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Absolute Electronegativity and Hardness: Applications to Organic Chemistry

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The recent concepts of absolute electronegativity, χ, and absolute hardness, η, are briefly reviewed. Experimental values for a large number of molecules and radicals are presented. The values are shown to be in good agreement with the known chemical behavior, both as to nucleophilic–electrophilic properties and as to rates of reaction. Applications are also given for the use of empirical rank orders of the local hardness, $\tilde{\eta}$. The uses of χ and η are consistent with frontier orbital theory. To make meaningful comparisons in a series of molecules, it is necessary that these orbitals remain the same. Also it is necessary that the observed I and A values of the molecules relate to the appropriate frontier orbitals.

The concept of hard and soft Lewis acids and bases was applied to organic chemistry in 1967.[1] A number of interesting, but qualitative, correlations were made.[2] A serious problem was that the terms hard and soft were not well defined, either theoretically or experimentally. Recently this deficiency has been corrected.[3] With use of density functional theory as a basis, the hardness of a chemical system has been rigorously defined. At the same time a related property, the electronic chemical potential, has been introduced.[4]

Any chemical system (atom, molecule, ion, radical) is characterized by its electronic chemical potential, μ, and by its absolute hardness, η. The exact definition of these quantities are

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \quad \eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \tag{1}$$

where N is the number of electrons and v is the potential due to the nuclei, plus any external potential.

Operational and approximate definitions are

$$-\mu = (I + A)/2 = \chi \qquad \eta = (I - A)/2 \tag{2}$$

where I is the ionization potential and A is the electron affinity.

Since $(I + A)/2$ is the Mulliken electronegativity for atoms, the value for any system, χ, is called the absolute electronegativity. For an equilibrium system it must be constant everywhere. The hardness, η, need not be constant and can have local values, but $(I - A)/2$ is the average or global value. The softness, σ, is simply the inverse of the hardness, $\sigma = 1/\eta$.

If two systems, B and C, are brought together, electrons will flow from that of lower χ to that of higher χ, until the chemical potentials become equal. As a first approximation, the (fractional) number of electrons transferred, ΔN, will be given by

$$\Delta N = \frac{\chi_C - \chi_B}{2(\eta_C + \eta_B)} \tag{3}$$

Obviously this is a convenient way of looking at generalized acid–base reactions

$$C + :B \rightarrow C:B \tag{4}$$

where C is the Lewis acid. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance.

There is an energy lowering due to electrons being transferred to a lower chemical potential. But this is only a small part of the total energy change, which must also include covalent bonding and ionic interactions. Even though (3) is incomplete, it is still useful because it measures the initial interaction between B anc C by using only properties of the isolated systems. Furthermore we can assume that the covalent bonding will show some proportionality to ΔN, since coordinate covalent bonding is involved. For neutral reactants the ionic binding will also depend on ΔN.

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[2] For example, see: Ho, T.L. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic Press: New York, 1977.

[3] Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 1503–1509.

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Table I. Experimental Parameters for Molecules (eV)

