at very low frequency, and several calculations demonstrate that the π-system offers very little resistance to bending about the central carbon.[26] Similarly, there may be very little resistance to the tilt of the ketenylidene ligand in III. If the ketenylidene is as highly compliant as carbon suboxide, the tilt of the CCO ligand may arise from very weak interactions, such as weak nonbonded interactions or possibly a weak bonding interaction between the β-carbon of CCO and Fe2.

Another interpretation of the structure of III can be derived from ideas proposed by Bradley[27] for the four-iron butterfly system using Wade's rules.[28] Following this alternative approach, the C atom is considered to be part of the cluster rather than a ligand, and the cluster framework is therefore a pseudotetrahedron consisting of three iron atoms and one carbon atom. The CO coordinated to the carbide appears to be slightly semibridging across any iron-carbon bond. The iron carbonyl distance is within the postulated range of a semibridging CO.[5] This CO is then poised for migration onto the iron framework.

Acknowledgment. The research was supported by NSF Grant CHE-8204401. We appreciate an informative discussion with Dr. Kenneth Wade.

Registry No. II, 87710-96-1; III, 87698-63-3; IV, 83220-20-6; V, 87698-65-5; VI, 87698-64-4; VII, 87698-67-7; [PPN][$Fe_3(CO)_{10}$(COC-OCH_3)], 69421-15-4.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors for both molecules as well as bond distances and angles of the tetraphenylarsonium counterions of III (132 pages). Ordering information is given on any current masthead page.

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Cation-Anion Combination Reactions. 24. Ionization Potentials, Solvation Energies, and Reactivities of Nucleophiles in Water[1]

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Abstract: An assumption is made and justified that free energies of bond dissociation in aqueous solution are approximately equal to enthalpies of bond dissociation in the gas phase. The free energies of bond dissociation in solution, thus estimated, are used in a thermochemical cycle to obtain free energies for one-electron transfer from various nucleophiles to the proton, standard electrode potentials vs. NHE for one-electron oxidations of the nucleophiles, and free energies of solution of the nucleophiles, all in aqueous solution. The one-electron oxidation potentials are shown to be correlated with the barriers to reactions of the nucleophiles with Pyronin cation [3,6-bis(dimethylamino)xanthylium cation]. The general problem of nucleophilic reactivity is discussed.

The experimental study of electrophile-nucleophile combination reactions has provided a wealth of data for testing various theories of nucleophilic reactivity.[1] It is fair to state that no general theory exists that is capable of giving even semiquantitative accord with the data.

One of the problems in attempts to formulate theories of nucleophilic reactivity is the sparsity of information on fundamental properties of the nucleophiles in solution. The only well-defined property for which data exist for a reasonable range of nucleophiles is basicity toward the proton, given by the pK_a's of the conjugate acids of the nucleophiles. Polarizabilities,[2] orbital energies,[3-5] hardness/softness,[6] and solvation energies[7] are some of the properties that have been postulated to affect reactivity but that are either poorly defined (hardness/softness), not presently obtainable for solution (anisotropic polarizability and orbital energies), or not generally available for species of interest (solvation energies).

For a few nucleophiles, the standard electrode potentials for oxidative dimerization

$$X^- = {}^1/_2X_2 + e^- \qquad (1)$$

are known and were once believed to be related to nucleophilic reactivity.[8] It was realized, however, that the bond dissociation energies of the X_2 species, which are an important variable component of the potentials for various X, should not be generally related to nucleophilic reactivity.[9] The relationship was modified[2] and later abandoned.[6]

The purpose of the present paper is to show that the standard electrode potentials for the half-cells

$$X^- = X\cdot + e^-$$
$$B = B^{+\cdot} + e^- \qquad (2)$$

for anionic, X^-, and neutral, B, nucleophiles can be estimated by

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[1] A preliminary report of this work was presented at the 2nd Conference on Physical-Organic Chemistry, Florianopolis, Santa Catarina, Brazil, April 5-8 1983. For previous paper in this series, see: Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 3573.

