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CHARGE-TRANSFER TRANSITION ENERGIES AND THE PREDICTION OF REACTIVITY IN ELECTROPHILE–NUCLEOPHILE REACTIONS

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The differences between charge-transfer transition energies calculated for donor–acceptor pairs at infinite separation and values determined experimentally for the charge-transfer complex geometry vary according to the charge type of the pairs and within a group of fixed charge type. It is argued that these differences provide a guide to the slope of the state–correlation curves for the product configuration in electrophile–nucleophile reactions of the corresponding charge type and that the observed variation invalidates the use of the simple expression $\Delta E = f\Gamma - \beta$ with constant f, derived from the curve-crossing model, to estimate energy barriers to reaction.

INTRODUCTION

The curve-crossing (configuration mixing) model (CMM)[1] has proved very useful in providing a qualitative insight into the origin of activation barriers in reactions between nucleophiles and electrophiles, such as nucleophilic substitution at saturated carbon.[2] According to the model, barriers to reaction arise as a result of the avoided crossing of potential energy curves that link the reactants at infinite separation in their ground states (Nu:, El) with an excited state of the product configuration and one connecting an excited state of the reactants ($Nu^{+\cdot}$, $El^{-\cdot}$) with the product in its ground state. The excitation process to product configuration is a vertical charge-transfer transition, and this provides the formal single electron shift that characterizes electrophile–nucleophile reactions.[3] More recently, attempts have been made to use the CMM to provide more quantitative estimates of reactivity in such reactions. The procedure used involves the evaluation of the energy gap between the ground and excited states of the reactant configuration, the so-called initial gap Γ_R, from which the activation barrier, $\Delta E^{\neq}$, is determined by means of the expression $\Delta E^{\neq} = f\Gamma_R - \beta$, where f is a proportionality constant dependent on the slope of the potential energy curves and β is the avoided crossing parameter. Values of f have usually been taken to be in the range 0·2–0·25 and β is taken to be about 10 kcal mol^{-1}. The constancy of f is based in part on estimates for S_N2 identity exchange reactions with values of 0·2–0·3 for a range of nucleophiles and leaving groups[4] and in part on the observation of linear correlations between log k for the reaction of a wide range of nucleophiles with the electrophiles, pyronin cation[5] and 2,4-dinitrophenyl acetate[6] and the gas-phase ionization potentials of the nucleophiles, the principal variable component of Γ_R.

These attempts at quantitation have met with mixed success, the most notable problem arising in dealing with reactivity in reactions between cation radicals of aromatic compounds and anionic or electrically neutral nucleophiles. In reactions involving cation radicals as nucleophiles, it is argued, additional excitation of the reactant configuration is necessary in order that the excited charge-transfer state, in this case ($Nu^{+\cdot}$, El), can form a covalent bond between the two components; El must be promoted to an excited triplet state. The additional excitation (ΔE_{ST}) means that, other things being equal, the avoided crossing of the potential energy curves must occur at higher energies, resulting in generally slower reactions than in comparable reactions of even-electron species.[7] Although this prediction is in line with some gas-phase data[7b,8a] and early results on cation radical–nucleophile reactivity in solution,[8b] it is

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at odds with more recent measurements on less stable cation radicals such as those generated from anthracene and 9-phenylanthracene.[9]

Attention has recently been drawn to the existence of differences between Γ_R and the experimentally observed electronic transition energy, $h\nu_{CT}$, of charge-transfer complexes, taken as models of an electrophile–nucleophile pair.[10] These differences arise because of differences in the energetics of association in the ground and excited states, and it was suggested that they should be taken into account in estimating initial gaps. In this paper we explore the matter further using new data on charge-transfer complexes of all the relevant electrical charge combinations for the electrophile–nucleophile pair, 0/0, +/0, 0/− and +/−.

