likely to encounter oxygen and form the benzaldehyde. The effect of oxygen, however, extends beyond that of a simple radical scavenger. An increase in the yields of primary recombination products, primarily of *p*-MAP, appears to indicate that most of the reaction occurs at the local supercage sites. It can be speculated on whether the paramagnetic oxygen molecules induce an enhanced rate of intersystem crossing of the radical pair. Such an effect is well documented and has been discussed by Scaiano[22] and others.[23] Oxygen, presumably being a faster random walker, may be able to induce intersystem crossing of the radical pair as it approaches the local supercage sites.

Finally, the result of carrying out the reaction at −20 °C also supports the percolation model. It is expected that a decrease in temperature should decrease the diffusion coefficient of all the species in the zeolite media. Low temperatures would therefore be expected to increase the role of local effects at all loadings as the mobility of the reaction intermediates is highly reduced. Such expectations are observed as the loading dependence of the product yields and the cage effect are substantially reduced (Figure 8). The yields of rearranged products, in relation to the results at room temperature, are increased substantially (70% to 90%) at all loadings. The yields of DPE indicate relatively small variations (30% to 5%), while consistently large cage effects are observed at all loadings (90% to 95%). A striking observation, which confirms the preferential formation of *p*-MAP at the local reaction sites, comes from the fact that the highest yields of this product (60–80%) are observed under these "diffusion-frozen" conditions. This interpretation, however, does not take into account temperature-induced changes in the rates of reaction.

Conclusions

The importance of loading on the dynamics of the radicals derived from the photolysis of DBK-d_5 in NaX has been demonstrated. The results presented here suggest that the effect of additives in the dynamics of intrazeolite reactions may be explained with the consideration of local and global space effects and by use of percolation theory. It is also suggested that the relative diffusion rates of the reactants and reaction intermediates should be taken into account in order to consider the applicability of a percolation model. Further work studying the effect of loading of various aromatic coadsorbates with different diffusion coefficients in zeolite media is currently under progress.

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[22] Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

[23] Kuz'min, V. A.; Levin, P. P. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1989**, 1291.

Use of Ionization Potentials, Electron Affinities, and Singlet–Triplet Excitation Energies for the Estimation of Reaction Barriers

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Abstract: The use of ionization potentials (I_D), electron affinities (E_A), and singlet–triplet excitation energies ($\Delta E_{ST}(\pi\pi^*)$) to estimate reaction barriers for donor (D)–acceptor (A) combination reactions i has been examined. It is evident from thermochemical cycles that these quantities are not a complete description of the energetics of the excitation of reactant ground-state configuration **1** to the first excited-state configuration **2**. The association constants of ground state ($K°$) and excited state (K^*) reactants must also be taken into account. Including a term for the latter gives rise to eq ii, in which *f* is a fraction and

$$D/A \rightarrow D^+\text{–}A^- \qquad \text{(i)}$$

$$\underset{\mathbf{1}}{D\!:\!A} \qquad \underset{\mathbf{2}}{{}^{+}D^{\bullet}\,{}^{\bullet}A^{-}}$$

$$\Delta E_{act} = f[(I_D - E_A) - RT \ln (K^*/K°)_{DA}] - B \qquad \text{(ii)}$$

B is the avoided crossing parameter, for the estimation of the reaction barrier using the state correlation diagram (SCD) analysis. It is concluded that linear correlations of ΔE_{act} vs $I_D - E_A$ are not expected to provide either *f* or *B*. The energies of excitation of **1** to **2** in acetonitrile, where D is an aromatic compound and A is tropylium ion, were observed to be lower than values calculated from $I_D - E_A$ by as much as 13–23 kcal/mol, indicating the need for a significant correction due to the $RT \ln (K^*/K°)_{DA}$ term. The consequences of the association equilibria of ground-state and excited-state complexes on excitation energies and reaction barriers are discussed for free-radical phenylation of aromatic compounds.

Introduction

Ionization potentials, electron affinities, and singlet–triplet excitation energies are frequently referred to in the discussion of reaction barriers.[2-7] When used to estimate barriers of bimolecular reactions, it is often necessary to combine two or more of the quantities corresponding to the two reactants. In doing so, the mutual interactions of the ground-state reactants to form the reactive complex, as well as the corresponding interactions

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[1] On leave from the Department of Chemistry, University of Kashmir, India.

[2] Epiotis, N. D.; Shaik, S. S. *J. Am. Chem. Soc.* **1977**, *99*, 4936.

[3] Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6218.

[4] Shaik, S. S. *J. Org. Chem.* **1987**, *52*, 1563.

[5] Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537.

