Nucleophilicity and Vertical Ionization Potentials in Cation–Anion Recombinations

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Nucleophilicity toward pyronin cation in aqueous solutions is shown to correlate with the vertical ionization potential of the nucleophile in solution. The curve crossing model is used to project the basis for this correlation and to derive an equation which is isomorphic with the empirical correlation. The physical significance of the correlation is discussed in terms of the variation in transition-state structure. A link is drawn between the above correlation and Ritchie's N^+ scale, with due implications on the physical significance of N^+.

Introduction

Cation–anion recombination (eq 1)[1] may seem the simplest possible process because it involves formation of a single covalent bond. Structure reactivity patterns are, however, not commensurate with this apparent simplicity and remain an intellectual challenge.[1a,f]

$$\mathrm{R^+\ (s) + X^-\ (s) \rightarrow R{-}X\ (s)} \qquad \text{(s = solvated)} \qquad (1)$$

Any conceptualization of this reaction must take into consideration that the ions are less stable in the gas phase than their corresponding radicals by ≥100 kcal/mol. The process owes its existence, entirely to solvation and involves extensive solvent reorganization in addition to bond coupling.[1]

It seems reasonable then to propose that the ions approach each other to a critical distance where an electron switches from X^- to R^+ and, simultaneously, covalent bonding and solvent reorganization occur.[1a,2]

Considerations of this kind have led Hoz[3] and Ritchie[1a,4] to investigate the correlation of nucleophilic reactivity of X^- with its adiabatic ionization potential, IP[X: (s)], in solution, as defined by eq 2.

$$\mathrm{X{:}^-\ (s) \rightarrow X^{\bullet}\ (s) + e^-}; \qquad \Delta G^\circ = \mathrm{IP[X{:}\ (s)]} \qquad (2)$$

Ritchie[4] has shown that the activation free energies—for the reactions of pyronin cation with various nucleophiles—correlate linearly with IP[(X: (s)] in aqueous solution. Later on, Ritchie has pointed out[5] that addition of nucleophiles like hydrazine and thiolates disrupts the correlation which becomes even poorer in Me_2SO.

Despite this "disappointment", the logic that has led to the above research direction persists, and it remains a challenge to understand reactivity patterns, of cation–anion recombination, in terms of fundamental properties of X^- and R^+.[1] As has been pointed out,[1a,5,6] the curve crossing models[2,7-9] may eventually provide some vital insight along these lines. However, application of these models requires vertical rather than the adiabatic values used by Hoz[3] and Ritchie.[4]

This paper presents a correlation of nucleophilic reactivity, toward pyronin cation with vertical ionization potentials of the nucleophiles in aqueous solution, IP[(X: (s)]*. The physical significance of the correlation is discussed using the curve crossing model.[2,7-9] Comments then follow regarding the relationship between the correlation and Ritchie's N^+ equation.[1c,10]

Results and Discussion

A. Vertical IP and Nucleophilic Reactivity. The vertical ionization potential refers to the energy change that accompanies loss of an electron from X: (s) under frozen geometry and solvent molecular orientations. Photoemission studies by Delahay[11] provide vertical ionization potentials for a few nucleophiles. Unknown values can be estimated by using the simple thermochemical cycle[11,12] in eq 3 (note that X: may be an anion or a neutral species and charges are deleted throughout).

$$\mathrm{X{:}\ (s) \rightarrow X{:}\ (g)}; \qquad \Delta G_1^\circ = -\Delta G_s^\circ(\mathrm{X{:}}) \qquad (3a)$$

$$\mathrm{X{:}\ (g) \rightarrow X^{\bullet}\ (g) + e}; \qquad \Delta G_2^\circ = \mathrm{IP[X{:}\ (g)]} \qquad (3b)$$

$$\mathrm{X^{\bullet}\ (g) \rightarrow X^{\bullet}\ (s)}; \qquad \Delta G_3^\circ = \Delta G_s^\circ(\mathrm{X^{\bullet}}) \qquad (3c)$$

$$\mathrm{X^{\bullet}\ (s) \rightarrow X^{\bullet}\ (s^*)}; \qquad \Delta G_4^\circ = \Delta G_{SR}^\circ \qquad (3d)$$

$$\mathrm{X{:}\ (s) \rightarrow X^{\bullet}\ (s^*) + e}; \qquad \Delta G^\circ = \mathrm{IP[X{:}\ (s)]^*} \qquad (3e)$$

The cycle involves desolvation, followed by gas-phase ionization and then solvation of the resulting $X^{\bullet}$. The final step in the cycle (eq 3d) involves reorganization of the solvent molecular orientations about $X^{\bullet}$ to the orientations that pertain to X:. The result is that the solvent molecules possess *disequilibrium* orientations about $X^{\bullet}$ as denoted by the asterisk. The energy associated with this process is the solvent reorganization energy, ΔG_{SR}°.

