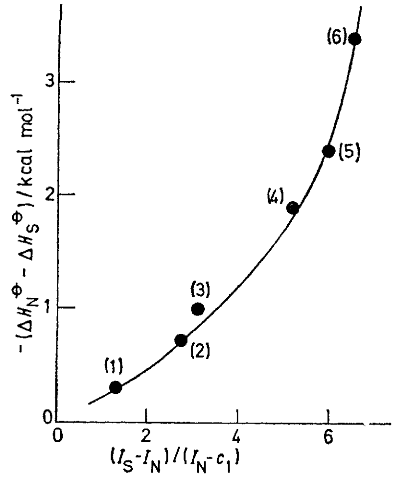
[2] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

[3] M. I. Foreman, R. Foster, and C. A. Fyfe, *J. Chem. Soc.* (*B*), 1970, 528.

[4] R. Foster and I. B. C. Martheson, *Spectrochim. Acta*, 1971, **27A**, 1171.

[5] R. Foster, 'Organic Charge-transfer Complexes,' Academic Press, London and New York, 1969, p. 195.

whose entropies of formation are very similar (1,3,5-trinitrobenzene 1·9—3·7 kcal mol^{-1}; fluoranil 2·0—5·4 kcal mol^{-1}). Although the difference could be rationalised by postulating that in the latter case E_0 is significantly dependent on the particular donor, it is difficult to see why this should be especially so for fluoranil complexes. Rather, with its greater electron affinity, one might expect there to be a greater contribution from charge-transfer in interactions with fluoranil than with 1,3,5-trinitrobenzene.



Plot of $-(\Delta H_N^{\ominus} - \Delta H_S^{\ominus})$ against $(I_S - I_N)/(I_N - c_1)$ for fluoranil–methylbenzene complexes in carbon tetrachloride, benzene as standard donor, S. Other donors: (1) toluene; (2) *p*-xylene; (3) mesitylene; (4) durene; (5) pentamethylbenzene; (6) hexamethylbenzene

Further, the value of $\Delta H^{\ominus}$ hitherto quoted may need to be modified because of the possible presence of termolecular species.[6,7] Indeed there seems little justification at present for attempting to place any particular significance in the *linearity* of the plot described by Sambhi. The only general conclusion which it is reasonable to make is that $-\Delta H^{\ominus}$ increases monotonically with decreasing ionisation potential of the donor for a set of complexes of a given acceptor with a series of related donors, a conclusion already reached in the original paper which reported the $\Delta H^{\ominus}$ values for the 1,3,5-trinitrobenzene and fluoranil complexes.[3] Since other properties, such as polarisability, increase with decreasing ionisation potential in such a series of donors, no direct argument concerning the possible involvement of charge-transfer stabilisation can be applied even to this observation.[8]

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[6] D. A. Deranleau, *J. Amer. Chem. Soc.*, 1969, **91**, 4050.

[7] B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc.* (*B*), 1971, 1283.

[8] See, for example, M. W. Hanna and J. L. Lippert in 'Molecular Complexes,' ed. R. Foster, Elek Science, London; Craine Russak, New York, 1973, ch. 1.