[6] Buncel, E.; Shaik, S. S.; Um, I.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1988**, *110*, 1275.

[7] Shaik, S. S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446.

0002-7863/91/1513-6218$02.50/0

in the excited state, are most often neglected. The results presented here show that excitation energies of ground-state reactant complexes to excited-state complexes may differ substantially from the corresponding energetics for excitation of the uncomplexed reactants.

The combination of a donor (D) with an acceptor (A) molecule can be considered to illustrate the problem. The configuration mixing (CM) model (or state correlation diagram (SCD) analysis) describes the combination reaction (1), the slash in D/A indicates

$$\mathrm{D/A} \rightarrow \mathrm{D^{+}\text{–}A^{-}} \tag{1}$$

a nonbonded complex, as an avoided crossing of the potential energy surfaces of reactant ground-state **1** and first excited-state **2** configurations. Configuration **2** is common to both reactant

$$\underset{\mathbf{1}}{\mathrm{D\!:\,A}} \qquad \underset{\mathbf{2}}{\mathrm{{}^{+}D^{\bullet}\,{}^{\bullet}A^{-}}}$$

and product.[8] The barrier for the reaction is then estimated from eq 2, where I_D is the ionization potential of D and E_A is the electron

$$\Delta E_{\mathrm{act}} = f(I_D - E_A) - B \tag{2}$$

affinity of A, f is a fraction, and B is the avoided crossing parameter. The difference $I_D - E_A$ is taken to represent the vertical excitation of **1** to **2** maintaining the geometry of **1** and is referred to as the initial gap. In this paper, the only aspect of the CM model that we consider is the energy terms, which must be taken into the initial gap.

Results and Discussion

Excitation Energies of Donor–Acceptor Complexes Relative to Those of Donor and Acceptor Molecules. In the following paragraphs, we derive the relationships between ionization potentials, electron affinities, and singlet–triplet excitation energies (ΔE_{ST}) of molecules and the corresponding energetics of excitation of donor–acceptor complexes. Three different cases are considered including (i) charge-transfer excitation of a donor–acceptor complex (D/A), (ii) singlet–triplet excitation of an aromatic compound complexed with phenyl radical, and (iii) the double excitation of a cation radical–nucleophile complex. The implications of these excitation energies on CM model initial gaps are then discussed in the following section.

As is evident from Scheme I, the term $I_D - E_A$ is not a complete description of the energetics of the excitation of configuration **1** to configuration **2**. This process can be broken down into four distinct steps involving dissociation of the ground-state complex (eq 3), the ionization of the free donor (eq 4), the attachment of an electron to the acceptor (eq 5), and finally the association of D^+ with A^- (eq 6). The free energies of these processes are summed in the thermochemical cycle (Scheme I) to give eq 7 where K° and K^* are the association constants for ground-state (eq 3) and excited-state (eq 6) reactants.

Scheme I

$$\mathrm{D\!:A} \rightleftarrows \mathrm{D\!:} + \mathrm{A} \qquad RT \ln K^{\circ}_{\mathrm{DA}} \tag{3}$$

$$\mathrm{D\!:} \rightleftarrows \mathrm{D^{+}} + e^{-} \qquad I_D \tag{4}$$

$$\mathrm{A} + e^{-} \rightleftarrows \mathrm{A^{-}} \qquad -E_A \tag{5}$$

$$\mathrm{D^{+}} + \mathrm{A^{-}} \rightleftarrows \mathrm{{}^{+}D^{\bullet}\,{}^{\bullet}A^{-}} \qquad -RT \ln K^{*}_{\mathrm{DA}} \tag{6}$$

$$\mathrm{D\!:A} \rightleftarrows \mathrm{{}^{+}D^{\bullet}\,{}^{\bullet}A^{-}} \qquad I_D - E_A - RT \ln (K^{*}/K^{\circ})_{\mathrm{DA}} \tag{7}$$

The initial gap for the reaction of a free radical with a neutral molecule has been assumed to be equal to the singlet–triplet excitation energy ($\Delta E_{ST}(\pi\pi^*)$) of the latter.[7] The process, illustrated for the excitation of the phenyl radical/aromatic compound complex $\mathrm{Ph^{\bullet}/ArH(\pi\pi)}$, corresponds to eqs 8–10 in Scheme II. The ratio of equilibrium constants $(K^*/K^\circ)_{ST}$ in (11) then refers to the association constants of reactants in the ground state (K°) and the excited state (K^*). The initial gap for singlet–triplet excitation of the $\mathrm{Ph^{\bullet}/ArH(\pi\pi)}$ complex is the free energy expression in (11).

