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Nucleophilic Attack on Cation Radicals and Cations. A Theoretical Analysis

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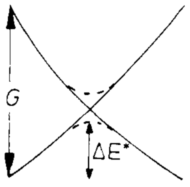
Abstract: The curve-crossing model is applied to the problem of barrier heights for nucleophilic attack on cation radicals, RH$^{\bullet+}$, and cations, R$^+$. It is shown that the barrier height depends on the ionization potential of the nucleophile, the electron affinity of the cation, and, for cation radicals, also on the singlet–triplet energy gap of the corresponding neutral molecule, RH. It is shown that in general, cation radicals are likely to be less reactive than cations (of the same acceptor ability) toward nucleophilic attack, because the product configuration for cation radicals is doubly excited (D$^+$ ^{3*}A$^-$), whereas that for regular cations is singly excited (D$^+$A$^-$). A semiquantitative analysis is presented that shows that those cases where cation radicals are likely to react rapidly with nucleophiles can be predicted in a straightforward manner.

In a recent communication[1] it was suggested that polar reactions could be usefully divided into "allowed" and "forbidden" categories, in analogy to Woodward and Hoffmann's pioneering classification of pericyclic reactions.[2] The basis for reaching this conclusion was the curve-crossing models[3-5] (configuration mixing (CM)[4] and state correlation diagram (SCD)[4a,5]) that provide a simple means for understanding barrier formation in chemical reactions. It was argued[1] that for certain reactions the electronic configuration describing the products was *singly* excited with respect to the reactants, while for others it was *doubly* excited. According to the curve-crossing diagrams the size of this energy gap, *G*, is of great importance in governing reactivity. A large gap is likely to lead to a high barrier, as illustrated in **1**, while a small gap is likely to lead to a low barrier, as illustrated in **2**, though there are exceptions (e.g., due to the effect of thermodynamics and curve slopes).[5b] Since in principle, double excitation leads to larger *G* values than single excitation, it is possible to classify reactions by the degree of excitation of the product configuration relative to that of reactants. Thus reactions whose product configuration is singly excited were formally classified as "allowed", while those where the product configuration is doubly excited were formally classified as "forbidden".



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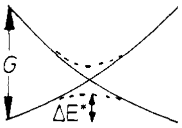

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To demonstrate the "allowed-forbidden" classification for polar reactions, it was applied to the reaction of both regular cations and cation radicals, with nucleophiles.[1] For cation radicals reacting with nucleophiles it was shown that the product configuration is doubly excited, and hence the reaction is formally classified as "forbidden". For regular cations however, the product configuration is singly excited and hence direct attack of a nucleophile is formally classified as "allowed". Consistent with this prediction, Eberson et al.[6] have pointed out that cation radicals are in many cases surprisingly resistant to nucleophilic attack.[6,7] By contrast however the reaction of cations with nucleophiles is generally a facile process.

In recent months evidence has appeared to suggest that certain cation radical reactions with nucleophiles are fast, and in some cases the reactions may even be barrier free. Specifically, Nibbering, Schwarz et al.[8] have studied the gas-phase reaction of ketene cation radical with ammonia, both experimentally and computationally, and found the reaction to be facile. Parker and Tilset[9] have studied the reaction of 9-phenylanthracene cation radical with nitrogen-centered nucleophiles and found them to be rapid (ca. 10^7–10^9 M^{-1} s^{-1}). Kochi and collaborators[10] have measured the rate of collapse of the aromatic cation radical–trinitromethyl anion ion pair obtained by photoexcitation within a solvent cage and measured rate constants as high as 10^9 M^{-1} s^{-1}. In this paper we present a semiquantitative analysis that enables reactivity and reaction pathways to be predicted in nucleophile–cation and nucleophile–cation radical reactions. The "allowed-forbidden" classification is then re-evaluated based on the semiquantitative analysis.

Discussion

The formal classification of polar reactions, as "allowed" and "forbidden", depends on whether the product configuration is singly or doubly excited with respect to the reactant configuration. It provides a rule of thumb for estimating relative reactivity. Of course, as a direct consequence of its simple nature, the classification cannot provide an infallible guide since we are aware that other factors[4a,5b,11] such as reaction exothermicity, the degree of avoided crossing, and variations in the curvatures of the intersecting curves can in principle change upon chemical substitution and thereby affect relative reactivity. In this sense the situation is analogous to Woodward and Hoffmann's use of the terms "allowed" and "forbidden".[2] Thus there are cases where "forbidden" reactions may have lower barriers than certain

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(1) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(3) For a recent review of the curve crossing models, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 218–222, 354–360, 381–382, 604–608.

(4) (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99.

(5) (a) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (b) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

(6) Eberson, L.; Blum, Z.; Helgee, B.; Nyberg, K. *Tetrahedron* **1978**, *34*, 731.

(7) For a number of cases it has actually been found that the cation radicals disproportionate to the dication and the neutral and that it is only at this dication stage that nucleophilic attack takes place. See: Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243.

(8) Drewello, T.; Heinrich, N.; Maas, W. P. M.; Nibbering, N. M. M.; Weiske, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 4810.

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

(10) (a) Masnovi, J. M.; Levine, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4356. (b) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7880. (c) Masnovi, J. M.; Huffman, J. C.; Kochi, J. K.; Hillinski, E. F.; Rentzepis, P. M. *Chem. Phys. Lett.* **1984**, *106*, 20. (d) Masnovi, J. M.; Kochi, J. K.; Hillinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 1126. (e) Sankaraman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824.

(11) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708.

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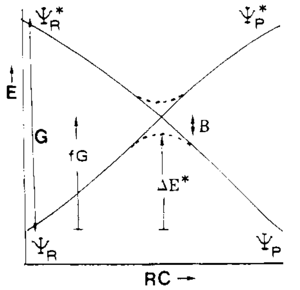

Figure 1. A curve crossing diagram for a one-step reaction. Ψ_R and Ψ_P are ground states of reactants and products, respectively. $\Psi_R{}^*$ and $\Psi_P{}^*$ are the corresponding excited states. The pair of states Ψ_R and $\Psi_P{}^*$ as well as the pair of states $\Psi_R{}^*$ and Ψ_P share the same electronic configuration, while the pair of states Ψ_R and $\Psi_R{}^*$ and the pair of states Ψ_P and $\Psi_P{}^*$ share the same geometry (that of reactants and products, respectively).