The components of the cycle sum up to eq 3e, which describes an electron loss from X: under *frozen solvent orientations*. The expression for the vertical ionization potential reads then as in eq 4.

$$\mathrm{IP[X{:}\ (s)]^*} = \mathrm{IP[X{:}\ (g)]} - \Delta G_s^\circ(\mathrm{X{:}}) + \Delta G_s^\circ(\mathrm{X^{\bullet}}) + \Delta G_{SR}^\circ \qquad (4)$$

Gas phase ionization potentials, as well as solvation energies, are available for a variety of neutral and anionic

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[1] For reviews, see: (a) Ritchie, C. D. *Can. J. Chem.*, invited review. (b) Ritchie, C. D. *Pure Appl. Chem.* **1978**, *50*, 1281. (c) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (d) Ritchie, C. D. *Pure Appl. Chem.* **1979**, *51*, 153. (e) Kessler, H.; Feigel, M. *Acc. Chem. Res.* **1982**, *15*, 2. (f) Arnett, E. M.; Molter, K. E. *Acc. Chem. Res.* **1985**, *18*, 339.

[2] Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. Pross, A.; Shaik, S. *Acc. Chem. Res.* **1983**, *16*, 363.

[3] Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904. Hoz, S. In Nucleophilicity; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1986.

[4] Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313.

[5] Ritchie, C. D. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1986.

[6] Correspondence between C. D. Ritchie and this author 1985–1986.

[7] For the earliest descriptions of this reaction in terms of curve crossing, see: Baughan, E. C.; Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1941**, *37*, 377. (b) Ogg, R. A., Jr.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 604.

[8] (a) Epiotis, N. D.; Shaik, S. *J. Am. Chem. Soc.* **1977**, *99*, 4936. (b) Shaik, S. S. *Progr. Phys. Org. Chem.* **1985**, *15*, 197. (c) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99.

[9] (a) Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6218. (b) Warshel, A. *Biochemistry* **1981**, *20*, 3167. (c) Warshel, A. *Acc. Chem. Res.* **1981**, *14*, 284.

[10] (a) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966. (b) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

[11] Delahay, P. *Acc. Chem. Res.* **1982**, *15*, 40.

[12] (a) Shaik, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 1227. (b) Reference 8b. (c) Buncel, E.; Shaik, S. S.; Um, I.-H.; Wolfe, S., submitted for publication in *J. Am. Chem. Soc.*

0022-3263/87/1952-1563$01.50/0

Table I. Calculated and Experimental Vertical Ionization Potentials (in kcal/mol) of Nucleophiles in Aqueous Solutions

entry	X:	IP[X: (s)]*, eq 4,5	IP[X: (s)]*, exptl[e]
1	F^-	238[a]	>232
2	Cl^-	202[a]	203
3	Br^-	183[b]	186
4	I^-	163[b]	166
5	HO^-	203[a]; 190–195[c]	195
6	CH_3O^-	177[a]	
7	HOO^-	171[a]	
8	$CF_3CH_2O^-$	179[a]	
9	PrS^-	165[a]	
10	PhS^-	160[a]	
11	N_3^-	176[a]	172
12	CN^-	200[a]	
13	SO_3^{2-}		166
14	$CH_3CO_2^-$	176[a]; 180[d]	180
15	H_2O	246[a]	232
16	piperidine (pip)	175[a]	
17	$PrNH_2$	190[a]	
18	N_2H_4	198[a]	

[a] Calculated with solvation energies from ref 4 and 5 and ionization potentials from ref 13. [b] Calculated with solvation energies from ref 8b. [c] Calculated with experimentally determined solvation energies from: Gomer, R.; Tryson, G. *J. Chem. Phys.* **1977**, *66*, 4413. [d] With gas-phase electron affinity of 78 kcal/mol from: Hiraoka, K.; Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 6833. [e] From ref 11.

nucleophiles.[4,8b,13] Solvent reorganization energies can be estimated by using Marcus' theory of nonequilibrium polarization.[14] $\Delta G_{SR}°$ can then be obtained from the solvation energies, $\Delta G_s°$, of X:⁻ and $X^{\bullet+}$ according to eq 5,[11,12] where ρ is the reorganization factor of the solvent.[15]

$$\Delta G_{SR}° = -\rho \Delta G_s°(X:) \qquad (X: = X:^-) \tag{5a}$$

$$\Delta G_{SR}° = -\rho \Delta G_s°(X^\bullet) \qquad (X^\bullet = X^{\bullet+}) \tag{5b}$$

Generally, ρ is large for solvents which possess organized and organizable superstructures. For example, for water, having the hydrogen bonding network, ρ is 0.56 (at T = 298 K), while for benzene ρ is 0.0093. Thus solvent reorganization energies will be extremely small for solvents whose superstructure is loose.[8b,16]

Aqueous solution IP[X: (s)]* values estimated by using eq 4 and 5 are shown in Table I together with available experimental data. The correspondence between the calculated and experimental values is reasonable. The origin of the significant *absolute* deviation for H_2O is not clear to us. This may indicate that eq 4 and 5 generally overestimate IP[X: (s)]* for neutral nucleophiles. It would perhaps have been, better to use ρ = 0.5 for neutral nucleophiles (eq 5b) as generally recommended by Delahay;[11] in this case calculated values for the neutral nucleophiles would be ≥5kcal/mol lower than the tabulated values. It is preferable though to leave ρ at its theoretical value[15] to allow IP* estimations methodically in various solvents.[8b,12]