molecule	I^a	A^a	χ	η	molecule	I^a	A^a	χ	η
SF_6	15.4	0.5	8.0	7.4	HCl	12.7	-3.3	4.7	8.0
O_3	12.8	2.1	7.5	5.4	CH_3CN	12.2	-2.8	4.7	7.5
SO_3	12.7	1.7	7.2	5.5	HCO_2CH_3	11.0	-1.8	4.6	6.4
Cl_2	11.6	2.4	7.0	4.6	CH_3CHO	10.2	-1.2	4.5	5.7
H_2	15.4	-2.0	6.7	8.7	C_2H_4	10.5	-1.8	4.4	6.2
SO_2	12.3	1.1	6.7	5.6	C_5H_5N	9.3	-0.6	4.4	5.0
N_2	15.58	-2.2	6.70	8.9	butadiene	9.1	-0.6	4.3	4.9
Br_2	10.56	2.6	6.6	4.0	H_2S	10.5	-2.1	4.2	6.2
C_2N_2	13.37	-0.58	6.40	6.98	C_2H_2	11.4	-2.6	4.4	7.0
O_2	12.2	0.4	6.3	5.9	$HCONH_2$	10.2	-2.0	4.1	6.1
BF_3	15.8	-3.5	6.2	9.7	styrene	8.47	-0.25	4.11	4.36
CO	14.0	-1.8	6.1	7.9	CH_3COCH_3	9.7	-1.5	4.1	5.6
I_2	9.4	2.6	6.0	3.4	PH_3	10.0	-1.9	4.1	6.0
BCl_3	11.60	0.33	5.97	5.64	C_6H_6	9.3	-1.2	4.1	5.3
CCl_4	11.5	$\sim 0.3^c$	5.9	5.6	AsH_3	10.0	-2.1^d	4.0	6.1
HNO_3	11.03	0.57	5.80	5.23	toluene	8.8	-1.1	3.9	5.0
CH_3NO_2	11.13	0.45	5.79	5.34	CH_3Cl	11.2	-3.7	3.8	7.5
PF_3	12.3	-1.0	5.7	6.7	*p*-xylene	8.4	-1.1	3.7	4.8
HCN	13.6	-2.3	5.7	8.0	1,3,5-trimethylbenzene	8.40	-1.03	3.69	4.72
PBr_3	9.9	1.6	5.6	4.2	cyclohexene	8.9	-2.1	3.4	5.5
S_2	9.36	1.66	5.51	3.85	DMF	9.1	-2.4	3.4	5.8
$C_6H_5NO_2$	9.9	1.1	5.5	4.4	CH_3F	12.5	-6.2	3.2	9.4
PCl_3	10.2	0.8	5.5	4.7	H_2O	12.6	-6.4	3.1	9.5
acrylonitrile	10.91	-0.21	5.35	5.56	$(CH_3)_3As$	8.7	-2.7	3.0	5.7
CS_2	10.08	0.62	5.35	5.56	$(CH_3)_3P$	8.6	-3.1	2.8	5.9
CH_2	10.0	0.6	5.3^e	4.7^e	c-C_3H_6	10.5^b	-5.0^d	2.8	7.8
HI	10.5	0.0	5.3	5.3	$(CH_3)_2S$	8.7	-3.3	2.7	6.0
CO_2	13.8	-3.8	5.0	8.8	NH_3	10.7	-5.6	2.6	8.2
HF	16.0	-6.0	5.0	11.0	CH_4	12.7	-7.8	2.5	10.3
CH_2O	10.9	-0.9	5.0	5.9	$C(CH_3)_4$	10.4	-6.1	2.2	8.3
CH_3I	9.5	0.2	4.9	4.7	$(CH_3)_2O$	10.0	-6.0	2.0	8.0
CH_3Br	10.6	~ -1.0	4.8	5.8	CH_3NH_2	9.0	-5.3^d	1.9	7.2
SiH_4	11.7	-2.0	4.8	6.8	$(CH_3)_3N$	7.8	-4.8	1.5	6.3

[a] For sources see ref 12, except as indicated. [b] Basch, H.; et al. *J. Chem. Phys.* **1969**, *51*, 52. [c] Reference 38. [d] Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985; Vol. III. [e] For singlet state.

The chemical potential and the hardness are molecular and not orbital properties. But the electrons will flow from a definite occupied orbital in B and will go into a definite empty orbital in C. Usually, but not always, there can be electron flow in both directions, as in σ- plus π-bonding. The overlap between the exchanging orbitals, and their nature, will be critical in determining energy changes. There is no conflict with the frontier orbital theory of chemical reactivity.

According to Koopman's theorem, the frontier orbital energies are given by

$$-\epsilon_{\text{HOMO}} = I \qquad -\epsilon_{\text{LUMO}} = A \tag{5}$$

Figure 1 shows the usual orbital energy diagrams for several molecules, where experimental values have been used for the frontier orbitals. The values of $\mu = -\chi$ are shown as dashed horizontal lines. The values of η are shown as dashed vertical lines. This shows very graphically what is meant by chemical hardness. Hard molecules have a large HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap.

The earlier, qualitative definitions of hardness were closely related to polarizability.[6] Soft acids and bases were those of high polarizability. This is consistent with Figure 1, since a small energy gap leads to easy polarization and a large gap to difficult polarization.