"allowed" ones. Also, it is possible to find formally "allowed" reactions that have large barriers so that, for all practical purposes, they are "forbidden".[12] It is a truism, that any reactivity rule in chemistry with just "on–off" alternatives can, at best, provide a rough conceptual framework for understanding reactivity problems. Chemical reactivity, being a quantifiable parameter that in practice stretches continuously over more than 20 orders of magnitude, of course cannot be fully described in terms of a "yes–no" type classification system. However, having made the above qualification we now propose to show that the simple rule governing reactivity in polar reactions is generally applicable and that apparent breakdowns may be understood by a more quantitative evaluation of the appropriate reactivity parameters.[5b,11]

The Relationship between Initial Energy Gap and Barrier Height. In recent papers we have described the height of the barrier for a given reaction, ΔE^*, by

$$\Delta E^* = fG - B \qquad (1)$$

The energy gap, G, is that between reactant (Ψ_R) and product ($\Psi_R{}^*$) configurations at the reactant geometry, B is the avoided crossing parameter, and f is some fraction that depends inter alia on the reaction thermodynamics and delocalization properties of the excited states.[5b,13] The relationship between these parameters is illustrated in Figure 1. If we arbitrarily describe rapid reactions as those whose barrier is less than 10 kcal/mol (equivalent to a rate constant of $>10^{5.6}$) and slow reactions as those whose barriers are more than 15 kcal/mol (equivalent to a rate constant of $<10^2$), we may generate a crude estimate of reactivity from the initial energy gap (G, in Figure 1). Since $f = 0.2 - 0.25$[13] and B has been estimated at 10 ± 3 kcal/mol,[13] we may propose that reactions whose initial energy gap is 60 kcal/mol or less will be rapid, while reactions whose initial barrier is 100 kcal/mol or more will be slow. Of course this is a very crude reactivity measure. But despite its crudeness, it will enable us to obtain a ballpark estimate for the reactivity of a particular system. In the course of specific analyses to follow, we will utilize these benchmark values of 60 and 100 kcal/mol as qualitative estimates of the limits of high and low reactivity.

Reaction of Nucleophiles with Cations and Cation Radicals. The reaction of a nucleophile with a cation and with a cation radical differ in their configurational description.[1] The reactant configuration for the cation–nucleophile reaction is depicted in **3** (a DA configuration, where D = donor, A = acceptor), while the configuration that describes the N–R combination product (described by D^+A^-) is depicted in **4**. It can be seen that all that is required to convert **3** to **4** is a single electron shift from $N\!:^-$ to R^+. For the addition reaction of a nucleophile to a cation

$$\begin{array}{ccc} \mathrm{N}\!:^{-}\ \ \mathrm{R}^{+} & \qquad & \mathrm{N}\bullet\ \ \bullet\mathrm{R} \\ \mathrm{D}\ \ \mathrm{A} & & \mathrm{D}^{+}\ \mathrm{A}^{-} \\ \mathbf{3} & & \mathbf{4} \end{array}$$

radical the situation is different. The reactant configuration, DA, is shown in **5**. However for the case of the cation radical the shift of a single electron from $N\!:^-$ to $RH^{\bullet+}$ to generate D^+A^-, **6**, merely

$$\begin{array}{ccccc} \mathrm{N}\!:^{-}\ \ \mathrm{RH}^{+\bullet} & \qquad & \mathrm{N}\bullet\ \ \mathrm{RH} & \qquad & \mathrm{N}\bullet\ \ (\bullet\dot{\mathrm{R}}\mathrm{H})^{*3} \\ \mathrm{D}\ \ \mathrm{A} & & \mathrm{D}^{+}\ \mathrm{A}^{-} & & \mathrm{D}^{+}\ \ {}^{3*}\mathrm{A}^{-} \\ \mathbf{5} & & \mathbf{6} & & \mathbf{7} \end{array}$$

generates the parent hydrocarbon, RH, together with the nucleophile in its oxidized form, $N^\bullet$. This configuration does not describe the products. The configuration which *does* describe the product of addition to the cation radical is depicted in **7** and may be termed $D^+\ {}^{3*}A^-$. In addition to an electron shift from the nucleophile to the cation radical, the hydrocarbon has undergone singlet–triplet excitation (signified as ${}^{3*}A^-$). The singlet–triplet excitation is necessary to generate an uncoupled electron in RH which may couple with the odd electron on $N^\bullet$ to form the N–RH covalent linkage. Thus addition of a nucleophile to a regular cation is described by a singly excited product configuration (D^+A^-), while addition to a cation radical is described by a doubly excited configuration ($D^+\ {}^{3*}A^-$). Let us now examine in a semiquantitative fashion the energy gaps for model systems.

Reaction of Model Cations and Radical Cations with NH_3. In order to assess the limitations of the "allowed-forbidden" classification of polar reactions, let us consider the energetics of three cation–nucleophile reactions: the reaction of ammonia with the methyl cation, CH_3^+, the ethylene radical cation, $CH_2{=}CH_2^{\bullet+}$, and the ketene radical cation, $CH_2{=}C{=}O^{\bullet+}$. In Table I are listed the appropriate physical parameters: vertical ionization potential of the nucleophile, N:, $I_{N:}{}^*$; vertical electron affinity of the electrophile, E, $A_E{}^*$; the singlet–triplet excitation energy, ΔE_{ST}; and the relevant energy gaps derived from these quantities for these three reactions. These are the key parameters that are utilized in estimating initial energy gaps in the application of the curve-crossing models (see Figure 1). For a reaction described by a DA – D^+A^- crossing the initial energy gap will be given by $I_{N:}{}^* - A_E{}^*$, the energy necessary to transfer an electron from D to A, while for those described by a DA – $D^+\ {}^{3*}A^-$ crossing the energy gap will be described by $I_{N:}{}^* - A_E{}^* + \Delta E_{ST}$; the gap is composed of the electron-transfer energy as well as the singlet–triplet excitation of the RH moiety.