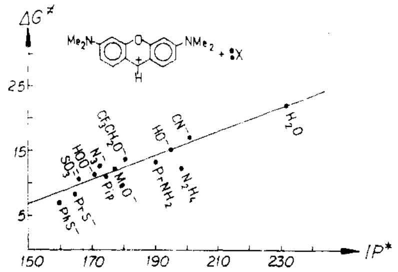

Figure 1. A correlation of the free energies of activation ($\Delta G^{\ddagger}$) with the vertical ionization potentials (IP*) of the nucleophiles (X:) for the aqueous solution recombination reactions of pyronin cation with nucleophiles (all values are in kcal/mol). Experimental IP* values are used when available.

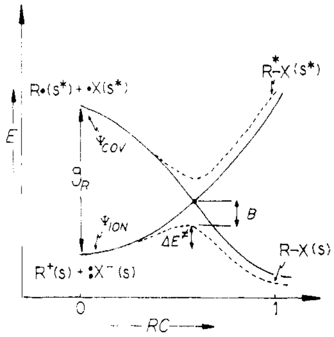

Figure 2. An avoided crossing diagram for recombination reactions of R^+ and X^-. The dashed lines are the energy curves after avoided crossing and mixing. The solvent configurations are common to the two curves. In parentheses, s means equilibrium solvation, while s* means disequilibrium solvation. On the right hand side, the excited state of the R–X bond is indicated by an asterisk above the bond.

Figure 1 is a plot of free energies of activation, $\Delta G^{\ddagger}$, against IP[X: (s)]* for a series of 13 nucleophiles reacting with pyronin cation.[4,5,17] The correlation coefficient, of 0.94, while not excellent is better than the corresponding correlation (c.c = 0.88) with the adiabatic IP values of X: (see eq 2).[4,5,18] Removal of the worst data point (N_2H_4) improves the correlation coefficient to 0.96. Removing delocalized nucleophiles (e.g., SO_3^{2-}, N_3^-), for reasons to be detailed later, further improves the correlation coefficient. With various combinations the correlation coefficients are in the range of 0.94–0.98. The equation for the line in Figure 1 is given in eq 6.

$$\Delta G^{\ddagger} \simeq 0.182\text{IP[X: (s)]}^* - 20.4 \text{ kcal/mol} \tag{6}$$

Since eq 6 is a correlation of reactivity with a fundamental property of the reactant, it is attempted in what follows to understand its basis. Does this correlation signify anything fundamental about the activation process of the reaction? Will the correlation persist for recombination reactions in other solvents and with other cations?

B. The Model. Interpretation of the Correlation. The barrier for the recombination reaction arises from an avoided crossing of ionic and covalent energy curves as shown in Figure 2. This diagram has been proposed in the past by several groups[7-9] and was recently calculated by Warshel and collaborators using empirical valence bond theory.[9a]

The "reaction coordinate" of Figure 2 is coveniently normalized to unity because the state-to-state correlation is independent of the details of the "reaction coordinate". Implicit in the "reaction coordinate" are the mutual approach of R and X, the internal geometric changes in R

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(13) (a) Vertical gas-phase ionization potentials for variety of amines and neutral nucleophiles can be found in: Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2. (b) Gas-phase ionization potentials of anionic nucleophiles X:⁻ are considered to be equal to the electron affinities (A) of X• and are taken from: Bartmess, J. E.; McIver, R. T., Jr., in ref 13a. Janousek, B. K.; Brauman, J. I., in ref 13a. Most of the A data used here is summarized in ref 4.

(14) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(15) $\rho = (\epsilon - n^2)/[n^2(\epsilon - 1)]$, where ϵ is the static dielectric constant, while n is the refractive index and n^2 is the optical dielectric constant.

(16) Shaik, S. S. *Isr. J. Chem.* **1986**, *26*, 367.

(17) Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279.

(18) The present correlation is also better than the corresponding rate equilibrium correlation. See discussion in ref 17.

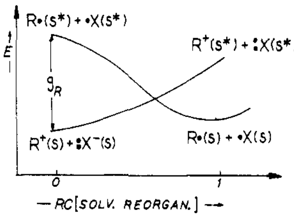

Figure 3. An avoided crossing diagram along a solvent reorganization coordinate. The resulting process is electron transfer.

and X, and the many motions of the solvent molecules which reorganize themselves in attempt to maintain equilibrium with the charges of the R,X system.[8b,12,16] Thus, Figure 2 describes a switchover of ionic and covalent configurations along a coordinate that involves a combination of all the motions that convert $R^+ + X^-$ to R–X. The recombination reaction can be described then as *a transformation that involves a single electron switch which is synchronized to bond coupling.*[2,8]

To elucidate the above description, consider a "reaction coordinate" that involves *only solvent reorganization*, while the rest of the movements remain frozen. At the *beginning of the reaction*, as in Figure 2, the *ionic curve* consists of the ions, R^+ (s) and $X:^-$ (s) *equilibrated* with the solvent, while the covalent curve consists of the radicals, $R^\bullet$ (s*) and $X^\bullet$ (s*), in *disequilibrium* with the solvent. As solvent reorganization takes place, the covalent configuration will be stabilized while the ionic configuration destabilized. If the initial gap (g_R) between the curves is small enough then solvent reorganization will suffice to promote crossing of the two curves and *a single electron transfer* will occur, as shown in Figure 3.[19] Such reactions have been in fact observed by Arnett et al.[1f,20] for cases that involve relatively unstable R^+ and X^-.