Chart I

case	ground-state complex	excited-state complex	$RT \ln (K^*/K^\circ)_{DA}$
1	D/A	D^+/A^-	large (+)
2	D^-/A	D/A^-	small
3	D/A^+	D^+/A	small
4	D^-/A^+	D/A	large (−)

Scheme II

$$\mathrm{Ph^{\bullet}/ArH(\pi\pi)} \rightleftarrows \mathrm{Ph^{\bullet}} + \mathrm{ArH(\pi\pi)} \qquad RT \ln K^{\circ}_{\mathrm{ST}} \tag{8}$$

$$\mathrm{ArH(\pi\pi)} \rightleftarrows \mathrm{ArH(\pi\pi^*)} \qquad \Delta E_{\mathrm{ST}}(\pi\pi^*) \tag{9}$$

$$\mathrm{Ph^{\bullet}} + \mathrm{ArH(\pi\pi^*)} \rightleftarrows \mathrm{Ph^{\bullet}/ArH(\pi\pi^*)} \qquad -RT \ln K^{*}_{\mathrm{ST}} \tag{10}$$

$$\mathrm{Ph^{\bullet}/ArH(\pi\pi)} \rightleftarrows \mathrm{Ph^{\bullet}/ArH(\pi\pi^*)} \qquad \Delta E_{\mathrm{ST}}(\pi\pi^*) - RT \ln (K^{*}/K^{\circ})_{\mathrm{ST}} \tag{11}$$

The CM model treatment of cation radical–nucleophile combination reactions involves reactant configurations **3**–**5**. The first

$$\underset{\mathbf{3}}{\mathrm{N\!:\,A^{\bullet+}}} \qquad \underset{\mathbf{4}}{\mathrm{N^{\bullet+}\,A}} \qquad \underset{\mathbf{5}}{\mathrm{N^{\bullet+}\,{}^{3*}A}}$$

excited-state reactant complex configuration **4** is not a product configuration, and the SCD analysis requires a further excitation to the doubly excited state **5** in order for an avoided crossing to afford product. The thermochemical cycle in Scheme III defines the energy of the initial gap for the combination of N: with $A^{\bullet+}$. Unlike the processes in Schemes I and II, the equilibrium constant ratio in the initial gap for this case refers to the dissociation of ground-state reactant complex and the association of the *doubly* excited-state reactant complex. The association and dissociation of the *singly* excited-state complex cancels in the two excitation terms.

Scheme III

$$\mathrm{N\!:/A^{\bullet+}} \rightleftarrows \mathrm{N\!:} + \mathrm{A^{\bullet+}} \qquad RT \ln K^{\circ}_{\mathrm{DA}} \tag{12}$$

$$\mathrm{N} \rightleftarrows \mathrm{N^{\bullet+}} + e^{-} \qquad I_D \tag{13}$$

$$\mathrm{A^{\bullet+}} + e^{-} \rightleftarrows \mathrm{A} \qquad -E_A \tag{14}$$

$$\mathrm{N^{\bullet+}} + \mathrm{A} \rightleftarrows \mathrm{N^{\bullet+}} + \mathrm{{}^{3*}A} \qquad \Delta E_{\mathrm{ST}}(\pi\pi^*) \tag{15}$$

$$\mathrm{N^{\bullet+}} + \mathrm{{}^{3*}A} \rightleftarrows \mathrm{N^{\bullet+}/{}^{3*}A} \qquad -RT \ln K^{*}_{\mathrm{ST}} \tag{16}$$

$$\mathrm{N\!:/A^{\bullet+}} \rightleftarrows \mathrm{N^{\bullet+}/{}^{3*}A} \qquad I_D - E_A + \Delta E_{\mathrm{ST}}(\pi\pi^*) - RT \ln (K^{*}_{\mathrm{ST}}/K^{\circ}_{\mathrm{DA}}) \tag{17}$$

Qualitative Expectations of the Magnitudes of the Association Terms. It is of interest to examine the conditions under which $(K^*/K^\circ)_{DA}$ might or might not be expected to be of significant magnitude. To do this, we can concentrate on the general D/A excitation portrayed in Scheme I. The expected effect of charge on the energetics of the ground state–excited state transformation is summarized in Chart I. When there is an overall change in charge between ground-state and excited-state complexes as in cases 1 and 4, the effect of $(K^*/K^\circ)_{DA}$ is expected to be most significant while in cases 2 and 3 where there is only a shift in charge it is likely to be less important. The energetics for the two extreme cases, 1 and 4, are illustrated qualitatively in Scheme IV. The equilibrium constant for interaction of neutral D and neutral A is generally expected to be less than unity corresponding to a positive free energy change in going to the D/A complex (case 1). On the other hand, the formation constant of the excited-state complex (D^+/A^-) is expected to be >1 due to a decrease in free energy. Thus, the charge-transfer energy (ΔE_{CT}) can be expected to be considerably less than $I_D - E_A$.