Let us first compare the nucleophilic attack of NH_3 on the methyl cation and ethylene cation radical. Reaction profiles for these two reactions, built up from the appropriate configuration curves, are illustrated schematically in Figure 2 (parts a and b), respectively. For the reaction of NH_3 with CH_3^+ the reaction profile is built up from the avoided crossing of reactant, DA and product, D^+A^- configurations. From the vertical ionization potential of ammonia and the vertical electron affinity of the methyl cation (i.e., the ionization potential of the methyl radical) the initial energy gap between DA and D^+A^- (Gap(Add)) is estimated as ca. 23 kcal/mol (Table I, reaction 1). This value is substantially less than our reference value of 60 kcal/mol and coupled with the strong thermodynamic driving force[14] (which ensures a small f value) suggests a barrier free reaction.[13b]

For the reaction with ethylene cation radical however (Table I, reaction 2), as discussed above, the reaction profile comes about from the avoided crossing of DA and the doubly excited product configuration, $D^+\ {}^{3*}A^-$. The double excitation involves both an electron shift from NH_3 to the ethylene cation radical as well as singlet–triplet excitation of the ethylene π-bond. Estimating the

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[12] For example, the trimerization of acetylene to benzene is an "allowed" reaction whose barrier is >60 kcal/mol despite a thermodynamic driving force of ca. −130 kcal/mol. See: (a) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797. (b) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837. There are also formally "forbidden" 2 + 2 cycloadditions between donor and acceptor olefins, which are quite fast and certainly faster than the "allowed" Diels–Alder reaction of ethylene and butadiene. See, for example: (c) Nishida, S.; Moritani, I.; Teraji, T. *J. Org. Chem.* **1973**, *38*, 1878.

[13] (a) Shaik, S. S. *J. Org. Chem.* **1987**, *52*, 1563. (b) Buncel, E.; Shaik, S. S.; Um, I.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1988**, *110*, 1275.

[14] The thermodynamic driving force of the reaction is the methyl cation affinity of ammonia: Meot-Ner, M.; Karpas, Z.; Deakyne, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3913.

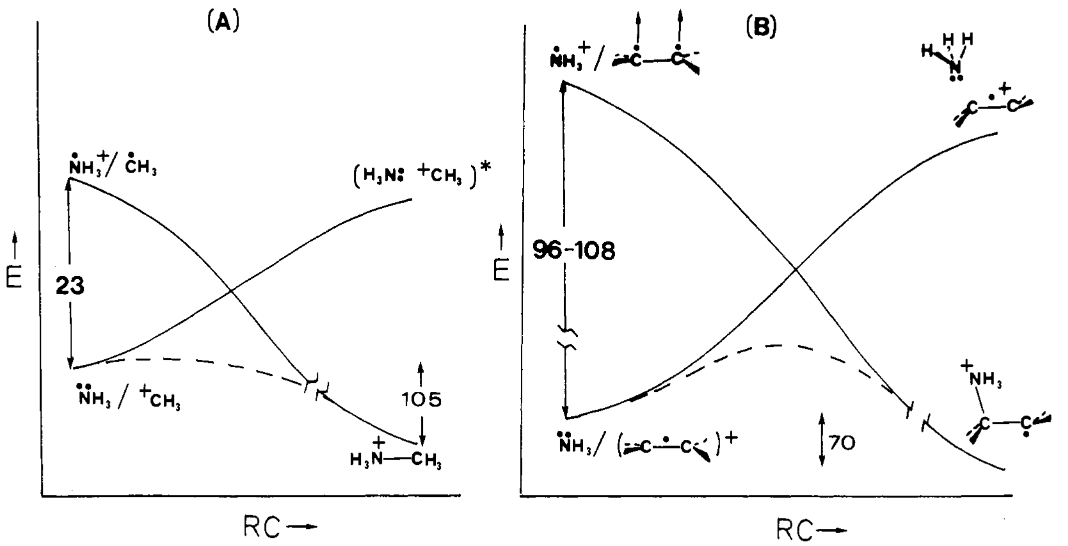


Figure 2. A curve crossing diagram for (A) the addition of ammonia to methyl cation and (B) the addition of ammonia to ethylene cation radical. In both cases the reaction coordinate is considered to begin from the geometry of the ion–dipole complex.

Table I. Gap-Related Quantities and Initial Energy Gaps[a] for Reactions (Nucleophilic Addition and Electron Transfer) of Cation Radicals and Cations with NH_3

cation	$I_{N:}$*(g)[a,b]	A_E*(g)[a,b]	$\Delta E_{ST}(\pi\pi^*)$[a]	Gap(Add)[c]	Gap(ET)[d]
(1) CH_3^+	250.2[e]	226.9[e]		23.3	23.3
(2) $H_2C{=}CH_2^{\bullet+}$	250.2[e]	242.5[f]	100,[g] 88[h]	96–108	7.7
(3) $H_2CCO^{\bullet+}$	250.2[e]	319.2[f]	100[g]	31	−69

[a] In kcal/mol. [b] $I_{N:}$*(g) is the gas-phase vertical ionization potential of the nucleophile (NH_3). A_E*(g) is the vertical electron affinity of the cation and is taken as the vertical ionization potential of the neutral species. The actual A_E*(g) may be <10 kcal/mol smaller than this value since these two values are not expected to be identical. [c] Gap(Add) is the initial energy gap for the nucleophilic addition pathway obtained from $I_{N:}$*(g) − A_E*(g) to which is added $\Delta E_{ST}(\pi\pi^*)$ for reactions of cation radicals. The gap refers to G in Figure 1. [d] Gap(ET) is the initial energy gap for the electron-transfer pathway obtained from $I_{N:}$*(g) − A_E*(g). The gap refers to G in Figure 1. [e] *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9. [f] Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley: New York, 1970. This is the π-electron affinity. [g] Estimated as a typical value for olefins. See: Jordan, K. D.; Burrow, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 6882. [h] The ΔE_{ST} is <100 kcal/mol because $C_2H_4^{\bullet+}$ in its ground state is 20° twisted (see: Koppel, H.; Cederbaum, L. S.; Domcke, W.; Shaik, S. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 210). Using a simple approximation of a $\cos^2\theta$ dependence of the twisting surface of triplet ethylene, the ΔE_{ST} value for a twisted $C_2H_4^{\bullet+}$ is 88 kcal/mol ($\Delta E_{ST} = \Delta E_{ST}(0°)\cos^2\theta$).

singlet–triplet gap as ca. 88–100 kcal/mol (see footnotes g and h in Table I) leads to an estimated energy gap of ca. 96–108 kcal/mol (Figure 2b). For the ethylene cation radical reacting with NH_3 this large initial energy gap suggests that this reaction will show a significant barrier.

Let us now compare the situation for the corresponding reaction of the ketene cation radical (Figure 3). In this case, because of the high electron affinity of this cation radical (Table I, reaction 3), the initial energy gap is just <31 kcal/mol, despite the contribution of the singlet–triplet excitation energy (<100 kcal/mol) to the gap. Thus in this particular case the $DA{-}D^+\,{}^{3*}A^-$ gap is not significantly different from the $DA{-}D^+A^-$ gap for the methyl cation reaction (23.3 kcal/mol).