Unlike the electron-transfer reaction, in the recombination reaction the single-electron switch is promoted by a combined deformation which involves all the motions, including the coupling of R to X. In this manner all the aspects of the reaction occur in a single step. This appears to be the exclusive pathway for the reactions, of pyronin cation, that are discussed in this paper.[1a]

Referring back to Figure 2, it can be seen that the barrier to cation–anion recombination reactions can be written as in eq 7, where $\Delta G^{\ddagger}$ replaces $\Delta E^{\ddagger}$.[8b] This equation states

$$\Delta G^{\ddagger} = f g_R - B \qquad (f < 1) \tag{7}$$

simply what *is* in Figure 2, namely, that the crossing point is some fraction (f) of the energy gap, g_R, between the curves and the barrier is the energy of the crossing point less the avoided crossing interaction B.

Since the diagram gap is the vertical electron-transfer energy from $X:^-$ (s) to R^+ (s), eq 7 becomes eq 8, where $A[R^+ \text{ (s)}]^*$ is the vertical electron affinity of R^+ (s).[21]

$$\Delta G^{\ddagger} = f(\mathrm{IP}[X\text{: (s)}]^* - A[R^+ \text{ (s)}]^*) - B \tag{8}$$

Equation 8 is not an explicit[22] or a "theoretically derived" equation but rather a parametric one that describes an activation process from reactants' point of view, as detailed below.

Scheme I

$$R^+ \ :X^- \longleftrightarrow R\bullet \quad \bullet X$$

The transition state for the reaction occurs at the proximity of the crossing point where the ionic and covalent configurations are equienergetic, as shown in Scheme I. Since the two configurations are initially separated by the vertical electron-transfer energy, deformations will be required to *destabilize* ($R^+ + :X^-$) (s) and *stabilize* ($R^\bullet + {}^\bullet X$) (s*). In this manner the gap is overcome, and the two configurations attain equal energy at the crossing point. *The deformation energy* (of ($R^+ + :X^-$) (s)) which is required to achieve crossing *is, then, a fraction of the vertical gap that must be overcome by the deformations.* This accounts for the first term in eq 8.

Once crossing has been achieved, energy is lowered by the resonance interaction between the two degenerate configurations (see Scheme I). This resonance interaction is B, the second term in eq 8. The equation describes then, the activation process as a deformation that is required to overcome the vertical electron-transfer energy so that an electron can switch from $X:^-$ (s) to R^+ (s) in synchronicity with bond coupling.

The barrier in eq 8 is seen to depend on four different factors. Thus, a priori, reactivity has to be conseptualized in terms of these four factors. This would probably be the case had we looked at a large set of data, changing X^-, R^+ and the solvent. Such is the case in other nucleophilic attacks that have been investigated.[8b]

Consider now a group of reactions that *happen* to possess constant f and B factors. Such a group will define a *reaction family* where the vertical electron transfer energy alone determines the reactivity trend. For a *reaction family* with a constant R^+ and a series of nucleophiles, the only variable is IP[X: (s)]*, and hence, eq 8 becomes eq 9.

$$\Delta G^{\ddagger} = f(\mathrm{IP}[X\text{: (s)}]^*) - C$$
$$(C = \text{constant};\ C = B + f(A[R^+ \text{ (s)}]^*)) \tag{9}$$

For such reaction families a plot $\Delta G^{\ddagger}$ vs. IP[X: (s)]* will be linear, with a slope and intercept equal to f and C, respectively. The reaction series of pyronin cation, that is described in Figure 1, exhibits roughly such a behavior as predicted in eq 9. Thus in this series, relative reactivity is largely dominated by variations in the vertical ionization potential of the nucleophile.

There arise now a few questions regarding this correlation. The foremost is, whether the correlation enfolds information about transition state structure. Answering this question requires a digression to discuss, in detail, how the various distortions and movements contribute to the energy variation of the two curves in Figure 2.

The covalent curve begins with the two radicals in a state of disequilibrium with the surrounding solvent. Along the "reaction coordinate" R and X approach one another and rehybridize, and as a result, the radicals are coupled to form a covalent R–X bond. Simultaneously, the solvent molecules reorganize and assume equilibrium configurations about R–X. Both these effects contribute to the descent of the covalent curve along the "reaction coordinate".