When the reactants are charged (case 4), the equilibrium constant for formation of the ground-state complex (D^-/A^+) can be expected to be considerably greater than unity and to be ac-

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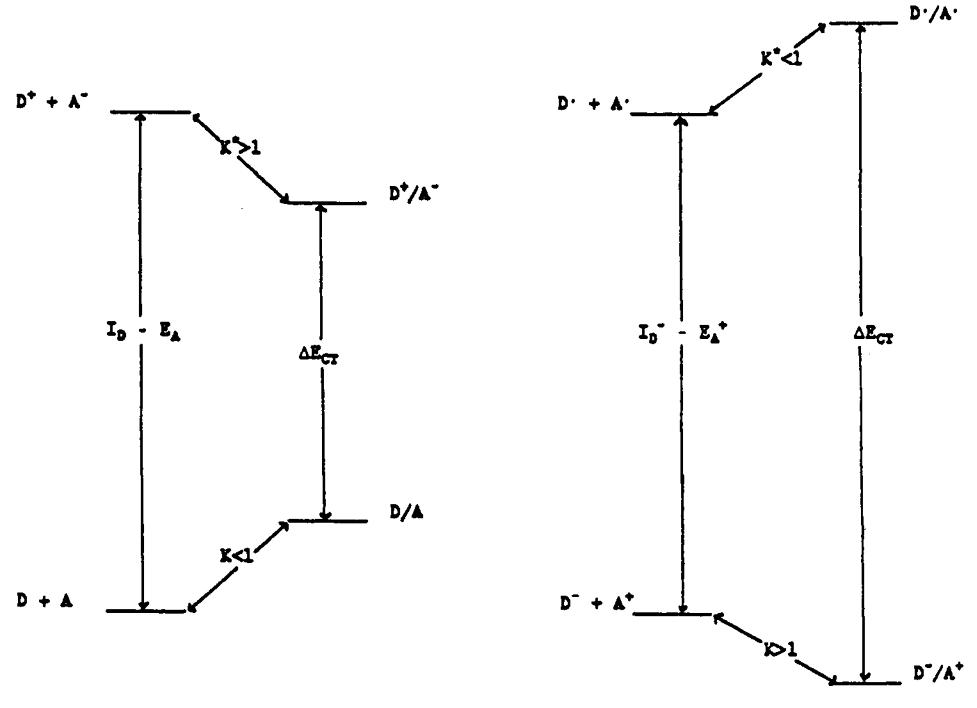
[8] Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

Scheme IV



Case 1

Case 4

Table I. Charge-Transfer Energies, Differences in Electrode Potentials, Ionization Potentials, and Solvation Energies of Aromatics

substance	$h\nu_{CT}$,[a] eV	$I_A - E_A$,[b] eV	$\Delta E°$,[c] V	$\Delta\Delta G_{solv}$,[d] V
toluene	3.95	2.58	2.69	0.11
1,2-dimethylbenzene	3.78	2.32	2.45	0.13
1,3-dimethylbenzene	3.78	2.32	2.46	0.14
1,4-dimethylbenzene	3.85	2.20	2.38	0.18
1,2,3-trimethylbenzene	3.54	2.18	2.18	0.00
1,2,4-trimethylbenzene	3.60	2.03	2.03	0.00
1,3,5-trimethylbenzene	3.55	2.18	2.43	0.25
durene	3.43	1.81	2.15	0.34
naphthalene	3.15	1.91	2.16	0.25
anthracene	2.54	1.19	1.55	0.36
anisole	3.42	2.15	2.00	-0.15
1,4-dimethoxybenzene	2.88	1.66	1.68	0.02

[a] From ref 9. [b] I_A listed in ref 9, E_A taken as I_A of tropyl radical from ref 11. [c] Oxidation potentials of aromatics from ref 12, that for tropyl radical from ref 15. [d] $\Delta E° = I_A - E_A$. The solvation energy of Tr^+ was estimated to be equal to -43.4 kcal/mol, using a value of -4.44 V for the absolute potential of the normal hydrogen electrode: Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955.