The conclusion is clear. Because of the small initial energy gap, the addition reaction of a nucleophile to both the methyl cation and the ketene cation radical are predicted to be rapid, with a small or zero barrier, and this despite the fact that for one the product configuration is singly excited, while for the other the product configuration is doubly excited. Ultimately therefore the classification of reaction 3 as "forbidden" is not predictive, since it is the *actual* energy gap that will govern the barrier height rather than the degree of the excitation (singly or doubly excited). The degree of the excitation is of course important but only to the extent that, in general, one would expect singly excited configurations to be of lower energy than doubly excited ones. Clearly though, this is true only when the electron affinities of R^+ and $RH^{\bullet+}$ are comparable.

The Choice of Reaction Channel. The previous discussion may also form a basis for predicting which particular reaction channel a set of reactants is likely to follow. Let us now apply the SCD model to determine the appropriate reaction channel for the reaction of NH_3 with each of the three model cations discussed above.

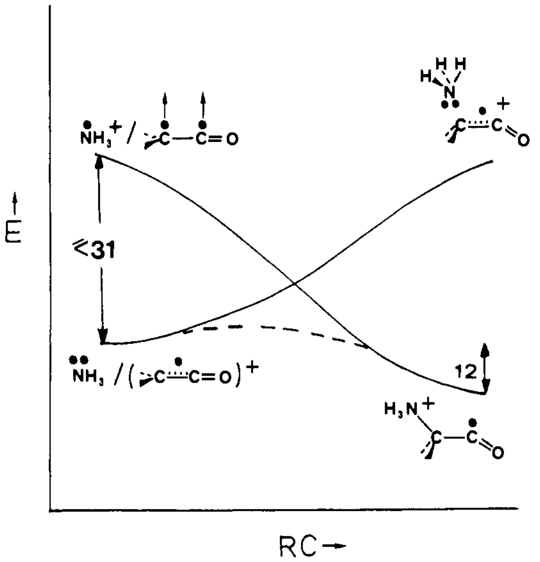


Figure 3. A curve crossing diagram for the addition of ammonia to the cation radical of ketene. The reaction coordinate is considered to begin from the geometry of the ion–dipole complex.

Consider the reaction of NH_3 with the ethylene cation radical (Table I, reaction 2). Two likely reaction channels that one might consider are the nucleophilic pathway, discussed above, and the

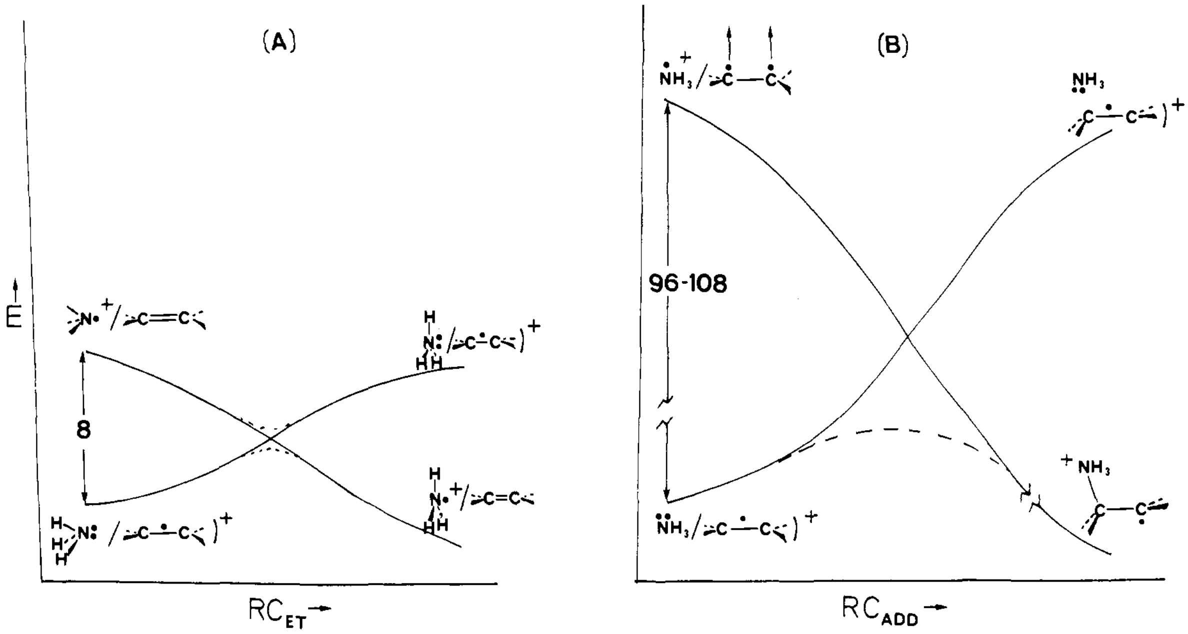


Figure 4. A curve crossing diagram for (A) the electron transfer from ammonia to the cation radical of ethylene and (B) the addition of ammonia to ethylene cation radical. RC$_{ET}$ is the ET reaction coordinate and involves nuclear intramolecular distortions of the two reactants but not their relative approach along the N---C bond-forming direction. In both cases the reaction coordinate is considered to begin from the geometry of the ion–dipole complex.

electron-transfer (ET) pathway. The two reaction profiles are illustrated in Figure 4. For all ET pathways, the reaction profile is built up from the avoided crossing of DA and D$^+$A$^-$ curves. In this particular case the DA–D$^+$A$^-$ energy gap is just ca. 8 kcal/mol (Table I and Figure 4A) so that in comparison to the addition pathway (Table I and Figure 4B) for which the DA–D$^+$ ^{3*}A$^-$ gap equals 96–108 kcal/mol, the barrier is likely to be significantly smaller. Thus based on a simple analysis of the relative energy gaps between reactant and product configurations for the two possible channels, we conclude that the ethylene cation radical will prefer to react with $\mathrm{NH_3}$ in an ET process.[15]

Competition between the addition and ET channels for reaction of $\mathrm{NH_3}$ with the ketene cation radical leads to the *opposite* prediction. As was stated above, an ET process involves a DA–D$^+$A$^-$ avoided crossing. However for the reaction of $\mathrm{NH_3}$ with the ketene cation radical the DA–D$^+$A$^-$ energy gap is *negative*, −69 kcal/mol! The negative sign signifies that the D$^+$A$^-$ curve lies substantially *below* the DA curve (shown schematically in Figure 5). It follows that the two configuration curves will not actually cross, and this means that an ET process will not therefore take place. Because of the large negative energy gap there simply may not be an energetically accessible reaction coordinate that connects reactants to ET products. This means that only by fluorescing or decaying in a radiationless process from the excited DA surface to the ground D$^+$A$^-$ surface are ET products likely to be formed. For the nucleophilic attack channel however, an avoided crossing does result (Figure 3). So for the ketene cation radical, our analysis suggests that a nucleophilic addition pathway will be preferred over an ET pathway.