RESULTS

Charge-transfer complex formation was studied using chloranil and tropylium ion as acceptors and durene and iodide ion as donors in acetonitrile solution. With these species, the four different charge combinations could be examined. Parameters of the complexes at 25 °C are given in Table 1; association constants were derived by the Benesi–Hildebrand technique,[11] the value for durene + tropylium ion being taken from recent work by Takahashi *et al.*[12]

Using the symbolism introduced by Pross and Shaik,[7b] the expressions for the initial gaps for the four donor–acceptor pairs in this present study are given by the following equations:

$$(0,0)\text{Case: } (\text{I}-\text{A})_{S^*} = (\text{I}-\text{A})_g + (\Delta G_{SD^+} + \Delta G_{SA^-}) - \rho(\Delta G_{SD^+} + \Delta G_{SA^-}) \quad (1)$$

$$(0/+)\text{Case: } (\text{I}-\text{A})_{S^*} = (\text{I}-\text{A})_g + (\Delta G_{SD^+} - \Delta G_{SA^+}) - \rho(\Delta G_{SD^+} + \Delta G_{SA^+}) \quad (2)$$

$$(-/0)\text{Case: } (\text{I}-\text{A})_{S^*} = (\text{I}-\text{A})_g - (\Delta G_{SD^-} - \Delta G_{SA^-}) - \rho(\Delta G_{SD^-} + \Delta G_{SA^-}) \quad (3)$$

$$(-/+)\text{Case: } (\text{I}-\text{A})_{S^*} = (\text{I}-\text{A})_g - (\Delta G_{SD^-} + \Delta G_{SA^+}) - \rho(\Delta G_{SD^-} + \Delta G_{SA^+}) \quad (4)$$

where the subscript S^* refers to vertical excitation in solution and g to the gas phase, ΔG_S values are ionic solvation energies (solvation of uncharged species is ignored) and ρ is the ratio of solvent reorganization energy (in passing from the S^* state to the relaxed solvated ion) to ΔG_S, the value for acetonitrile being 0·54. Ionic solvation energies were obtained from the appropriate electrode potentials, placed on an absolute scale using a value of 4·44 for the absolute potential of the hydrogen electrode,[13] in conjunction with the energy of the corresponding adiabatic ionization process in the gas phase.

Table 2. Electrode potentials and ionic solvation energies of donors and acceptors in acetontrile

Substance	Process	*E*(V vs NHE)	*IP* or *EA*[a]	ΔG_{solv}[b]
Durene	Oxidation	2·07[c]	8·05[c]	−1·54
Chloranil	Reduction	0·35[d]	2·78[e]	−2·01
Iodide	Oxidation	1·00[f]	3·13[g]	−2·31
Tropylium	Reduction	−0·08[c]	6·24[c]	−1·88

[a] Adiabatic gas phase values in eV. The pertinent quantities are the ionization potentials (*IP*) for the oxidations and the electron affinities (*EA*) for the reductions.
[b] Ionic solvation energies in eV; $\Delta G_{solv} = E + 4 \cdot 44 - IP$.
[c] Values quoted in Ref. 10; the oxidation potential from Ref. 16.
[d] From Ref. 17.
[e] From Ref. 18.
[f] Value from Ref. 19, adjusted to acetonitrile.
[g] From Ref. 20.

From the results in Tables 1–3 it can be seen that, for all the charge types, there is a substantial discrepancy, labelled $\Delta\Gamma_R$ and defined as $h\nu_{CT} - \Gamma_R$, between the calculated initial gap (which refers to the reactants at infinite separation) and the excitation energy observed for the corresponding complex. In each case, $\Delta\Gamma_R$ is substantial and lies outside the combined uncertainties in the experimental data used in the calculations. Electronic excitation leads to increased interaction (and a decrease in energy) between reactants in all four cases to various extents. Caution should be exercised in relating the magnitude of the discrepancies to charge type alone, since our earlier analysis based on Takahashi *et al.*'s data[12] for the complexation of aromatic hydrocarbons with tropylium ion in acetonitrile showed that, within that rather homogeneous group, $\Delta\Gamma_R$ varies from −0·5 to −1·0 eV.