Soft molecules can easily change both their number of electrons and the distribution of charge within the molecule. Two such molecules, one a donor and one an acceptor, can interact with each other in several favorable ways.[7,8] This is the basis of the HSAB principle, "hard acids prefer to coordinate to hard bases, and soft acids to soft bases".[6] Hard acids and bases must rely on existing charges and dipoles as a source of ionic bonding.[9]

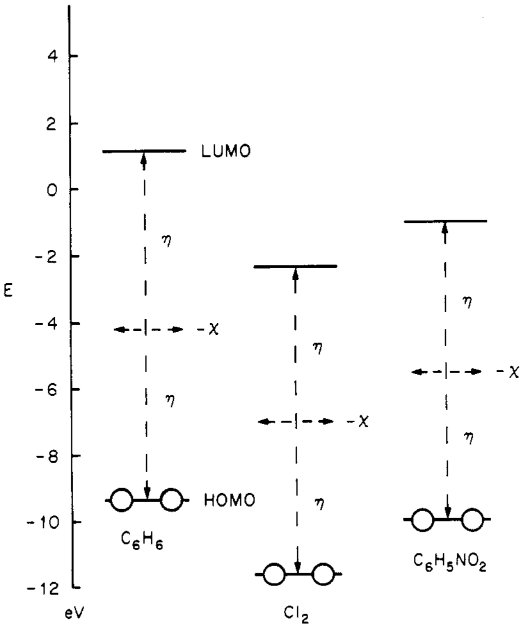

Figure 1. Orbital energies for several molecules, showing χ and η.

The energy gap in Figure 1 is also related to vis-UV spectra. However the energy of the first absorption band is only about half of $(I - A)$. The difference arises from the extra electron-electron repulsion that comes with the

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Table II. Values of ΔN Calculated for Reaction of Cl_2 with Substituted Benzenes

reactant	χ,[a] eV	η,[a] eV	ΔN
$C_6H_5NHCH_3$	3.05	4.25	0.22
$C_6H_5N(CH_3)_2$	3.10	4.35	0.22
$C_6H_5NH_2$	3.3	4.4	0.21
$C_6H_5OCH_3$	3.55	4.65	0.19
1,3,5-$C_6H_3(CH_3)_3$	3.7	4.7	0.18
p-$C_6H_4(CH_3)_2$	3.7	4.8	0.18
C_6H_5SH	3.8	4.6	0.17
C_6H_5OH	3.8	4.8	0.17
$C_6H_5CH_3$	3.9	5.0	0.16
$C_6H_5CH{=}CH_2$	4.1	4.4	0.16
C_6H_5I	4.1	4.6	0.16
C_6H_5Br	4.1	4.8	0.15
C_6H_5Cl	4.1	4.9	0.15
C_6H_5F	4.1	5.0	0.15
C_6H_6	4.1	5.3	0.14
$C_6H_5CO_2CH_3$	4.7[b]	4.6[b]	0.12
$C_6H_5COCH_3$	4.8[b]	4.5[b]	0.12
C_6H_5CHO	5.0[c]	4.6[c]	0.11
$C_6H_5CO_2H$	4.9[b]	4.8[b]	0.11
C_6H_5CN	5.0[c]	4.7[c]	0.11
$C_6H_5NO_2$	5.5	4.4	0.08
p-$C_6H_4(NO_2)CN$	6.1	4.5	0.05
thiophene	3.8	5.0	0.17
furan	3.5	5.3	0.18
pyrrole	2.9	5.4	0.21
anthracene	3.8	3.3	0.26
azulene	4.1	3.3	0.18
phenanthrene	4.1	3.8	0.17
naphthalene	4.0	4.2	0.17
biphenyl	4.0	4.3	0.17

[a] References same as for Table I, except as indicated. [b] Reference 39. [c] Chowdhury, S.; Heinis, T.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 4662.

electron affinity. Still, for related molecules there will be a linearity between $Nh\nu$ and $(I - A)$, which can be very useful.[10] Also, as expected, there is a strong correlation between chemical reactivity and the first absorption bond of most molecules.[11]

Table I contains experimental values of I, A, χ, and η for a number of molecules of interest. Other values have been published elsewhere,[12] and more are given in the tables to follow. It turns out that most common molecules have negative values of A, and it is fortunate that recently the technique of electron transmission spectroscopy has been developed to measure them.[13] These are vertical values, obviously, which is what is required by density functional theory, as in eq 1.

The molecules are arranged in order of decreasing values of χ, so that Lewis bases are at the bottom. The ordering must *not* be taken as an order of acid or base strength, but of the inherent preference for accepting or donating electrons. The strength depends strongly on other features, such as charges or dipole moments, and the orbitals that accept or donate electrons.

The main purpose of the paper will be to see if numbers, such as those in Table I, can be correlated with the known chemical reactivity of various classes of organic molecules. A prototype molecule will be selected to see if χ and η are consistent with known behavior. Then eq 3 will be applied to a series of related molecules reacting with a common substrate. The assumption is that a large value of ΔN is favorable for reaction.