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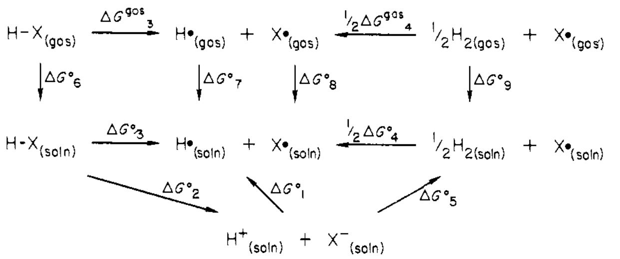
Scheme I

(A) Neutral HX



(B) Cationic BH^+

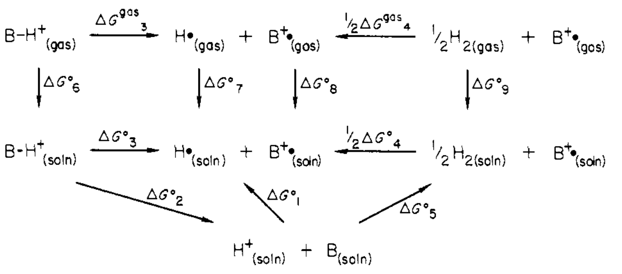


Table I. Oxidation Potentials of Nucleophiles[a]

H-X	ΔH^{gas}_3	ref	$\Delta G°_2$	$\Delta G°_5$
H-OOH	88.6	16	16.0	20.5
$H-OC_6H_5$	86.5	12	13.7	20.7
H-ONO	78	17	4.4	21.5
$H-SCH_2CH_2CH_3$	88.6	14	14.8	21.7
$H-SC_6H_5$	83.3	17	8.9	22.3
H^+-piperidine	90	11[b]	15.2	22.7
$H-OCH_3$	102	18	22.6	27.3
$H^+-H_2NCH_2CH_2CH_3$	99	11[b]	14.4	32.5
$H-OCH_2CF_3$	102	18[c]	17.0	32.9
$H-N_3$	92.5	13	6.4	34
H-OCl	98	23	10.3	35.6
$H-O_2CCH_3$	106	17	6.4	47.5
H-CN	123.8	12	12.6	59.1
H-OH	119.3	12	21.5	45.7
H^+-OH_2	137.4	*d*	0[e]	85.3

[a] All values are in kcal/mol. Quantities are defined in Scheme I, and standard states are given in the text. Values of $\Delta G°_2$ are from ref 20–22. [b] These values are corrected as directed in the footnotes to the tables in ref 11. [c] Reference 18 shows that the bond dissociation energies are independent of alkyl group for simple groups. It is assumed that the same is true for the polar trifluoromethyl group. [d] From $\Delta H_a = 161$, ref 11, and the ionization potential of 290 for water, ref 27. [e] From the standard state of pure liquid for water.

the use of gas-phase data for bond dissociations and solution pK_a values in a simple thermochemical cycle. These potentials can then be used to obtain estimates of the solvation energies of the nucleophiles. Finally, it will be shown that potentials for half-cells (eq 2) are correlated with reactivity of the nucleophiles toward Pyronin cation [3,6-bis-(dimethylamino)xanthylium ion] in water.

Standard Electrode Potentials

The standard potentials for the half-cells (eq 2) are equivalent to the free energies for the reactions

$$H^+ + X^- \xrightarrow{\Delta G°_5} {}^1/_2H_2 + X\cdot$$

$$H^+ + B \xrightarrow{\Delta G°_5} {}^1/_2H_2 + B^{+}\cdot \qquad (3)$$

in aqueous solution. Throughout this paper, standard states are taken in the gas phase as the ideal gas 1-atm pressure and 25 °C and in solution as the ideal 1-molar solution at 25 °C.

Equations 4 and 5 follow obviously from the quantities defined in the thermochemical cycles of Scheme I:

$$\Delta G°_5 = \Delta G°_3 - \Delta G°_2 - {}^1/_2\Delta G°_4 \qquad (4)$$

$$\Delta G°_3 = \Delta G^{gas}_3 - \Delta G°_6 + \Delta G°_7 + \Delta G°_8 \qquad (5)$$

Reasonably accurate values for ΔG^{gas}_3 are available for many nucleophiles of interest in electrophile–nucleophile combination reactions[10–18] Values for $\Delta G°_6$ are, in principle, measurable, and some are available.[19] They will not be used in the present section for reasons that will become clear.

For aqueous solutions, it is quite remarkable that the free energies of solution of alcohols, ethers, amines, and carboxylic acids are all approximately equal to −3 ± 2 kcal/mol.[19] For many of the species of interest here, then, we confidently expect $\Delta G°_6$ and $\Delta G°_8$ for HX to be ca. −3 kcal/mol. There is also a nearly linear relationship between $\Delta G°_6$ and size of the molecule even when $\Delta G°_6$ is different from −3 kcal/mol, as for noble gases, diatomic molecules, and hydrocarbons.[19] Even for charged species, Aue and Bowers[11] have shown that free energies of solution vary monotonically with size for primary, secondary, and tertiary ammonium ions with no apparent deviations attributable to different numbers of H-bonding sites. This behavior should lead to a nearly perfect cancellation of $\Delta G°_6$ and $\Delta G°_8$ in eq 5 for all species of interest here.