The ionic curve begins with the two ions equilibrated with the surrounding solvent. It is worthwhile to consider separately the ions and the solvent subsystems, as discussed extensively by Warshel.[9,23] Initially, the bare ions

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(19) Theories of solvent reorganization-promoted electron transfer in terms of avoided crossing, along a solvent reorganization coordinate, are described in: (a) Salem, L. *Science (Washington, D.C.)* **1976**, *191*, 822. (b) Warshel, A. *J. Phys. Chem.* **1982**, *86*, 2218.

(20) (a) Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172. (b) Arnett, E. M.; Troughton, E. B.; Molter, K. E. *J. Am. Chem. Soc.* **1984**, *106*, 6726.

(21) The corresponding expression is

$$A[R^+ \text{ (s)}]^* = \mathrm{IP}[R^\bullet \text{ (g)}] + (1 + \rho)\Delta G_s{}^\circ(R^+) - \Delta G_s{}^\circ(R^\bullet).$$

(22) For explicit equations, see: (a) Reference 8b, Appendix A, equation A.15. (b) Shaik, S. S.; Schlegel, H. B.; Wolfe, S., to be published.

attract one another along the "reaction coordinate", and this attraction persists up to a critical distance which is the sum of the ionic radii of R^+ and X^-.[2,9a] Beyond this point, further approach becomes repulsive, and this will be augmented by geometric distortions (rehybridization) of R^+ and X^-. Eventually, at the distance which corresponds to the R–X molecule, the ionic curve correlates with a singlet valence excited state of R–X.[24,8,9]

Along the same "reaction coordinate", the solvent molecules undergo reorganization which results in a loss of solvation[23] of the two ions. This persists until the solvent molecules occupy disequilibrium configurations about the ionic excited state of R–X.

The sum of the above two effects leads to the shape of the ionic curve in Figure 2. Thus, initially ionic attraction is opposed by solvation loss, and the resulting curve is relatively flat.[23] At distances closer than the sum of the ionic radii, the loss of solvation is augmented by nonbonded ionic repulsion and geometric distortions of the ions. It is this branch of the curve that rises sharply and is responsible for the barrier to the cation–anion recombination.[2,9a]

We can return now to the question of transition-state structure for the pyronin cation reactions. The barrier is contributed then, *in general*, by a combined deformation energy that involves nonbonded repulsions between R and X, geometric distortions (rehybridization) of R and X, and loss of solvation energy (due to prevention, by bulk solvent, of optimal packing of the solvation shells about the ions[23a]). This combined deformation will take place just to the extent required to overcome the *vertical electron transfer* energy and achieve a transition state at the crossing point of $R^+ \,{:}X^-$ and $R^\bullet \,{}^\bullet X$ (see Scheme I).[25]

The approximate adherence of the pyronin cation series to eq 9 means that the extent of deformations will be determined largely by the vertical ionization potential IP[X: (s)]*. Thus, the larger the IP* the greater, generally, the deformations in the transition state. This means that the transition state for RS^- + pyronin$^+$ is the least deformed while that for H_2O + pyronin$^+$ is the most deformed. Thus, *the larger the recombination barrier the more advanced the transition state in terms of its total deformation from the initial state*.[25]

If the distortions that constitute the total deformation are linearly synchronized, then the above statement means that as the IP* and $\Delta G^{\ddagger}$ increase along the series of Figure 1 the transition states become tighter (in terms of the R–X bond order), the R and X suffer more geometric distortions, and the solvent molecules undergo more reorganization. This, however, may not always be the case, because the various distortions along the "reaction coordinate" do not have to depend linearly on each other.[26] Empirical VB calculations (such as Warshel's[9,19b,23]) may have to be carried out for further clarification. It must be emphasized though that regardless of the advancement of the various distortions, *the charges of the transition state are approximately constant* ($R^{0.5+}\,X^{0.5-}$). This is so, because the transition state is in the proximity of the crossing point which is a resonance hybrid of the two degenerate configurations $R^+ \,{:}X^-$ and $R^\bullet \,{}^\bullet X$ as shown above in Scheme I.

Another feature of the pyronin series that requires attention is the approximate constancy of the avoided crossing interaction, *B* (Figure 2). A rough estimate of *B* can be achieved by using the value of the intercept in eq 6 and its theoretical expression in eq 9. The vertical electron affinity of pyronin cation can be reasonably bracketed between 42 and 78 kcal/mol.[27] Using the slope in eq 6 as the value of the model parameter *f* in eq 9, we obtain *B* values of 6–13 kcal/mol. Such values are not uncommon[9,28] in VB computations.

If there exists then a correspondence between the empirical correlation (in Figure 1 and eq 6) and its modeling (in Figure 2 and eq 9), then the above result means that the resonance energies *B*, of the transition states of the series, are approximately constant in the range of 6–13 kcal/mol. Both lower and upper limit *B* values indicate significant overlap between pyronin and the X's in the transition states, though the lower limit value corresponds to fairly "early" transition states.[9a]

Be the value of *B* as it may, its approximate constancy does not in any way require[8b,25c] "a constant transition-state structure". *B* is proportional to the overlap between the bond hybrids of R and X at the transition state.[29] The overlap itself is a function of distance and hybridization, while the proportionality constant varies roughly as the bond strength.[29] Clearly, analysis of experimentally derived *B* values will have to be done, in the future, by theoretical means that enable estimation of the R–X distances in the transition state.