For the reaction of $\mathrm{NH_3}$ with the methyl cation, the two possible reaction profiles, for addition and ET, are illustrated in Figure 6. Both involve a DA–D$^+$A$^-$ avoided crossing, since in both the configurational change involves the transfer of a single electron. However due to the significantly lower energy of the addition product (Figure 6A) and the larger *B* values[13a] compared to the ET products (Figure 6B), the addition pathway is predicted to be substantially preferred.

We see therefore that a more detailed analysis of the configuration curves enables an assessment to be made regarding the choice of reaction channel likely to be followed in a particular case.

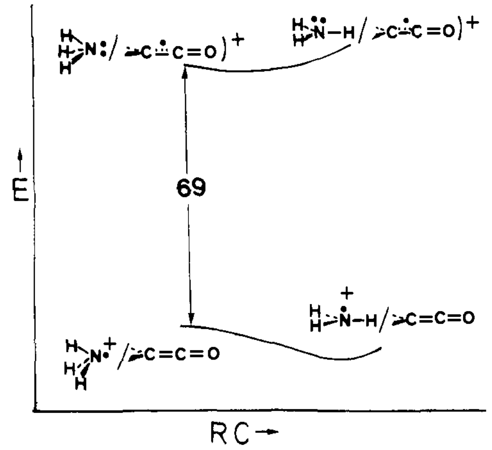
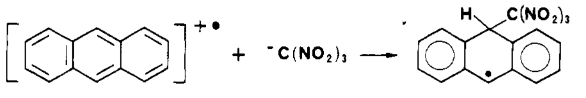


Figure 5. Curves for the putative electron transfer from ammonia to ketene cation radical. The reaction coordinate involves the relaxation of $\mathrm{NH_3}^{\bullet+}$. Note that the two surfaces do not cross.

Competition between Radical Cation–Nucleophile and Radical Cation–Radical Combination Reactions. In a series of very elegant experiments, Kochi and co-workers[10] have been able to study the competitive reaction of aromatic cation radicals. A$^{\bullet+}$ (A = anthracene or substituted anisoles), with the anionic nucleophile, $^-$C(NO$_2$)$_3$, or with $^\bullet$NO$_2$ radical within the triad [A$^{\bullet+}$, $^-$C(NO$_2$)$_3$, $^\bullet$NO$_2$]. The triad is generated within a cage by the photochemical excitation of the charge-transfer complex of the aromatic moiety and tetranitromethane, [A, C(NO$_2$)$_4$] to give [A$^{\bullet+}$, C(NO$_2$)$_4^{\bullet-}$]. The radical cation, C(NO$_2$)$_4^{\bullet-}$, then rapidly breaks up (within 3ps) to form the separate $^-$C(NO$_2$)$_3$ anion and $^\bullet$NO$_2$ radical within the triad [A$^{\bullet+}$, $^-$C(NO$_2$)$_3$, $^\bullet$NO$_2$]. At this point two reaction channels are available; in one the radical cation undergoes a combination reaction with the anionic group (ion pair collapse), while in the second channel the radical cation undergoes a combination reaction with the radical group (radical pair collapse). Kochi et al.[10] have found that different cation radicals and solvents affect the choice of reaction channel. Let us examine the data more closely.

The first result is that anthracene cation radical (as well as substituted derivatives) reacts rapidly ($k = 10^9$ s^{-1}) with the $^-$C(NO$_2$)$_3$ anion by ion pair collapse to yield the hydranthyl adduct (eq 2),[10a] while 1,4-dimethoxybenzene reacts by the second channel, radical pair collapse,[10c] to yield the Wheland intermediate as derived from aromatic nitration (eq 3).



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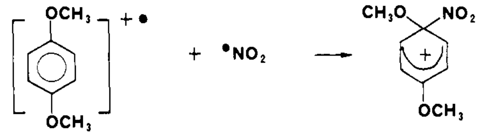


(3)

Two questions arise. Why is ion pair collapse, which involves nucleophilic attack on a cation radical of anthracene, so fast despite the product configuration being doubly excited? Secondly, why do two cation radicals with essentially the same electron affinity (E° values for anthracene and dimethoxybenzene are 1.23 and 1.30 V, respectively)[10e] react by different channels?

Examination of the relevant physical parameters in Table II provides a possible answer to both questions. The initial energy gap between reactant and product configurations for the addition reaction of $^-C(NO_2)_3$ anion to anthracene cation radical in dichloromethane (entry 1) is estimated at ca. 52–62 kcal/mol. In benzene (entry 3) the gap is actually close to zero. Thus despite the fact that the gap is composed of both an electron transfer and a singlet–triplet excitation the initial gap is relatively small. Given our rule of thumb, described above, for assessing reactivity, such a process is predicted to be extremely fast, as indeed is observed by Kochi.[10a] So once again, we see that reactions proceeding via a doubly excited configuration may in certain cases be rapid.

The different reaction channels followed by anthracene and dimethoxybenzene cation radicals within the triad is intriguing. Kochi et al.[10e] have noted that as the aromatic moiety becomes a better acceptor, the tendency to undergo ion pair collapse rather than radical pair collapse increases. This is also consistent with the curve crossing model since as the aromatic moiety becomes a better acceptor the initial energy gap (governed by $I_{N:}^* - A_E^*$) decreases, and the reaction barrier is thus predicted to decrease. However for the case of anthracene and dimethoxybenzene cation radicals this behavior is not observed. If anything, the dimethoxybenzene cation radical is a *better* acceptor than that of anthracene yet it undergoes radical collapse rather than ion-pair collapse.[10e] Examination of the data in Table II (entries 1 and 5) provides an explanation for this anomalous behavior. The data reveal that despite the small difference in the electron affinities between the cation radicals of dimethoxybenzene and anthracene, the initial energy gap for the dimethoxybenzene cation radical reaction with $^-C(NO_2)_3$ (80–90 kcal/mol) is substantially larger than for the corresponding reaction of anthracene (52–62 kcal/mol). The reason for the difference in gap size stems from the difference in the singlet–triplet excitation for the two aromatics. Anthracene has a substantially lower singlet–triplet excitation (42.4 kcal/mol) than the family of substituted benzenes (ca. 80 kcal/mol), and this appears to be the factor responsible for the different pathways followed by these two cation radicals. Thus ion-pair collapse does *not* necessarily take place with the better cation radical acceptor since the rate of ion-pair collapse depends not only on the donor–acceptor pair ability (the $I_{N:}^* - A_E^*$ term) but also on the singlet–triplet excitation gap as well.