Reasonably sized saturated hydrocarbons, diatomic molecules (X–X), and noble gases all have free energies of solution in water of ca. 4 kcal/mol.[19] From an extrapolation of the data for noble gases,[19b] we estimate that the free energy of solution of the hydrogen atom in water is +5 kcal/mol. This value for $\Delta G°_7$ could then be used in eq 5 to obtain $\Delta G°_3$ from ΔG^{gas}_3. There is, however, an even simpler way to proceed.

Dissociation of a molecule into a hydrogen atom and other fragment in the gas phase has an entropy of reaction equal to the entropy of the free hydrogen atom plus any symmetry contributions.[11,12] To a reasonable approximation (ca. ±1 kcal/mol), $T\Delta S^{gas}_3 = +7$ kcal/mol for ordinary HX and BH^+ species. With this approximation, and those above for $\Delta G°_6$, $\Delta G°_7$, and $\Delta G°_8$, eq 5 becomes simply

$$\Delta G°_3 = \Delta H^{gas}_3 - 2 \text{ kcal/mol} \qquad (6)$$

With the same approximations applied to the dissociation of hydrogen molecule

$$\Delta G°_4 = \Delta H^{gas}_4 - 2 \text{ kcal/mol} \qquad (7)$$

and eq (4) becomes the final working equation, eq 8:

$$\Delta G°_5 = \Delta H^{gas}_3 - {}^1/_2\Delta H^{gas}_4 - \Delta G°_2 \qquad (8)$$

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Table II. Electron Transfer and Solvation Energies[a]

Nuc	ΔG°_1	EA	ref	$-\Delta G^{gas}_1$	$-\Delta G^\circ_{soln}$-(X^-)	$-\Delta G^\circ_8$-($B^+\cdot$)
OH^-	99	42.1	27	271	106	
CN^-	112	88.1	27	226	73	
N_3^-	87	62.1	28	252	74	
HOO^-	73	27.4	16	286	94	
CH_3O^-	80	36.7	18	277	92	
$CF_3CH_2O^-$	86	51.2	*b*	262	84	
$C_6H_5O^-$	74	48.7	*c*	265	74	
n-$PrNH_2$	85	197	10	117		69
piperidine	76	181	10	133		62
H_2O	138	290	27	24		109
n-PrS^-	75	46.1	14	268	78	
$C_6H_5S^-$	75	56.9	15	257	68	
OCl^-	89	64	27	250	74	
$CH_3CO_2^-$	101	73	*d*	231	77	
NO_2^-	75					
F^-	133	78.4	12	235	104	

[a] All values are in kcal/mol. Quantities are defined in Scheme I and eq 11 and 12. EA is the gas-phase adiabatic ionization potential. The value of −260.5 for $\Delta G^\circ_{soln}(H^+)$ is from ref 26. [b] From $\Delta H_a = 364$, ref 12, and ΔH^{gas}_3 given in Table I. [c] From $\Delta H_a = 351.4$, ref 12. [d] From $\Delta H_a = 347$; taken from the value relative to HF in ref 29 and adjusted to the acidity of HF given in ref 12.

where the 1-kcal difference between ΔG°_3 and $^1/_2\Delta G^\circ_4$ is neglected as insignificant.

The value of ΔH^{gas}_4 is taken as 104.2 kcal/mol,[23] and other quantities in eq 8 are given in Table I, together with the calculated values of ΔG°_5, for a range of nucleophiles.

A value for ΔG°_5 for hydroxide ion in aqueous solution has been reported,[24] which is based partly on electrochemical measurement and partly on a thermochemical cycle. The value of 46.6 kcal/mol is in reasonable agreement with that of 45.7 kcal/mol obtained here. A similar evaluation of ΔG°_5 for peroxide ion in aqueous solution gave 18.3 kcal/mol,[24] which may be compared with the present value of 20.5 kcal/mol. The agreement indicates at least a reasonable consistency of approximations.