Table II. Differences in Charge-Transfer Excitation Energies and Initial Gaps

substance	I_V,[a] eV	$I_V - I_A$,[b] eV	$(I_V - E_V)_s$, eV	$-\Delta$Gap, kcal/mol
tropyl radical	6.28[c]	0.04[d]		
toluene	8.92[e]	0.10[f]	4.72	17.8
1,2-dimethylbenzene	8.73[e]	0.17[f]	4.54	17.5
1,3-dimethylbenzene	8.58[e]	0.02[f]	4.40	14.3
1,4-dimethylbenzene	8.58[e]	0.14[f]	4.42	13.0
1,2,3-trimethylbenzene	8.68[e]	0.26[f]	4.43	20.5
1,2,4-trimethylbenzene	8.46[e]	0.19[f]	4.21	14.1
1,3,5-trimethylbenzene	8.68[e]	0.26[f]	4.55	23.0
durene	8.34[e]	0.29[f]	4.25	18.9
naphthalene	8.26[g]	0.11	4.13	22.5
anthracene	7.55[h]	0.12	3.47	21.4
anisole	8.39[i]	0.00	4.07	15.1
1,4-dimethoxybenzene	7.90[j]	0.00	3.66	18.0

[a] Vertical ionization potential. [b] Adiabatic ionization potential. [c] Value from ref 17. [d] I_A from ref 11. [e] I_V from ref 30. [f] I_A from tabulation in ref 9. [g] Reference 18. [h] Reference 19. [i] Reference 29. [j] Reference 20.

companied by a significant decrease in free energy. In this case, the excited-state reactants, $D^•$ and $A^•$, are neutral and formation of $D^•/A^•$ is likely to demand an increase in free energy. The overall result expected is that ΔE_{CT} should be greater than $I_D^- - E_A^+$. This situation is illustrated in the right-hand diagram of Scheme IV.

Semiquantitative Estimation of the Magnitude of Association Energies. The charge-transfer excitation of tropylium ion/aromatic compound complexes[9] in acetonitrile provides examples of case 3 systems. Since the excitation (eq 18) involves a shift in

$$ArH/Tr^+ \rightarrow ArH^{•+}/Tr^• \qquad (18)$$

rather than the production of charge, the difference between $I_D - E_A$ and ΔE_{CT} is expected to be less than would be anticipated for either case 1 or case 4 systems (Scheme IV). Data are available that allow the evaluation of the relative magnitudes of association energies of ground-state and excited-state complexes.

Charge-transfer excitation energies corresponding to (18) have been reported for a range of aromatic substrates.[9] Data are summarized for a number of aromatic compounds in Table I. The ΔE_{CT} (equal to $h\nu_{CT}$) were obtained in acetonitrile.[9] The column labeled $I_A - E_A$ gives the values of the differences in adiabatic ionization potentials of the aromatic compound[10] and tropyl radical.[11] The electrode potentials for most of the aromatic compounds have been tabulated[12] from earlier work,[13,14] and the $\Delta E°$ refer to the difference in oxidation potentials of the aromatic compounds and of tropyl radical.[15] The differences in solvation energies of the cation radical of the aromatic compound and that

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(9) Takahashi, Y.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2954.

(10) Tabulated in ref 9 from literature data.

(11) Thrush, B. A.; Zwoienik, J. J. *Discuss. Faraday Soc.* **1963**, *35*, 196. Elder, F.; Parr, A. *J. Chem. Phys.* **1969**, *50*, 1027.

(12) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987; Chapter 3.

(13) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98.

(14) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567.

(15) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand.* **1980**, *B34*, 91.

of tropylium ion were calculated from eq 19. The adiabatic term ($I_A - E_A$) is appropriate since solvation energies refer to the relaxed configurations after the electronic transitions.

$$\Delta\Delta G_{\mathrm{solv}} = \Delta E^{\circ} - I_A - E_A \qquad (19)$$

Vertical ionization potentials (I_V) are gathered in Table II, and the differences in I_V and I_A are tabulated. $(I_V - E_V)_s$ refers to the vertical ionization reactions in acetonitrile solution and were calculated from eq 20. In eq 20, ρ is a solvent parameter, equal

$$(I_V - E_V)_s = (I_V - E_V)_{\mathrm{gas}} + \Delta\Delta G_{\mathrm{solv}} - \rho[\Delta G(\mathrm{ArH}^{\bullet+}) + \Delta G(\mathrm{Tr}^+)]_{\mathrm{solv}} \qquad (20)$$