Kochi's observation that solvent polarity has a strong influence on the reaction channel can also be understood in terms of the curve crossing model. The effect of solvent polarity on the energetics of anthracene cation radical and $^-C(NO_2)_3$ anion combination is shown in Table II. The effect of solvent[18] on both ionization potential and electron affinity is substantial. Thus in benzene (entry 3) an initial gap of just 2–12 kcal/mol is estimated, while in the more polar acetonitrile (entry 2), a gap of 70–80 kcal/mol is estimated. It follows that radical combination, which is not expected to show a significant solvent effect, can compete more effectively as the solvent polarity increases since the initial energy gap, and hence the barrier to ion-pair collapse, increases with it.

In light of the data in Table II (entries 7 and 8), the rapid (10^7–10^9 M^{-1} s^{-1}) rates of reaction of amine nucleophiles with the cation radicals derived from anthracene derivatives, as reported by Parker and Tilset,[9] pose a dilemma since it is difficult to reconcile the rapid rates with the large initial energy gaps (ca. 100 kcal/mol). It is of course possible that other factors that govern the curve crossing diagram, which we cannot estimate quantitatively, are involved. On reviewing the data, however, we wish to propose an alternative explanation for the rapid rates, which is consistent with both the experimental data and the theoretical analysis presented above.

The mechanistic scheme described in Scheme I exhibits the same kinetic behavior and stoichiometry as the direct nucleophilic attack pathway but involves an initial rate-determining electron transfer from the nucleophile to the phenylanthracene cation radical ($PA^{\bullet+}$). This scheme is consistent with our analysis since a rapid reaction could be predicted for an ET process. The initial energy gap for an ET reaction ($I_{N:}^* - A_E^*$) is significantly lower than for the direct nucleophilic attack pathway ($I_{N:}^* - A_E^* + \Delta E_{ST}$). For example, the gap for the piperidine–anthracene cation radical reaction in dichloromethane (entry 8) is 49 kcal/mol for the ET pathway, consistent with a rapid reaction. This is in contrast to the direct attack pathway for which the initial gap is estimated to be 101 kcal/mol. On the other hand, the reaction with pyridine has high gaps for both mechanisms, and we cannot offer a good explanation for the rapid rates. As pointed out by a referee, the rates of the addition correlate with the basicity of the amine, which suggests that pyridine and piperidine may share a common mechanism. We conclude therefore that further examination of this problem, both theoretically and experimentally, is required to establish the origins of the very rapid rate of the reaction of amines with anthracene cation radical.

Scheme I

$$PA^{\bullet+} + Nu \xrightarrow{RDS} PA + Nu^{\bullet+}$$

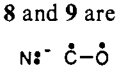
$$PA^{\bullet+} + Nu^{\bullet+} \rightarrow PA^+\text{–}Nu^+$$

$$PA^+\text{–}Nu^+ + Nu \rightarrow PA(Nu)_2^{2+}$$

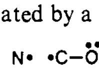
$$\overline{\underline{2PA^{\bullet+} + 2Nu \rightarrow PA + PA(Nu)_2^{2+}}}$$

The Nature of Polar Organic Reactions. On the basis of the above discussion it is evident that reactions whose product configuration is doubly excited may be rapid despite the double excitation. However the idea that reactions whose product configuration is singly excited are favored over those where it is doubly excited seems to typify organic chemical reactivity in a broad sense. Let us discuss this point in greater detail.

A cursory examination of the basic reactions of organic chemistry reveals a remarkable feature. With few exceptions the electronic configuration that describes products is singly excited with respect to the reactants. Let us illustrate the point by considering nucleophilic addition to a carbonyl group. The reactant configuration is described by **8** (a DA configuration), while the product configuration is described by **9** (a D^+A^- configuration). Since **8** and **9** are related by a single electron shift,



8



9

D^+A^- is a singly excited configuration with respect to DA. Most of the polar reactions of undergraduate organic chemistry belong

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(15) It should be noted that for ET processes the *B* value is commonly presumed to be <1 kcal/mol.[16] A small *B* value will tend to increase the barrier, thereby reducing the likelihood of ET pathways.[17] However despite this an ET pathway is predicted to be favored over the addition pathway due to the very small *G* value for the ET pathway.

(16) (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Heidelberg, 1987. (b) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(17) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

(18) Shaik, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 1227.

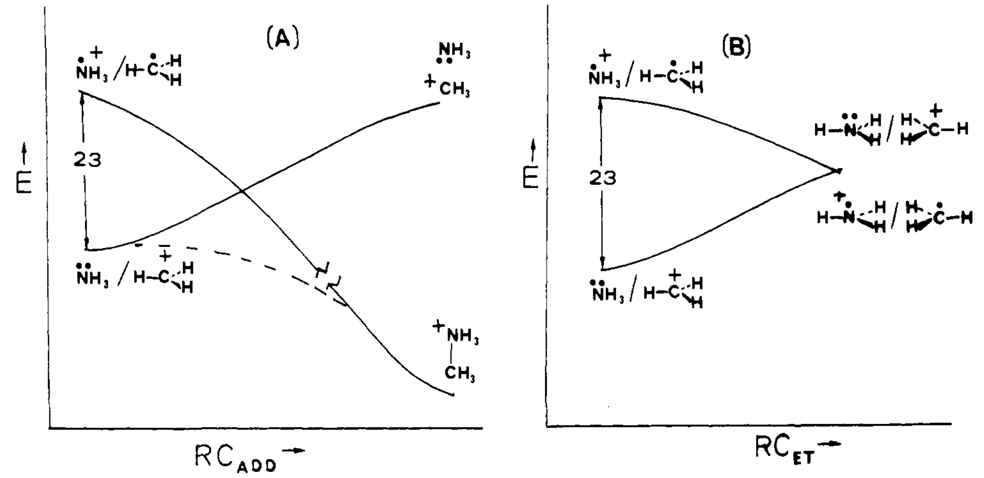

Figure 6. A curve crossing diagram for the (A) addition of ammonia to methyl cation and (B) the electron transfer from ammonia to methyl cation. The RC_{ADD} is the addition reaction coordinate which involves both reactants' approach and intramolecular geometric changes. The RC_{ET} is the reaction coordinate for electron transfer and involves only intramolecular geometric changes within the ammonia and methyl cation moieties. In both cases the reaction coordinate is considered to begin from the geometry of the ion-dipole complex.