One further check of values is possible. The standard potential for the half-cell

$$^1/_2(CN)_2 + H^+ + e^- = HCN \qquad (9)$$

has been reported[24] to be 4.2 kcal/mol. this value, together with the values of ΔG°_2 and ΔG°_5 from Table I, can be used to calculate the free energy of bond dissociation of cyanogen in aqueous solution. The value obtained, 135 kcal/mol, may be compared with the enthalpy of bond dissociation in the gas phase. This latter value has been the subject of some controversy but is quoted as a "median value" of 134 kcal/mol.[23]

Solvation Energies of Nucleophiles

From Scheme I, it is obvious that values for ΔG°_1 can be obtained from quantities already evaluated:

$$\Delta G^\circ_1 = \Delta G^\circ_5 + {}^1\!/_2\Delta G^\circ_4 \qquad (10)$$

The comparable quantity for the gas phase, ΔG^{gas}_1, can be calculated from the electron affinity of X·, or the ionization potential of B, and the ionization potential of the hydrogen atom (313.6 kcal/mol[23]). Equations 11 and 12 follow from the definitions

$$\Delta G^\circ_{soln}(X^-) = \Delta G^{gas}_1 - \Delta G^\circ_1 + \Delta G^\circ_7 + \Delta G^\circ_8 - \Delta G^\circ_{soln}(H^+) \qquad (11)$$

$$\Delta G^\circ_{soln}(B^+\cdot) = \Delta G^\circ_1 - \Delta G^{gas}_1 - \Delta G^\circ_7 + \Delta G^\circ_{soln}(B) - \Delta G^\circ_{soln}(H^+) \qquad (12)$$

where the ΔG°_{soln}'s are the free energies of transfer from the gas phase to aqueous solution. We have already estimated that ΔG°_7 = 5 kcal/mol. We shall assume that $\Delta G^\circ_8 = -3$ for all X, although this is a less accurate approximation than that used in the derivation of eq 8. It would be better to use the earlier approximaion and equate the free energies of solution of HX and X·, but the free energies of solution of many of the HX of interest are not available. The free energies of solution of the B species of interest are available. Values[11] of −2.5 kcal/mol for *n*-propylamine and of −0.8 kcal/mol for piperidine, and a calculated value, from vapor pressure,[22] for water of −2.1 kcal/mol are used. The calculated values are shown in Table II.

Table III. Reactions of Nucleophiles with Pyronin[a]

nucleophile	$\Delta G^\dagger$	ΔG°_{ion}	$\Delta\Delta G^\circ_{BDE}$
H_2O	21.9[b]	−25[c]	60
CN^-	17.3		
OH^-	15.1	+3.4	49
N_3^-	12.7[d]	−8.2[d]	26
$CF_3CH_2O^-$	13.8[e]	−1.5[e]	31
CH_3O^-	12.2[e]		
piperidine	11.2	+1.8	25
n-$PrNH_2$	13.2	+0.3	33
HOO^-	11.5	+3.4	24
$C_6H_5S^-$	6.7[f]	+1.2[f]	24
n-PrS^-	8.2	+7.0	29

[a] Reactions in water at 25 °C. Data are from ref 27, unless otherwise noted. Quantities are defined in eq 13 and 14 and are in kcal/mol. $\Delta G^\dagger$ is the free energy of activation for the combination reaction. [b] Estimated from relative rate constants for OH^- and H_2O with $DMAPTr^+$, ref 50, and for OH^- with Pyronin. [c] The pK_a of the conjugate acid of the alcohol is estimated to be −7. See: Ritchie, C. D.; Wright, D. J.; Huang, D.-S.; Kamego. A. A. *J. Am. Chem. Soc.* 1975, *97*, 1163. [d] Estimated from the reactions of OH^- and N_3^- with tri-*p*-anisylmethyl cation and OH^- with Pyronin. See: Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* 1973, *95*, 2701. [e] Estimated from the reactions of OH^- and alkoxides with $DMAPTr^+$, ref 1. [f] Estimated from the reactions of OH^- and thiophenoxide ion with $DMAPTr^+$, ref 1.

The free energies of solution could equally well have been obtained from gas-phase and solution acidity measurements.[11,25] The calculation is completely equivalent to that used here since the gas-phase acidities, electron affinities, and gas-phase bond dissociation energies are interdependent quantities.[11,12] For this reason, the free energies of solution for the $B^+\cdot$ species reported in Table II are equal to the free energies of solution of the corresponding BH^+ species reported by Aue and Bowers,[11] except for the symmetry contributions that we have neglected.

It does not appear that free energies of solution of any of the X^- species considered in Table II have been estimated in any previous work, except that for fluoride ion, which we have included specifically for comparison. From an entirely different cycle and set of assumptions, a value of −104 kcal/mol[26] was obtained, which is identical with the value found here.