to 0.54 for acetonitrile,[16] which reflects the differences in solvation energies of ions formed in vertical and adiabatic ionization processes. The vertical ionization potential of tropyl radical[17] was obtained from the photoelectron spectrum as were those of the other aromatic compounds with the exception of anthracene and naphthalene in which I_V are from electron impact.[18,19] Since I_V refer to Franck–Condon transitions, their experimental determination is less ambiguous than the corresponding I_A. The I_V listed for 1,4-dimethoxybenzene, for example, is from a well-defined photoelectron spectrum,[20] which makes an identical value for I_A somewhat suspect. In any event, $I_V - I_A$ for the compounds in this study are relatively small, and the errors associated with this difference do not significantly affect our results. The final column in Table II lists ΔGap, defined as the differences between ΔE_{CT} and $(I_V - E_V)_s$ (kcal/mol), which according to the thermochemical cycle (Scheme I) is equal to $-RT \ln (K^*/K^{\circ})$. These values range from −13 to −23 kcal/mol.

The large values observed for ΔGap as well as the extensive scatter in this quantity for this series of compounds (Table II) were not expected. This cannot be due to experimental errors in either I_V or $h\nu_{CT}$. These quantities are reported to a precision of 0.01 eV,[9] and errors are generally accepted to be of the order of 0.05 eV or less. Still unrecognized factors, other than those taken into account in Scheme I, may contribute to the magnitude of ΔGap. For this reason, we make no attempt to calculate numerical values of $(K^*/K^{\circ})_{DA}$ from the corresponding ΔGap. However, this in no way detracts from our suggestion that the energetics of association reactions of ground- and excited-state reactants cannot be neglected when considering the magnitudes of SCD initial gaps.

Application of the CM Model to the Analysis of Barriers for the Free-Radical Phenylation of Aromatic Compounds. The barriers for the reactions of phenyl radical with aromatic compounds can be formulated in the same way as those for radical additions to olefins as in (21) with reactant configurations **6** and **7**.[7]

$$\Delta E_{\mathrm{act}} = f\Delta E_{\mathrm{ST}}(\pi\pi^*) - B \qquad (21)$$

$$\underset{\mathbf{6}}{\mathrm{Ph}^{\bullet}/\mathrm{ArH}(\pi\pi)} \qquad \underset{\mathbf{7}}{\mathrm{Ph}^{\bullet}/\mathrm{ArH}(\pi\pi^*)}$$

We have shown in Scheme II that $RT \ln (K^*/K^{\circ})_{\mathrm{ST}}$ must be subtracted from $\Delta E_{\mathrm{ST}}(\pi\pi^*)$ in order to give the SCD initial gap. However, to be consistent with how the model has been applied in the past, kinetic data for this reaction series will first be analyzed in terms of (21). It is commonly assumed that correlations of free energies of activation for a reaction series with the initial gap should give rise to a linear relationship in which the slope can be equated to f and B can be obtained from the intercept.[4,6]

Table III. Second-Order Rate Constants, Free-Radical Phenylation Activation Free Energies, and Singlet–Triplet Excitation Energies of Aromatic Hydrocarbons[a]

hydrocarbon	log k, $M^{-1}\ s^{-1}$	ΔG^*, kcal/mol	ΔE_{ST}, kcal/mol
benzene	5.65	9.75	83.9
naphthalene	6.93	8.01	60.9
anthracene	8.31	6.12	42.0
pyrene	7.86	6.74	48.7
chrysene	7.56	7.15	56.6
triphenylene	7.25	7.57	66.6
1,2-benzanthracene	8.26	6.19	47.2
phenanthrene	8.74	5.54	62.2

[a] In dichloromethane at 298 K. ΔE_{ST} values from ref 24.

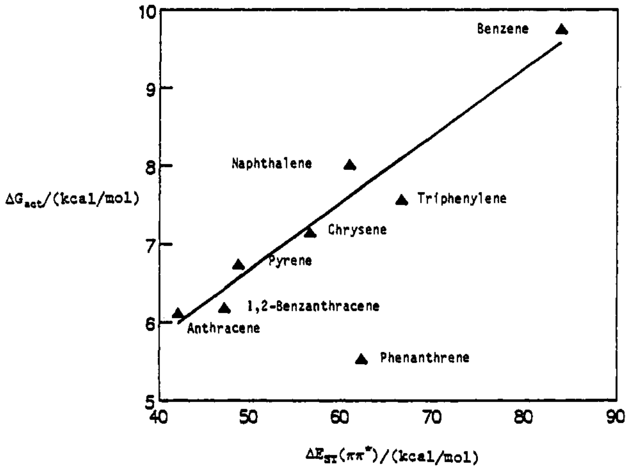

Figure 1. Correlation of free energies of activation vs singlet–triplet excitation energies for the reactions between phenyl radical and aromatic compounds in dichloromethane at 298 K.