Meaningful comparisons can only be made for a series of molecules where the interacting orbitals remain essentially the same. Also it is necessary that experimental I and A values are related to these frontier orbitals.

In certain cases it has been found that, for a series of moleceuls, ΔN is proportional to bond energies.[12,14] These are cases where ΔN is small, as in charge-transfer complexes. If ΔN is large, there will be too much ionic bonding, which is dominated by size factors. More generally, since eq 3 only gives the initial effect, it is expected that ΔN values will be related to energy barriers to reaction.

For anions and polyatomic cations it is possible to obtain rank orderings of hardness, but not absolute values, nor electronegativities. It will be shown that such rank orders can also be useful, even though eq 3 cannot be used.

Aromatic Electrophilic Substitution. Taking benzene as the prototype, its value of $\chi = 4.1$ eV shows that it is primarily an electron donor, or base. An η value of 5.3 eV is relatively soft. We expect acid-base complexes to form with molecules well above it in the Table, as well as with certain metal ions. These complexes may eventually lead to electrophilic substitution.

Figure 1 shows that electrons will flow spontaneously from benzene to chlorine. Also nitrobenzene will donate electrons to Cl_2 a little less readily. Taking Cl_2 as the common reagent, we next calculate ΔN for the substituted benzenes where I and A values are known. The results are given in Table II. They are quite encouraging, since it is clear that an almost perfect order of reactivity toward electrophilic substitution is followed by ΔN.

Some heteroaromatic molecules are also listed in Table II. The values of ΔN are seen to vary just as do the relative values of reactivity in electrophilic substitution.[15]

	benzene	thiophene	furan	pyrrole
ΔN	0.15	0.17	0.18	0.21
k_{rel}	1	10^3	10^5	10^{12}

Also included in the table are data for some polynuclear aromatics. These are also in the right order, with anthracene being very reactive and biphenyl somewhat more reactive than benzene.[16] None of these results, of course, give any indication of the position of reaction in the aromatic molecule. This question is answered by considering the electron density of the HOMO at various positions (vide infra).

As far as reactions with nucleophiles go, it can be seen that multiple substitution of benzene with groups such as NO_2 and CN, will be needed. These substituents will raise χ and increase electrophilic behavior.

Reactions of Olefins. The characteristics of ethylene, $\chi = 4.4$ eV and $\eta = 6.2$ eV, suggest similarity to benzene; nucleophilic addition becomes somewhat more probable, but electrophilic addition still is dominant. Table III contains values of χ and η for a number of olefins, as well as the relative rates of bromination in methanol.

For Br_2, $\chi = 6.6$ and $\eta = 4.0$, so that it is the electrophile. As before, ΔN can be calculated from eq 3, and these are also in the Table. Again there is a near perfect correlation between relative rates and the amount of electron density transferred. Since the same order of reactivity is found

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(16) For a review of rate data for Diels–Alder reactions, see: Sauer, J.; Sustman, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807.

Table III. Values of ΔN and Relative Rates of Olefin Reactions with Bromine

reactant	χ^a	η^a	ΔN	k_{rel}
$CH_2{=}CH_2$	4.4	6.2	0.11	1
$CH_2{=}CHCH{=}CH_2$	4.3	4.9	0.13	$\sim 50^d$
$CH_3CH{=}CH_2$	3.9	5.9	0.14	61
trans-$CH_3CH{=}CHCH_3$	3.5	5.6	0.16	1700
cis-$CH_3CH{=}CHCH_3$	3.45	5.7	0.16	2000
$(CH_3)_2C{=}CH_2$	3.5	5.7	0.16	5400
$(CH_3)_2C{=}CHCH_3$	3.3	5.5	0.17	1.3×10^5
$(CH_3)_2C{=}C(CH_3)_2$	3.0	5.3	0.19	1.8×10^6
$CH{\equiv}CH$	4.4	7.0	0.10	10^{-3}
$CH_2{=}CHCN$	5.4	5.6	0.06	v. slow
$CH_2{=}CHCHO$	5.3^b	4.9^b	0.08	v. slow
$CH_2{=}C{=}CH_2$	3.8	5.1	0.14	$\sim 12^d$
$CH_2{=}CHOAc$	4.3^c	5.5^c	0.12	$\sim 120^d$

[a] References same as for Table I, except as indicated. [b] Electron affinity, 0.40 eV is theoretical value, Lindholm, E. *J. Phys. Chem.* **1988**, *92*, 1794. However it gives results in good agreement with vis–UV spectrum. [c] Electron affinity from ref 19; ionization potential from Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937. [d] Estimated from rates of hydration. Tidwell, T. T.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 3395. Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 2683.