Electrode Potentials and Nucleophilic Reactivity

In recent work,[1,27] rate and equilibrium constants for the reactions of a variety of nucleophiles with Pyronin cation in aqueous solution have been obtained. The reactions of Pyronin are believed to be relatively free of complications from steric effects, believed present in reactions of triarylmethyl cations,[27] and from the uncertainty of position of attack on the aryltropylium cations. These reactions are, therefore, believed to be particularly appropriate for the study of "inherent" nucleophilicity in electrophile–nu-

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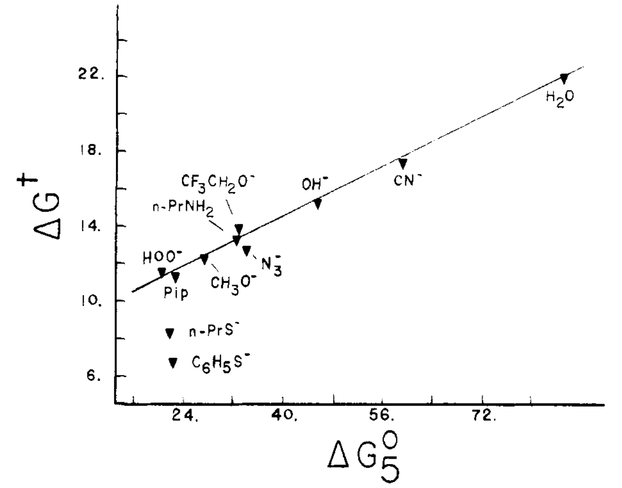

Figure 1. Plot of electrode potential vs. free energy of activation for reactions of nucleophiles with pyronin in water. Data are from Table I and III.

cleophile combination reactions.

Pertinent data for the free energies of activation are shown in Table III. A plot of these free energies of activation vs. the appropriate values of $\Delta G°_5$ is shown in Figure 1. With the exception of the thiolate ions, there is an excellent linear relationship between the quantities with a slope, $\Delta\Delta G^{\dagger}/\Delta\Delta G°_5$, of 0.18.

From the equilibrium constants for reactions of the nucleophiles with Pyronin, values of the free energy for ionic dissociation of the adducts, $\Delta G°_{\text{ion}}$, can be obtained. If the standard electrode potential for reduction of Pyronin, $\Delta G°_{R^+}$, were known, the cycle

$$\begin{tikzcd} & \text{R-Nuc} \arrow[dl, "\Delta G°_{\text{ion}}"'] \arrow[dr, "\Delta G°_{\text{BDE}}"] & \\ R^+ + \text{Nuc}^- \arrow[rr, "\Delta G°_{\text{ET}}"] & & R\bullet + \text{Nuc}\bullet \end{tikzcd} \tag{13}$$

could be used to obtain $\Delta G°_{\text{BDE}}$, since $\Delta G°_{\text{ET}} = \Delta G°_5 - \Delta G°_{R^+}$. Since the value is not known, we can only obtain relative values of $\Delta G°_{\text{BDE}}$, $\Delta\Delta G°_{\text{BDE}}$, from

$$\Delta\Delta G°_{\text{BDE}} = \Delta G°_{\text{ion}} + \Delta G°_5 \tag{14}$$

Experimental and calculated quantities are shown in Table III.

Discussion

Factors Affecting Oxidation Potentials. Since the values of $\Delta G°_5$ or, more directly, $\Delta G°_1$ may be thought of as relative measures of "solution electron affinities", there is an obvious temptation to relate them to orbital energies of the HOMO's of the nucleophilic species through a naive application of Koopmans' theorem. Such a relationship is almost certainly not correct. Even in the gas phase, Koopmans' theorem is not always applicable, particularly when "adiabatic" electron affinities or ionization potentials are considered.[18,31] In the case of ionization potentials of amines, the difference between adiabatic and vertical processes amounts to ca. 20 kcal/mol.[11] In solution, the solvation energy difference between ionic and neutral species involved is always a large quantity and completely invalidates the application of Koopmans' theorem to the adiabatic processes.

The relative values of $\Delta G°_5$ for the various species considered in Table I do not appear to be dominated by any single factor. The gas-phase electron affinities span a tremendous range and are not correlated with the equally large range of solvation energies of anions and neutrals. The energies associated with changes in geometries from vertical to ground states in the gas phase of the ionized species vary from nil for OH^-[31] to small for alkoxides[18] to large for amines.[11]

Nucleophilic Reactivities. Before discussing the correlation shown in Figure 1, it is appropriate to consider some of the ideas relating to nucleophilic reactivity that have developed over the years.