Table II. Gap-Related Quantities and Initial Energy Gaps[a] for Reactions of Cation Radicals of Anthracene, $A^{\bullet+}$, and 1,4-Dimethoxybenzene, $DMB^{\bullet+}$, with Nucleophiles

reaction	$I_{N:}^*(s)^{a,b}$	$A_E^*(s)^{a,b}$	$\Delta E_{ST}(\pi\pi^*)^{a,c}$	Gap(Add)[a,d]
(1) $(NO_2)_3C^- + A^{\bullet+}$ in dichloromethane	131–141	121	42.4[e]	52–62
(2) $(NO_2)_3C^- + A^{\bullet+}$ in acetonitrile	138–148	110	42.4[e]	70–80
(3) $(NO_2)_3C^- + A^{\bullet+}$ in benzene	103–113	143	42.4[e]	2–12
(4) $(NO_2)_3C^- + A^{\bullet+}$ in the gas phase	70–80[f]	172[f,g]	42.4[e]	−60–(−50)
(5) $(NO_2)_3C^- + DMB^{\bullet+}$ in dichloromethane	131–141	131	80[c]	80–90
(6) $(NO_2)_3C^- + DMB^{\bullet+}$ in the gas phase	70–80[f]	182[f,g]	80[c]	−22–(−32)
(7) pyridine + $A^{\bullet+}$ in dichloromethane	191	121	42.4[e]	112.4
(8) piperidine + $A^{\bullet+}$ in dichloromethane	170	121	42.4[e]	101.4; (49)[h]

[a] In kcal/mol. [b] Asterisks signify vertical values. $I_{N:}(s)^*$ is the vertical solution phase ionization potential of the nucleophile, and $A_E^*(s)$ is the vertical solution phase electron affinity of the cation radical and is taken as the ionization potential of the neutral species. Solution values are determined using information in the Appendix and in ref 5c, 13, and 18. [c] Estimated from substituent effect using the relation of excitation energies with ionization potentials and electron affinities. See: Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. [d] Gap(Add) is the initial energy gap for the nucleophilic addition pathway obtained from $I_{N:}^*(s) - A_E^*(s) + \Delta E_{ST}(\pi\pi^*)$. [e] McGlynn, S. P.; Azumi, T.; Kinoshita, M. *The Triplet State*; Prentice Hall: NJ, 1969. [f] Gas-phase values. [g] These are the gas-phase ionization potentials of the neutral molecules from the following: (i) Herndon, W. C. *J. Am. Chem. Soc.* **1976**, *98*, 887. (ii) Bock, H.; Wagner, G.; Kroner, J. *Chem. Ber.* **1972**, *105*, 3850. [h] Energy gap for the corresponding ET pathway, Gap(ET).

Table III. Physical Data for Nucleophiles

		ΔG_S ($N:^-$ or $N^{\bullet+}$)			ρ		
nucleophile	$I_{N:}^*(g)$	CH_3CN	CH_2Cl_2	C_6H_6	CH_3CN	CH_2Cl_2	C_6H_6
$(NO)_{23}C:^-$	70–80	−44	−43	−33	0.54	0.415	0.0093
Py	221.4		−52		0.54	0.415	0.0093

to this same category. Thus nucleophilic addition and substitution and electrophilic addition and substitution are all governed by a single electron shift (i.e., they are described by a $DA-D^+A^-$ avoided crossing) and are therefore all in the category of reactions whose product configuration is singly excited.[3-5] In fact within this basic grouping it is only elimination[19] and pericyclic reactions[4b,5] that are described by a doubly excited product configuration. Indeed these reactions appear to occur only because the transition state is stabilized through the additional mixing of a third or "foreign" configuration, which is singly excited. For elimination reactions, this configuration is the carbanion or carbocation configuration, while for pericyclic reactions the additional configuration is the charge-transfer configuration, D^+A^-. In terms of Figure 1 and eq 1 this means a large *B* value.[20] So while reactions described by a singly excited product configuration dominate organic chemistry, it is apparent that reactions in which the product configuration is doubly excited are possible.

Conclusion

The "allowed-forbidden" classification of polar reactions in terms of singly and doubly excited product configurations is analyzed in a semiquantitative manner. The present paper both clarifies and qualifies the way in which this classification should be utilized. Our key conclusions are as follows.

(i) In a broad sense, reaction classes which involve a single excitation in the gap (G of Figure 1) are expected to be more common than classes that involve double or higher excitations. This is especially true in organic chemistry of first row elements where excitations are usually large energetic quantities.[20c]

(ii) For the specific case of $N:/R^+$ and $N:/RH^{\bullet+}$ combinations, where R^+ and $RH^{\bullet+}$ possess the same electron affinity, A_E^*, it is always true that the $N:/R^+$ reaction will be preferred, though both reaction types may be fast in an absolute sense. The rapid rates are due to the fact that these reactions normally exhibit very small (or even negative) gaps in the gas phase, and it is only solvation that causes the gaps to be moderately large.

(iii) Specific semiquantitative comparisons between $N:/R^+$ and $N:/RH^{\bullet+}$ systems can be made by use of the actual values of the energy gap, *G*. This physical parameter appears to be an important

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(19) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187.

(20) In problems of stereochemical selection (e.g., 4s + 2s vs 4s + 2a) the gap is constant, and it is now the avoided crossing parameter *B* that governs reactivity. *B* values for allowed reactions are much larger than those for forbidden reactions. See: (a) Bernardi, F.; Olivucci, M.; McDouall, J. J. W.; Robb, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 544. (b) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (c) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086.

index of chemical reactivity.[20,21]

We conclude therefore that the curve crossing models and the physical parameters on which they rest provide useful insight into one of the most basic of chemical reactions—nucleophile–electrophile combination.

Appendix

(I) Estimation of $I_{N:}*(s)$ Values. Following ref 5b, 13, and 18 the vertical ionization of a nucleophile (N:) is given by equation A.1

$$I_{N:}*(s) = I_{N:}*(g) - \Delta G°_S(N:) + \Delta G°_S(N^\bullet) + \Delta G°_{SR} \qquad (A.1)$$

Here $I_{N:}*(g)$ refers to the vertical ionization potential of N: in the gas phase, $\Delta G°_S$ refers to solvation free energies of the corresponding parenthetical species, and $\Delta G°_{SR}$ is the solvent reorganization energy associated with the ionization.