Relative rate constants were obtained by competition kinetics using the reduction of phenyldiazonium ion by iodide ion to generate phenyl radicals[21,22] in dichloromethane containing two aromatic compounds in large excess of $[\mathrm{PhN_2}^+]$. Absolute rate constants were then derived with the value[23] reported for the reaction of phenyl radical with benzene, $4.5 \times 10^5\ M^{-1}\ s^{-1}$, as the standard. The reliability of this rate constant has been tested by comparison with relative values obtained by indirect methods.[23] Our second-order rate constants measured at 298 K for the reaction of phenyl radical with a series of alternant aromatic hydrocarbons are summarized in Table III. The corresponding singlet–triplet energies are listed as well.[24]

The observed free energies of activation correlate linearly with $\Delta E_{\mathrm{ST}}(\pi\pi^*)$ of ArH (Figure 1). Only the point for phenanthrene deviates significantly from the line (eq 22) and was omitted in

$$\Delta G_{\mathrm{act}} = 0.086\Delta E_{\mathrm{ST}}(\pi\pi^*) + 2.4\ \mathrm{kcal/mol} \qquad (22)$$

the correlation ($r = 0.97$). Directly relating eq 22 to eq 12 leads to problems. The constant, +2.4 kcal/mol, would have to be equated to $-B$, the avoided crossing parameter.[25] This is a highly unlikely situation since a negative B implies an increase rather than a decrease in energy as configuration mixing takes place. The appropriate term, in addition to $\Delta E_{\mathrm{ST}}(\pi\pi^*)$, to use in the correlation is derived in Scheme II and results in (23).

$$\Delta E_{\mathrm{act}} = f[\Delta E_{\mathrm{ST}}(\pi\pi^*) - RT \ln (K^*/K^{\circ})_{\mathrm{ST}}] - B \qquad (23)$$

The observation that ΔE_{act} is linearly related to $\Delta E_{\mathrm{ST}}(\pi\pi^*)$ does not imply that the reaction barrier is also linearly related to $\ln (K^*/K^{\circ})_{\mathrm{ST}}$. Because of this, the observed correlation parameters, slope 0.086 and intercept 2.4 kcal/mol, have no direct bearing on eq 23. Thus, lacking $(K^*/K^{\circ})_{\mathrm{ST}}$ data, we are unable to relate

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(16) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306.
(17) Koenig, T.; Chang, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 2240.
(18) Van Brunt, R. J.; Wacks, M. E. *J. Chem. Phys.* **1964**, *41*, 3195.
(19) Wacks, M. E.; Dibeler, V. A. *J. Chem. Phys.* **1959**, *31*, 1557.
(20) Bock, H.; Wagner, G.; Kronor, J. *Chem. Ber.* **1972**, *105*, 3850.
(21) Singh, P. R.; Kumar, A. *Aust. J. Chem.* **1972**, *25*, 2133.
(22) Tilset, M.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 281.
(23) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.
(24) Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9.
(25) Values of 0.2–0.25 are frequently used for f in recent discussions[16] and B values of 10–20 kcal/mol are commonly[19,20] assigned.

reaction barriers to a state correlation diagram.[26] These data illustrate the difficulty of interpreting a linear relationship between reaction barriers and singlet–triplet excitation energies.

Conclusions. Thermodynamic considerations require that the energetics involved in association of ground-state and dissociation of excited-state reactants be taken into account when formulating initial gaps for excitation of ground-state to excited-state complexes from ionization potentials, electron affinities, and singlet–triplet excitation energies of molecules. If the association of reactants, alone, is considered, the erroneous conclusion that since the association energy is negligibly small, the association constants can be neglected may appear reasonable. However, it is not a single association constant but rather the ratio K^*/K° that determines the magnitude of the effect. It is not acceptable to neglect this term without attempts to evaluate its magnitude.

Our overall conclusion is that when linear correlations between observed activation barriers and $I_D - E_A$ or $\Delta E_{ST}(\pi\pi^*)$ are found, the significance of the correlation parameters is usually not obvious. The uncertainties in the initial gap arising from the neglect of the association constants may explain the apparent failure[16,27] of the CM model analysis to correctly predict the barrier for the reaction of 9-phenylanthracene cation radical with pyridine. Further work is required to clarify the energetics of this and other ion-radical reactions.

Once again, the arguments presented in this paper are restricted to the terms that must be taken into consideration for the initial gap for excitation of ground-state donor–acceptor complexes to the corresponding excited states. The uncertainties that may arise can render the CM model analysis inappropriate for semiquantitative estimation of the reaction barrier. However, this added uncertainty is not expected to affect the qualitative use of the theory.