The second question regarding the correlation in Figure 1 is when can we anticipate such reaction families? The qualification of a reaction family is the constancy of the *f* factor in the parametric form of eq 7. In that equation, *f* is the ratio between the energy of the crossing point and the energy gap at the reactant side of Figure 2. Explicitly,[22] this ratio depends on the curvatures of the curves,[8b,26b] on the energy level of the excited state at the product side,[24] and on the free energy change of the reaction. The lack of such data, for the cation–anion recombination reaction, prevents the anticipation of ideal reaction families. The remaining strategy then is to search "approximate reaction families" by empirical correlations, e.g., of the type presented in Figure 1.

One clarification, regarding relative values of *f* factors, may be made though, which rests upon previous experience with such correlations.[12,25b,c] Thus, the *f* factor is normally found to be larger for delocalized nucleophiles as PhO^-, PhS^-, and so on.[12,25b] Such an effect is obtained because

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(23) (a) Warshel, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 5250. (b) Warshel, A.; Russell, S. *Q. Rev. Biophys.* **1984**, *17*, 283.

(24) For simple alkyl R, the ionic curve correlates with the $\sigma\sigma^*$ valence excited state of the R–X bond (see discussions in ref 8b). For complex R groups, like pyronin, the $\sigma\sigma^*$ valence state should be mixed with adjacent $\pi\pi^*$ states. The importance of $\sigma\sigma^*$ states is being now revived. See, (a) Robin, M. B. *Can. J. Chem.* **1985**, *63*, 2032. (b) Elsevier, C. J.; Vermeer, P.; Gedanken, A.; Runge, W. *J. Am. Chem. Soc.* **1985**, *107*, 2537.

(25) For this methodology, see: (a) References 8b, 12c, and 16. (b) Shaik, S. S. *Can. J. Chem.* **1986**, *64*, 96. (c) Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642.

(26) For such considerations in S_N2 and NVS reactions, see: (a) Reference 8b, pp 290–294. (b) Cohen, D.; Bar, R.; Shaik, S. S. *J. Am. Chem. Soc.* **1986**, *108*, 231.

(27) The vertical IP[$R^\bullet$ (*g*)] of pyronin can be estimated between 120 and 140 kcal/mol from data in: Turner, D. W. *Adv. Phys. Org. Chem.* **1964**, *4*, 47. Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162. Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. The solvation energy of carbenium ions of the pyronin size and electronic delocalization type is 40–50 kcal/mol, see: Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1893. Wolf, J. F.; Harch, P. G.; Taft, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 2904. Using these values and the equation in ref 21 (here) provides the vertical electron affinity of pyronin cation.

(28) Hiberty, P. C.; Sevin, A., submitted for publication in *J. Am. Chem. Soc.*

(29) See p 315 in ref 8b. In effective-one-electronic VB theory this becomes

$$B = 2^{1/2}\langle\varphi_R|\hat{H}|\varphi_X\rangle \simeq k\langle\varphi_R|\varphi_X\rangle = kS_{RX}$$

For approximate ways to evaluate such matrix elements, see p 318 of ref 8 b and ref 9a.

delocalization of the odd electron in $X^\bullet$ causes a shallow descent of the covalent curve toward R–X (Figure 2).[8b,25c,26b] The result is that, relative to a case of a localized nucleophile, the energy of the crossing point is raised and this corresponds to a larger f in eq 7. This in turn means greater R and X deformations, tighter transition states, and larger extents of solvent reorganization.[8b,12c,16,25,26b]

The above effect on f depends critically on whether or not the present crossing, in Figure 2, requires strong R to X coupling. For weak coupling, localized and delocalized nucleophiles may share a similar f value and lie on the same correlation line (Figure 1). The fact that PhS^-, N_3^-, and SO_3^{2-} do not deviate[30] strongly from the line in Figure 1 may indicate that the R to X coupling is not prominent in achieving the crossing and, hence, the transition state in Figure 2. Such a description would be more compatible with the B value of 6 kcal/mol. Addition of other delocalized nucleophiles such as $CH_3CO_2^-$, NO_2^-, and so on are needed to ascertain whether a large slope family line will accommodate delocalized nucleophiles as in other nucleophilic reactions[8b,12c] or whether the recombination reaction is different, in this sense, from other nucleophilic reactions.

Delocalization, but in a different sense than the above, may be responsible for the enhanced reactivity of N_2H_4. The vertical species $N_2H_4^+$, is ineffectively delocalized owing to the small overlap between the hybrids on the nitrogen atoms. Effective delocalization is achieved via extensive geometric reorganization, which involves rotation and rehybridization.[31] If these motions become part of the reaction coordinate, in the recombination reaction, then the so acquired delocalization of $N_2H_4^+$ will come to the fore as a higher resonance interaction B at the transition state. The large negative deviation of hydrazine from the line in Figure 1 may originate in this effect.