Perhaps the earliest substantial attempt at an empirical correlation of nucleophilic reactivities was the development of the Swain–Scott equation[32] for application to S_N2 reactions. Only shortly thereafter, Edwards began attempts[2,8] to relate general nucleophilic reactivities to physicochemical properties of the nucleophiles. The first formulation of the Edwards equation[8] postulated a relationship between reactivity and some combination of basicity and oxidation potential of oxidative dimerization of the nucleophiles.

After some difficulties with the original formulation, including the bond energy problem[9] mentioned in the introduction and some examples of negative coefficients of the oxidation potentials in correlations,[2] oxidation potentials were replaced by polarizabilities. In actual practice, the anisotropic polarizabilities desired were not available in many cases and were "evaluated" by application of the four-parameter equation to reactivity data.[2,8]

In further development of the Edward's equation,[2b] another factor, the "α-effect", was postulated to be important in addition to the basicity and polarizability of the nucleophile. There have been numerous attempts[4,33,34] to relate the α-effect to physicochemical properties of the reagents.

In the mid-1960s, Pearson[6] expressed the pessimistic opinion that the general quantitative correlation of nucleophilic reactivities is an unattainable goal and put forward the qualitative, and somewhat ill-defined, Soft–Hard Acid–Base concept. Although the concept has been quite popular, it has not deterred efforts to understand nucleophilic reactivity in more fundamental terms.

During the same time that the development of the Edwards' equation was taking place, Miller[35] had taken a different approach to nucleophilic reactivity in SNAr reactions. The energy difference (enthalpies were actually considered) between reactants, $ArX + Y^-$, and the intermediate Meisenheimer complex, $ArXY^-$, was divided into contributions from the bond dissociation energy, into $ArX^-\cdot + Y\cdot$, the electron affinity of $Y\cdot$, solvation energies of Y^-, $ArXY^-$, and $ArX^-\cdot$, and bond-energy changes on going from ArX to the Meisenheimer complex. The energy difference between the complex and the transition state was then assumed to be some fraction, ca. 20–30% taken from an assumed curve, of the $ArXY^-$ bond dissociation energy. The assumed curve of fraction of bond dissociation energy vs. exothermicity of the reaction was based on the Hammond postulate of variable transition states. According to this scheme, the activation enthalpy for the reaction of a nucleophile with ArX is the sum of all of the contributions listed above for the formation of the intermediate complex, less 20–30% of the bond dissociation energy. It was recognized that the fraction of bond dissociation energy used might underestimate the actual extent of bond dissociation and contain contributions from, for example, solvation energies of Y^-. The relative reactivities of various Y^- are actually calculated, then, from the electron affinities, solvation energies, and C–Y bond dissociation energies. Many of the quantities entering these calculations were empirically estimated, and some of the electron affinities and solvation energies used are seriously different from currently accepted values, so that the agreement with experiment must be regarded as, at least partly, fortuitous. The scheme is notable as the first recognition that electron affinities and solvation energies of the nucleophiles might be important contributors to reactivity.

There have been a number of suggestions that orbital energies of the HOMO's of nucleophilic reagents are important in determining reactivity.[3,5] As already discussed, however, the entire concept of orbital energies in solution is quite complex[5] and nu-

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merical data have not been produced. It has also been recognized, at least qualitatively, that the α-effect might be due to orbital energies or ionization potentials.[33,34] Jencks[33] particularly noted that stabilization of the cation radical produced from ionization of a neutral α-effect nucleophile should lead to "unusually" low ionization potentials. Hoz[34] has carried the argument further.

There have been several notable recent developments in the realm of nucleophilicity in S_N2 reactions. The application of Marcus theory to S_N2 reactions[36] has recast the problem in terms of factors influencing the "inherent barriers" for the reactions. Brauman[37] has shown that these seem to be related to the gas-phase methyl cation affinities of the nucleophiles, which are, of course, equal to the methyl–X bond dissociation energies plus the energy of electron transfer from X^- to CH_3^+.