Experimental Section

Reagents. Benzenediazonium tetrafluoroborate was prepared by a standard procedure,[28] recrystallized from dry methanol and ether, and stored at −5 °C. Tetrabutylammonium tetrafluoroborate (Aldrich) was used as received. Dichloromethane was distilled over calcium chloride in a nitrogen atmosphere. All solid reagents and reference compounds were checked for purity by GLC. Some of these were recrystallized before use.

Procedure. Phenyl radicals were generated from $PhN_2^+BF_4^-$ by reduction with $Bu_4N^+I^-$ in dichloromethane. A solution of the aromatic hydrocarbon and $PhN_2^+BF_4^-$ in dichloromethane was allowed to come to thermal equilibrium at 298 K under a nitrogen atmosphere before an excess of a solution of $Bu_4N^+I^-$ was injected in the same solvent. The very rapid reaction was allowed to go to completion with efficient stirring and then allowed to stand for 0.5 h. The reaction mixture was then treated with 10% $Na_2S_2O_3$ solution to destroy iodine and extracted with pentane. The combined extracts were dried over anhydrous $MgSO_4$ before GLC analysis. The analysis was carried out with a Varian 3700 gas chromatograph in conjunction with a Hewlett-Packard 3390 A integrator. GLC response factors were determined by measurements on mixtures of known composition. All other aspects of the analysis were similar to those described earlier.[22]

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Registry No. Benzene, 71-43-2; naphthalene, 91-20-3; anthracene, 120-12-7; pyrene, 129-00-0; chrysene, 218-01-9; triphenylene, 217-59-4; 1,2-benzanthracene, 56-55-3; phenanthracene, 85-01-8; phenyl radical, 2396-01-2.

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(26) In order to observe "reasonable" values of f and B, the K^*/K° term would have to be significantly large. For example, considering only the data for benzene and anthracene, log $(K^*/K^\circ)_{ST}$ values of 24 and 4, respectively, would give rise to $f = 0.25$ and $B = 2.9$. This implies a linear relationship between log $(K^*/K^\circ)_{ST}$ and $\Delta E_{ST}(\pi\pi^*)$ with a slope equal to 0.48.

(27) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521.

(28) *Vogel's Textbook of Practical Organic Chemistry*; Longman: Harlow, Essex, U.K., 1978; p 705.

(29) Kobayoshi, T.; Nagokura, S. *J. Chem. Soc. Jpn.* **1974**, *47*, 2563.

(30) Klessinger, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 525.

Chelation of 2-Substituted-1-lithoxides: Structural and Energetic Factors of Relevance to Synthetic Organic Chemistry

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Abstract: A number of lithium 2-(methylamino)-, 2-(dimethylamino)-, 2-methoxy-, and 2-(isopropylthio)-substituted-1-phenyl-1-propoxides were studied as models for asymmetric synthetic strategies for which lithium chelation between two electronegative atoms has frequently been invoked. The heats of formation of these alkoxides were determined by deprotonating the alcohols with lithium bis(trimethylsilyl)amide in a solution calorimeter. Aggregation numbers for the substituted alcohols and their corresponding lithium alkoxides were obtained with freezing point depression and vapor pressure osmometry in THF, benzene, and dioxane. In several cases, solution structures were obtained through ^1H, ^6Li, and 2D ^6Li–^1H NOE (HOESY) NMR spectroscopy. Solid-state structures of lithium (+)-*N*-methylpseudoephedrate and (−)-*N*-methylephedrate (+)-*N*-methylpseudoephedrate and (−)-*N*-methylephedrate (as the benzene solvate) were obtained by X-ray crystallography, and both were found to be present as tetramers in which the dimethylamino nitrogen atoms were coordinated to the lithium cations to form five-membered chelate rings. The lithium alkoxides were either tetramers or hexamers in nonpolar solvents; however, the alkoxides' solution structures were very complex in THF as evidenced by several ^6Li resonances observed in the ^6Li NMR spectra at low temperatures. Intramolecular lithium chelation was found to occur in each alkoxide in dioxane and benzene. The enthalpies of chelational stabilization were estimated by comparing their heats of deprotonation with those of nonchelatable 2-alkyl-substituted analogues. The stabilization enthalpies ranged from 5 to 11 kcal/mol per alkoxide molecule.

Introduction

Important progress toward asymmetric synthesis has been made in the last two decades through the use of organolithium compounds in low polarity solvents, usually at low temperatures. Especially successful has been the use of lithium enolates in the modern aldol reaction.[1,2] Although the actual reactive inter-

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