A third and final question concerns the possibility of observing a correlation such as eq 6 in solvents other than water. There exist two reasons why such a correlation may be less extended in solvents like acetonitrile, Me_2SO, and so on. The first reason is the possible involvement of ion-pair intermediates and barriers[1e,32] to their formation. In water, as a solvent, there is almost complete cancellation of the electrostatic attraction energy by the loss of solvation energy as R^+ and X^- approach one another.[23] In other solvents the cancellation is not complete and ion-pair minima may become significant.[33] The experimental barrier to cation–anion recombination will then be a sum of terms. This may cause deviations from the correlation of $\Delta G^\ddagger$ vs. IP*, especially if neutral nucleophiles are also included. The second reason is that the variation in the IP* values decreases in nonhydroxylic solvents[8b,16] and IP* may cease to be the dominant factor of $\Delta G^\ddagger$ variation.[34]

The net result of all the above is that "reaction families" in nonhydroxylic solvents may become less extended than in water. Examination of Arnett's data[1f,20] can clarify some of the above points but will have to be delayed until IP and solvation energy data become available.

C. The IP* Correlation and the N^+ Equation. Consider a reaction family that obeys eq 9, and let us define a reaction with a certain nucleophile as a standard reaction, having activation energy $\Delta G_0^\ddagger$. Reactivity of any nucleophile, relative to the standard one, will read then as in eq 10 and in a logarithmic rate format as in eq 11.

$$\Delta G^\ddagger - \Delta G_0^\ddagger = f(\mathrm{IP}[X{:}\ (s)]^* - \mathrm{IP}[X{:}\ (s)]_0^*) = f\Delta[\mathrm{IP}^*] \qquad (10)$$

$$\log\,[k/k_0] = -f\Delta[\mathrm{IP}^*]/2.303RT \qquad (11)$$

Equation 11 means that relative reactivities of nucleophiles depend only on the differences between their vertical ionization potentials. On the other hand, k_0 is the rate of the standard reaction and depends on the identity of the cation. This is the case of an ideal reaction family in the sense of eq 7 and 9.

Equation 11 is isomorphic with Ritchie's N^+ equation,[1c,10] and we may therefore equate the N^+ parameter with the right hand side of eq 11; that is, eq 12 obtains.

$$N^+ = -f\Delta[\mathrm{IP}^*]/2.303RT;\ \Delta[\mathrm{IP}^*] = \mathrm{IP}[X{:}\ (s)]^* - \mathrm{IP}[X{:}\ (s)]_0^* \qquad (12)$$

Following the discussions of eq 7 and 9, the N^+ parameter is seen to possess a physical significance pertaining to transition-state structure. Thus, the N^+ scale can be described as a *measure of the total deformation (solvent and structure) experienced by X: (relative to a standard nucleophile) in its recombination reaction with a given R^+*.

Since in an ideal reaction family f is a constant then the N^+ parameter, in a reaction family, is proportional only to the vertical ionization potential differences. The behavior of N^+ in different series rests therefore on the constancy of f for different electrophiles. Considering the above discussion of f, deviations and breakdowns in the generality of the N^+ parameter can be expected.[1a,35]

A few other f factors are available for nucleophilic attacks on arylacetate esters.[12c] These factors for localized nucleophiles range between 0.14 and 0.19 and are fairly close to the value of 0.18 obtained in this study. Delocalized nucleophiles such as N_3^-, $CH_3CO_2^-$, PhS^-, PhO^-, and NO_2^- were found to have larger f values and are therefore expected to lead to breakdowns in the constancy of the N^+ values. Also, there is some dependence of the f factor on the identity of the electrophile.[12c]

It appears therefore that the N^+ and the *IP** correlations both result because sometimes nucleophilicity can be attributed to a single fundamental property of the nucleophile. When such correlations are observed the present study suggests that this fundamental property is associated with the (standardized) deformation of the nucleophile required to switch an electron to the electrophile while simultaneously forming a new bond.

Conclusions

Nucleophilicity toward pyronin cation in aqueous solutions correlates with the vertical ionization potential of the nucleophile in solution. This correlation retains a similar sense to the correlation found by Ritchie[4,5] but differs in taking into account solvent and structural reorganization energies. The curve crossing diagram[2,7-9] projects the basis

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(30) The status of SO_3^{2-} is not clear because it may react also via the sulfur center.

(31) (a) Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45. (b) Mautner, M.; Nelsen, S. F.; Willi, M. R.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 7384. (c) Nelsen, S. F.; Blackstock, S. C.; Yumibe, N. P.; Frigo, T. B.; Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 143. (d) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131.

(32) Di Vona, M. L.; Doddi, G.; Ercolani, G.; Illuminati, G. *J. Am. Chem. Soc.* **1986**, *108*, 3409.