The reorganization energy can be related to the solvation free energy of the charged species in the following manners

$$\Delta G°_{SR} = -\rho \Delta G°_S(N:); \qquad \text{for } N: = N:^- \qquad (A.2a)$$

$$\Delta G°_{SR} = -\rho \Delta G°_S(N^\bullet); \qquad \text{for } N^\bullet = N^{\bullet +} \qquad (A.2b)$$

where ρ is the solvent reorganization factor, which is a function of the static (ϵ_S) and optical (ϵ_{op}) dielectric constants of the solvent, as follows:

$$\rho = (\epsilon_S - \epsilon_{op})/[\epsilon_{op}(\epsilon_S - 1)]; \qquad \epsilon_{op} = n^2 \qquad (A.3)$$

Here n is the refractive index of the solvent.

Equations A.2 become accordingly

$$I_{N:}*(s) \cong I_{N:}*(g) + (1 + \rho)\Delta G°_S(N:); \qquad N: = N:^- \qquad (A.4a)$$

$$I_{N:}*(s) \cong I_{N:}*(g) + (1 + \rho)\Delta G°_S(N^\bullet); \qquad N^\bullet = N^{\bullet +} \qquad (A.4b)$$

The $I_{N:}*(g)$ value of $(NO_2)_3C:^-$ is not known to us. However, as discussed by Kochi et al.,[10] the radical anion $C(NO_2)_4^{\bullet -}$ decomposes to $NO_2^\bullet + (NO_2)_3C:^-$ rather than NO_2^- and $(NO_2)_3C^\bullet$. This means that the ionization potential of the trinitromethyl anion is larger than that of NO_2^- (56 kcal/mol). To be on the safe side we used a high value of 70–80 kcal/mol (Table II, entry 4) which is the ionization potential of very stable anions (e.g., halides, carboxylates, and so on; see, for example, *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapters 9 and 10).

The solvation energy of $(NO_2)_3C:^-$ was taken as −43 kcal/mol in CH_2Cl_2. This value is roughly equal to the $\Delta G°_S$ value of picrate which is reported in the following: Abraham, M. H.; Liszi, J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 143 (values on the molar scale). The same value of $\Delta G°_S$ is used in CH_3CN using free energy of transfer data from Abraham and Liszi. In benzene $\Delta G°_S = -33$ kcal/mol from data in Abraham and Liszi.

The gas-phase vertical ionization potential of pyridine is taken from the following: *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: Vol. 2, Chapter 9.

The solvation energy of the radical cation of pyridine was assumed equal to the value of PyH^+ (see discussion in Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109). The latter solvation energy was derived from the revised pK_a data in solution by the following: Arnett, E. M.; Scorrano, G. *Adv. Phys. Org. Chem.* **1976**, *13*, 83. The derivation relies on equation A.5.

$$\Delta G°_S(PyH^+) = PA - 1.3634pK_a + \Delta G°_S(Py) - 269 \text{ kcal/mol} \qquad (A.5)$$

The last number in the equation involves the sum of the solvation energy of H^+ (−260.5 kcal/mol) and an 8 kcal/mol correction, of the proton affinity (PA), to the free energy scale (see p 46 in Chapter 9, Vol. 2 of *Gas Phase Ion Chemistry*). The solvation energy in CH_2Cl_2 was estimated from ΔG_t data (for free energy of transfer, see: Marcus, Y. *Pure Appl. Chem.* **1983**, *55*, 977. Abraham, M. H.; Liszi, J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 143). A value of ~5 kcal/mol was judged appropriate for PyH^+.

All the relevant data are summarized in Table III.

(II) Estimation of $A_E*(s)$ Data. Following analyses in ref 5b, 13, and 18 the electron affinity of a radical cation follows equation A.6:

$$A_E*(s) = A_E*(g) + (1 + \rho)\Delta G°_S(E) \qquad (A.6)$$

Here $\Delta G°_S(E)$ is the solvation free energy of the radical cation, symbolized as the electrophile, E, and $A_E*(g)$ is the vertical electron affinity in the gas phase. Unless large geometric changes separate the ion and the corresponding neutral species, the $A_E*(g)$ value may simply be taken as the ionization potential of the neutral species, $I_{neutral}(g)$ so that equation A.7 can be used:

$$A_E*(s) \cong I_{neutral}(g) + (1 + \rho)\Delta G°_S(E) \qquad (A.7)$$

The solvation energies of a variety of arene radical cations were estimated as −40 kcal/mol in CH_3CN (Fukuzumi, S. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 7599), and the solvation energies used in this study are −41.1 kcal/mol (CH_3CN), −35 kcal/mol (CH_2Cl_2), and −29 kcal/mol (C_6H_6) where ΔG_t data are estimated from Abraham and Liszi. The same values are used for *p*-dimethoxybenzene. The identical solvation energies of the two radical cations is apparent from the fact that the gas-phase ionization potentials of the two differ by 1.4 kcal/mol (Bock, H.; Wagner, G.; Kroner, J. *Chem. Ber.* **1972**, *105*, 3850. Herndon, W. C. *J. Am. Chem. Soc.* **1976**, *98*, 887), while the redox potential in CH_3CN differs by 1.6 kcal/mol, in the same direction (Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824).

Registry No. $A^{\bullet +}$, 34512-28-2; $DMB^{\bullet +}$, 34478-03-0; $H_2C{=}CH_2^{\bullet +}$, 34470-02-5; $H_2CCO^{\bullet +}$, 64999-16-2; NH_3, 7664-41-7; CH_3^+, 14531-53-4; $(NO_2)_3C^-$, 20143-63-9; pyridine, 110-86-1; piperidine, 110-89-4.

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(21) In response to a referee's comment we note that in some cases, reactions with smaller G values are also more exothermic. In such cases there will also exist a simple rate–equilibrium relationship, and therefore it may well be that some of the trends discussed here can be discussed in those terms. This however is not the general case, and there exist many reactions where smaller G values do not coincide with improved exothermicity. For a discussion of such cases see, for example, pp 224–231, 253–259 in ref 5b. For cation–nucleophile combination reactions in particular it is well established that rate–equilibrium relationships break down (see: Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279) so that using such relationships to understand reactivity in the systems discussed in this paper is likely to be of limited utility.