From the beginning of the present series of papers,[7,38] it has been obvious that nucleophilic reactivity in electrophile–nucleophile combination, ENC, reactions is quite different from that in S_N2 reactions. One of the striking examples is the order of reactivity $N_3^- > OH^- > CN^-$ found in ENC reactions, which is the reverse of the order in S_N2 reactions. It has also been shown[27] that Marcus theory cannot be justifiably applied to ENC-type reactions. The basic problem is that there is no a priori method of establishing the position of the transition state for a reaction with $\Delta G^\circ = 0$, and no answer to this problem is apparent in recent work.[39]

There is another problem that needs confrontation before proceeding with the discussion of the ENC reactions. Pearson's pessimism[6] about general correlations of nucleophilicity reactivity has considerable foundation even for ENC reactions. Although reasonably consistent patterns of nucleophilic reactivity are observed toward widely different electrophiles,[40,41] there are frequent inexplicable deviations from this pattern.[41,42] A few examples should suffice to make the point. For the reactions of a wide range of anionic and neutral nucleophiles, there is an excellent correlation of rates for reaction with 2,4-dinitrofluorobenzene and with $DMAPTr^+$ ([*p*-(dimethylamino)phenyl]tropylium ion) in aqueous solution; azide ion, however, deviates badly from the correlation[41] with no apparent reason. Thiolate ions are particularly unreactive, relative to other nucleophiles, in reactions with carbonyl carbon.[42] Particularly pertinent to the present work, the correlation of reactions of Pyronin with those of $DMAPTr^+$ is far less than perfect;[27] again for no apparent reason, both primary and secondary amines, relative to other nucleophiles, have rate constants nearly a factor of 10 greater toward Pyronin than toward $DMAPTr^+$.

With the above reservations, there is an impressive body of data on ENC reactions reasonably well correlated by the simple N_+ relationship,[40] and at least semiquantitative orders of reactivity exist that are worthy of attempts at understanding.

The correlation of nucleophilic reactivity with oxidation potentials shown in Figure 1 is particularly impressive in that it incudes anionic, neutral, and α-effect nucleophiles. The deviations of the points for thiolates suggests that the correlation may be limited to nucleophiles derived from first-row elements, and this might be ascribed to polarizability effects.[43]

Although the theoretical arguments for the involvement of orbital energies in nucleophilic reactivity[3,5] might be considered to be suggestive of the present correlation, as already pointed out, the relationship between orbital energies and the present oxidation potentials in solution is not straightforward. The most directly suggestive previous work is Hoz's discussion of the importance of partial electron transfer in the α-effect.[34] Simultaneously with, and independently of, the present work, Hoz has noted that the ionization potentials of azide, hydroxide, and cyanide ions in aqueous solution, evaluated from a cycle and assumptions quite similar to those used here, are in accord with the order of reactivity in ENC reactions.[44] Most of the earlier attempts to rationalize the orders of reactivity in ENC reactions have focused on desolvation of the nucleophiles,[1,7,40,45] which is only one of the components determining oxidation potentials.

The slope of the correlation shown in Figure 1, 0.18, is much too small to be consistent with a mechanism involving an actual electron-transfer step. An electron transfer from any of the nucleophiles studied to any of the cations studied would have a large positive ΔG°_{ET}, and the rate constants for the transfers would certainly[46] give $\Delta G^\dagger/\Delta G^\circ_{ET} = 1$.

Some idea of the magnitudes of ΔG°_{ET} can be obtained. There are some reports of electrochemical measurements of reduction potentials for some of the cations of interest.[47,48] The most directly pertinent report is to a cyclic voltammetry study of tropylium cation, and phenylxanthylium cation, in 75% aqueous ethanol.[47b] Although the report of "near reversability", and other considerations,[49] should cause considerable skepticism about the reported potentials, the reported[47b] study of rates of reactions of the cations with $Cr(ClO_4)_2$, and an independent estimate of the potential for tropylium ion, to be given below, indicates that the potentials are, at least, approximately correct. Conversion of the reported potential to standard potential vs. NHE gives $E^0 = -0.19$ V (−4.4 kcal/mol).

For the electron transfer from hydroxide ion to tropylium cation, then, $\Delta G^\circ_{ET} = 50.1$ kcal/mol. We may estimate this value in an entirely different way. The bond dissociation energy (gas phase) of Tr–H is 73 kcal/mol.[17] The difference in bond dissociation energies of benzyl–H and benzyl–OH is 7 kcal/mol,[17] leading to an estimate of the Tr–OH bond dissociation energy of 66 kcal/mol. By use of the same approximations as those in the derivation of eq 8, the free energy of dissociation of Tr–OH in aqueous solution is the same, $\Delta G^\circ_{BDE} = 66$ kcal/mol. The equilibrium constant for the ionic dissociation of Tr–OH in aqueous solution[50] gives $\Delta G^\circ_{ion} = 12.7$ kcal/mol, and from eq 13, we obtain $\Delta G^\circ_{ET} = 53$ kcal/mol, in reasonable agreement with the above value.