(33) Even ion-dipole minima can persist in nonhydroxylic solvents, see; Hayami, J.; Koyanagi, T.; Hihara, N.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 891. Hayami, J.; Tanaka, N.; Hihara, N.; Kaji, A. *Tetrahedron Lett.* **1973**, 385. Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 2794.

(34) This is observed for example in S_N2 where the relative reactivity in water $I^- > Br^- > Cl^- > F^-$ (dominated by IP*) is reversed or upset in nonhydroxylic solvents. The treatment in terms of curve crossing is detailed in a monograph: Shaik, S. S.; Mitchell, D. J.; Schlegel, H. B.; Wolfe, S. *Theoretical Physical Organic Chemistry. Application to the S_N2 Transition State*; Wiley-Interscience: New York, in preparation.

(35) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 6082.

for such a correlation and leads to a parametric barrier equation (eq 9) which is isomorphic with the empirical correlation (eq 6). The physical significance of the correlation is shown then to derive from the notion that the activation process is a deformation that is required to overcome the vertical electron transfer energy gap. A relationship between the N^+ equation and the present correlation can be drawn in terms of the above physical picture.

Greater insight into the problem can be achieved when more necessary vertical data becomes available and when full VB computations[9] are carried out for these reactions. Both goals appear to be attainable.[9,24,28]

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Registry No. F^-, 16984-48-8; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; HO^-, 14280-30-9; CH_3O^-, 3315-60-4; HOO^-, 14691-59-9; $CF_3CH_2O^-$, 24265-37-0; PrS^-, 20733-14-6; PhS^-, 13133-62-5; N_3^-, 14343-69-2; CN^-, 57-12-5; SO_3^{2-}, 14265-45-3; $CH_3CO_2^-$, 71-50-1; H_2O, 7732-18-5; $PrNH_2$, 107-10-8; N_2H_4, 302-01-2; piperidine, 110-89-4; pyronin cation, 17817-77-5.

Synthesis of Terpenes Containing the Bicyclo[3.1.1]heptane Ring System by the Intramolecular [2 + 2] Cycloaddition Reaction of Vinylketenes with Alkenes. Preparation of Chrysanthenone, β-Pinene, β-*cis*-Bergamotene, β-*trans*-Bergamotene, β-Copaene, and β-Ylangene and Lemnalol

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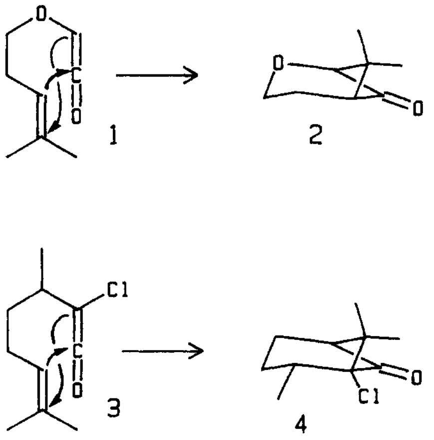
Treatment of geranoyl chloride (**20**) with triethylamine in toluene at reflux gave the vinylketene **21** which underwent a [2 + 2] cycloaddition to give 7,7-dimethyl-2-methylenebicyclo[3.1.1]heptan-6-one (**24**) in 43% yield. Isomerization over Pd gave chrysanthenone (**6**) in quantitative yield. Wolff–Kishner reduction gave β-pinene (**5**) in 70% yield. A similar sequence of reactions starting from (*Z,E*)- and (*E,E*)-farnesoyl chloride gave ketones **51** and **57**, which were converted to β-*cis*-bergamotene (**8**) and β-*trans*-bergamotene (**9**), respectively. β-Copaene (**10**) and β-ylangene (**11**) were prepared from **57** by a three-step sequence. Treatment of the imidazolide **59** with tri-*n*-butyltin hydride in toluene at reflux gave a 46% yield of a 1:1 mixture of **10** and **11**. Selenium dioxide oxidation of **11** gave the antitumor agent lemnalol. The mechanisms of the regiospecific ketene generation and the [2 + 2] cycloaddition reaction have been explored, and the reactivity of the novel bicyclo[3.1.1]heptanones has been examined.

The stereospecific [2 + 2] cycloaddition of ketenes to alkenes is a valuable method for the synthesis of cyclobutanones and compounds that can be derived from them; it is one of the few general methods for the carbofunctionalization of alkenes. We have recently initiated a program to develop the intramolecular [2 + 2] cycloaddition of ketenes to alkenes into a general synthetic method.[2-5] Initial studies indicated that electronic effects of substituents on the alkene rather than the connectivity pattern controls the regiochemistry of the cycloaddition. Specifically, ketenes **1** and **3**, in which the terminal carbon of the double bond is more highly substituted, cyclize regiospecifically to the bicyclo[3.1.1]heptan-6-ones **2** and **4**.[2]



Several mono- and sesquiterpenes contain the bicyclo[3.1.1]heptane ring system. Numerous monoterpenes, including the readily available essential oil β-pinene (**5**), chrysanthenone (**6**),[6] and the monoterpenoid glycoside paeonoflorin (**7**),[7] which was isolated from the traditional

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