Table 1. Absorption maxima, molar absorptivities and formation constants for charge-transfer complexes in acetonitrile at 298 K

Donor	Acceptor	λ (nm)	ε (l mol^{-1} cm^{-1})	*K* (l mol^{-1})
Durene	Chloranil	460	1460	1·10
Durene	(Tropylium)$^+$	361	1650	0·82
I$^-$	Chloranil	448	2020	5·25
I$^-$	(Tropylium)$^+$	486	2600	3·95

Table 3. Parameters used in calculations of Γ_R and $\Delta\Gamma_R$ from equations (1)–(4)[a]

Donor	Acceptor	Equation	I_g	A_g	$(I-A)_s$	$h\nu_{CT}$[d]	$\Delta\Gamma_R$
Durene	Chloranil	(1)	8·34[b]	2·78[c]	3·93	2·67	−1·26
Durene	(Tropylium)$^+$	(2)	8·34[b]	6·28[b]	4·25	3·40	−0·85
I^-	Chloranil	(3)	3·13[c]	2·78[c]	2·98	2·74	−0·24
I^-	(Tropylium)$^+$	(4)	3·13[c]	6·28[b]	3·30	2·53	−0·77

[a] Units are eV.
[b] Values quoted in Ref. 10.
[c] Adiabatic values, see Table 2.
[d] Derived from the λ values in Table 1.

DISCUSSION

In a reaction between an electrophile and a nucleophile, leading to covalent bond formation, the reactants in the initial state may be regarded as being at infinite separation; calculated values of Γ_R refer to charge-transfer excitation in this situation. The next state in the reaction is the formation of an encounter complex. In the gas phase, such encounter complexes, by virtue of electrostatic interactions (ion–ion, ion–dipole, dipole–dipole) have a much lower energy than the separated reactants,[14] and this perhaps makes the complex a sensible starting point in assessing the magnitude of the barrier to covalent bond formation.[4] The encounter complex in solution, however, has an energy much less different from that of the separated reactants because of the effects of solvation. We believe that a donor–acceptor complex represents a reasonably good model of an electrophile–nucleophile pair in the reactant configuration at the encounter complex geometry, and the magnitudes of the equilibrium constants in Table 1 confirm that, for the complexes we have studied, the interaction energy in the ground state is less than 1·0 kcal mol^{-1}.

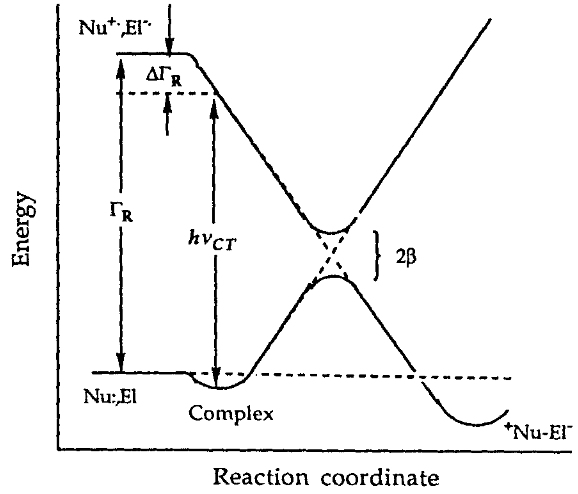

Figure 1. Curve-crossing diagram for the configuration mixing model description of the electrophile–nucleophile interaction starting from the geometry of the charge-transfer complex