Accepting the reduction potential of tropylium cation as approximately correct, then, the least positive free energy of electron transfer that can be obtained for the nucleophiles considered in Table I is +25 kcal/mol for peroxide ion. Most of the cations that have been studied in ENC reactions are expected to be less easily reduced than is tropylium cation (for example, tri-*p*-anisylmethyl cation has a reported $E_0 = -0.6$ V, vs. NHE[47]), and the free energies of electron transfer will be even greater than those calculated here.

The conclusion that appears to be forced by these considerations is that the slope of 0.18 in the correlation of Figure 1 results from only partial electron transfer at the transition states. The correlation then indicates that there is a remarkable proportionate involvement of all of the factors determining the oxidation potentials in solution: solvation, "vertical" electron affinity, and geometrical changes of the nucleophiles. No rationalization of this behavior is apparent.

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Registry No. OH^-, 14280-30-9; CN^-, 57-12-5; N_3^-, 14343-69-2; HOO^-, 14691-59-9; CH_3O^-, 3315-60-4; $CF_3CH_2O^-$, 24265-37-0; C_6H_5-O^-, 3229-70-7; *n*-$PrNH_2$, 107-10-8; H_2O, 7732-18-5; *n*-PrS^-, 20733-14-6; $C_6H_5S^-$, 13133-62-5; OCl^-, 14380-61-1; $CH_3CO_2^-$, 71-50-1; NO_2^-, 14797-65-0; F^-, 16984-48-8; piperidine, 110-89-4; pyronine, 92-32-0.

Induction of the Cholesteric Mesophase in Nematic Liquid Crystals: Mechanism and Application to the Determination of Bridged Biaryl Configurations

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Abstract: It is shown that the helicity of optically active bridged biaryl molecules is the main factor determining their high twisting power in biphenyl nematic liquid crystals. A mechanism of induction of the cholesteric phase was deduced from the orientation of the solute molecules, determined by linear dichroism and from the solvent effect. These results show that it is also possible to correlate the absolute configurations of optically active bridged biaryl compounds to the sign of their twisting power in biphenyl nematics.

When a chiral "guest molecule" is dissolved in a nematic liquid crystal, its molecular chirality is transferred to the solvent which becomes organized in a macrostructural helical cholesteric structure.[2–4]

A cholesteric structure is characterized by its handedness and pitch. Equal amounts of enantiomeric "guests" of equal enantiomeric purity induce helical structures with identical pitch and opposite handedness.[3] Different substances show a different ability to twist a nematic phase. The twisting power of a chiral dopant can be defined as[5,6]

$$\beta_{\mathrm{M}} = (pcr)^{-1}$$

where p is the pitch (μm^{-1}), c is the concentration (moles of solute/moles of solution), and r is the enantiomeric purity of the dopant.

The twisting power β_{M} and its sign [(+) for a P helix and (−) for an M helix of the induced cholesteric] characterize the chiral solute in a way similar to the specific optical rotation [α]. However, the physical origin of the two quantities is entirely different. The origin of the optical rotation depends on interactions between light and molecules, while the twisting power originates from interactions between molecules of solute and solvent.[6–8] Quantity β_{M}, a molecular property dependent on the liquid crystalline matrix, can give information on the chiral dopant. On the one hand, the passage from molecular to macrostructural chirality somehow amplifies the molecular asymmetry, and this can be used to detect traces of optically active substances,[9] to follow racemization kinetics on extremely small scale experiments,[10] and also to characterize molecules with very low optical rotations such as compounds chiral by isotopic substitution.[11] On the other hand, the variations of β_{M} with the molecular structure of the inducing chiral compound and, for a given dopant, with the liquid crystal used as solvent can give information concerning the mechanism of induction and also allow the formulation of an interaction model between solute and solvent, able to predict the handedness of the induced cholesteric mesophase.

In a previous work[4] on optically active *trans*-stilbene oxide and related molecules, we proposed a model of induction in which the chirality is transferred from the chiral inducer to the nearest neighbor molecule of the solvent through chiral conformations; the latter serves as a template for the near neighbor and so on, thus justifying the observed high values of β_{M}.

In this paper we report our results on the chiral biphenyl system. Optically active twisted biaryls should display strong interactions with liquid crystals of the biaryl type because of their structural analogy, and therefore a study of their twisting powers should also give evidence to confirm or disregard our hypothesis on the mechanism of induction. We specifically restricted our study to only bridged derivatives where the helicity of the biaryl system is unambiguous in order to apply our model to the correlation of configurations.

Results and Discussion

Pitch values were determined by means of the Grandjean–Cano method which is based on the observation of the discontinuity lines appearing when a cholesteric liquid crystal is inserted into a cell

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