Electronic excitation of the charge-transfer complex takes the energy of the system to a point on the potential energy curve of the product configuration at the same geometry as the ground-state complex. This is shown in Figure 1, which in other respects is of the sort used in discussions of the CMM approach to organic reactivity. The excitation energy represents the gap between reactant and product configurations at a point some way along the reaction coordinate towards the curve-crossing point, and it could be argued that this energy might be a better one from which to estimate activation barriers if values of $h\nu_{CT}$ were available for electrophile–nucleophile pairs. They are not, of course, and in any case we prefer to regard the discrepancy, $\Delta\Gamma_R$, as an experimental indication of the slope of the potential energy curve for the product configuration. In doing this, we make the assumption that, in the systems that we have studied, the geometry of the charge-transfer complex in the ground state corresponds to the same extent of progress alone the hypothetical electrophile–nucleophile reaction coordinate. If we make the further assumption that the slope of the curve in its initial stages is a guide to the slope as it approaches the crossing point, then the value of $\Delta\Gamma_R$ may be related to the energy of the system at the curve-crossing point. On this basis, a large negative value of $\Delta\Gamma_R$ would correspond to a high negative slope for the potential energy curve and consequently a low value of the factor f and of the activation barrier to covalent bond formation. Conversely, a value of $\Delta\Gamma_R$ that is less negative would imply a correspondingly larger activation barrier. For the purposes of this paper, we wish merely to call attention to our observation that the discrepancies are widely variable over a range of about 1·0 eV between reactant pairs of different charge types, and that they vary substantially between reactant pairs of the same charge type even though these are closely related structurally. Under these circumstances, we believe that the CMM method of estimating reaction barriers in electrophile–nucleophile reactions using a constant value of the parameter f is unreliable as a general procedure. This calls into question the significance of the observed linear free energy relationships which encouraged the notion of a constant f; a more detailed investigation of this aspect seems desirable.

The constancy of f has been much discussed and it has been argued that its magnitude should vary according to the degree of charge localization in the excited reactant configuration. Thus, the curve connecting $El^{-\cdot}$ and $Nu^{+\cdot}$ and the combination product is expected to show a less steep dependence on the reaction coordinate when delocalization hinders the odd electron pairing, and this will lead to a high f and $\Delta E^{\neq}$. Conversely, with localized charge, f will be smaller. For example, in the case of S_N2 identity reactions of CH_3X, f has been equated with the weighting (b^2) of $CH_3{:}{\cdot}X^-$ in the VB descriptions of the reactant anion radical and found to have values in the range 0·2–0·3 for a variety of X.[4] Analogous considerations of charge localization led to analysis of nucleophilic reactivity in the reactions with 2,4-dinitrophenyl acetate into low f (0·14) reactions with, e.g., HO^- and high f (0·29) reactions with, e.g., $CH_3CO_2^-$.[5] It is our contention, however, that such treatments are valuable only in dealing with trends within closely related groups of reactions and that the theory cannot be securely applied to predict absolute reactivity.

Simple considerations in any case suggest that f is unlikely to be constant with a series of reactions, however closely related structurally the reactants may be. Figure 2 shows a curve-crossing diagram in which, for mathematical simplicity, the correlation lines are rectilinear. Using the symbolism shown, it can easily be shown that, in this case, $f = \Gamma_P/(\Gamma_R + \Gamma_P - \Delta H^\circ)$. Although hardly realistic, this simplified picture makes it clear that f is intimately related to more features of the reaction system than are incorporated in the initial gap.

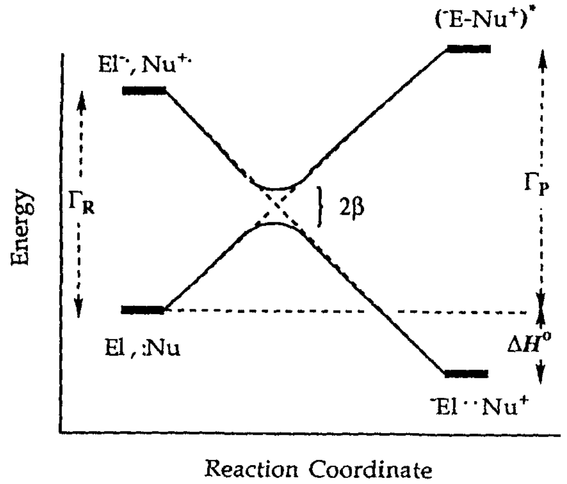

Figure 2. Curve-crossing diagram for the configuration mixing model description of the electrophile–nucleophile interaction starting from the isolated reactants

CONCLUSION

In its present form, the CMM provides an unreliable means of predicting reactivity in electrophile–nucleophile reactions. The weakness seems to reside in the use of the expression $\Delta E = f\Gamma_R - \beta$ with a constant value for f. Further examination of the possibility of using excitation energies of charge-transfer complexes to model the early stages of electrophile–nucleophile reactions could prove fruitful.

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