Table IV. Calculated Values of ΔN and Rate Constants for Reactions of Olefins with 1,3-Cyclopentadiene

reactant	χ^a	η^a	ΔN	k,[b] $M^{-1}\ s^{-1}$
$C_2(CN)_4$	7.3	4.5	0.19	4.3×10^8
$NCCH{=}C(CN)_2$	6.8	4.7	0.17	4.8×10^6
$CH_2{=}C(CN)_2$	6.5	4.9	0.14	4.6×10^5
maleic anhydride	6.3	4.7	0.13	5.5×10^4
p-benzquinone	5.7	3.9	0.11	9.0×10^3
maleonitrile	6.2	5.6	0.12	9.1×10^2
fumaronitrile	6.2	5.6	0.12	8.1×10^2
$CH_2{=}CHCN$	5.4	5.6	0.08	10
C_2H_4	4.4	6.2	0.03	$10^{-4\,c}$
cyclopentadiene	3.8	5.8	0.00	0.9

[a] Data as in Table I except ionization potentials of the cyano derivaives. Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Sc.* **1976**, *98*, 937. [b] At 20 °C. Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183. [c] Reference 16. From relative gas-phase data.

for rates of hydration in acid solution as for bromination, a few rates have been estimated in this way.

Olefins with electron-withdrawing substituents can also act as electron acceptors. Because of the nature of the LUMO, they will react most favorably with π-bases. It has already been shown that eq 3 works very well in predicting relative equilibrium constants for binding of olefins to transition metal atoms.[12] Zero-valent metal atoms act as π-donors by way of filled d orbitals.

Another type of π-donor will be suitable dienes in the Diels–Alder reaction.[16] Cyclopentadiene, $\chi = 3.8$, $\eta = 4.8$, is much more reactive than butadiene, $\chi = 4.3$, $\eta = 4.9$, as expected. Table IV contains calculated values of ΔN and rate constants for reaction of a number of olefins with 1,3-cyclopentadiene in dioxane. The correlation is seen to be quite good. Not only are activated olefins correlated, but even cyclopentadiene itself, acting as an olefin. The low reactivity of ethylene is not explained, however.

Reactions of Free Radicals. Table V lists experimental values of χ and η for a number of important free radicals. These numbers can be useful in two ways. In combining two such radicals to form a molecule, the difference in χ values is a major factor in determining the polarity of the bond. This can then be used as basis for deciding which part of the molecule is the Lewis acid and which part is the base.[12,17] For example, methanol should be considered as CH_3^+, OH^- and not HO^+, CH_3^-.

The second use of the table is to estimate the reactivity of radicals in the same ways that are used for stable molecules. The acid–base character of radicals has been recognized for some time, and it is customary to speak of electrophilic radicals, such as Cl, and nucleophilic radicals, such as $(CH_3)_3C$. Table V is a quantitative order of such descriptions.

When a nucleophilic radical reacts with olefins, electron-withdrawing substituents on the olefin speed up the rate of reaction. When an electrophilic radical reacts, the effect is reversed.[18] Such results are consistent with the use of eq 3. An electron-withdrawing substituent will increase χ, and hence ΔN, for reaction with a nucleophile. Table VI shows the values of ΔN calculated for a series of olefins reacting with $(CH_3)_3C$. There is very good agreement between the ΔN sequence and the second-order rate constants in 2-propanol at 300 K.[19]

Table VII has listed the rate constants at 437 K for a series of radicals reacting with ethylene. The calculated values of ΔN are also listed and are nearly in the same order as the rate constants. The more electrophilic radicals react the fastest.

Even if the radical (R) and the substrate (S) have the same electronegativity, the hardness of each should have an effect on the rate. The SOMO (singly occupied MO) of the radical acts as both an acceptor orbital and a donor orbital, and the substrate must also play a dual role. It should be advantageous for the sum $(\eta_R + \eta_S)$ to be small, which facilitates changes in electron density.

Indeed this effect is well known in radical abstraction reactions that are not endothermic.

$$R + X - Y \rightarrow R - X + Y \qquad (6)$$

For a given radical, and a related series of $X - Y$ molecules, the activation energy is usually a linear function of the reciprocal polarizability of $X - Y$, $E_a = C/\alpha_{XY}$, where C is a constant.[20] Since the polarizability is roughly proportional to the softness, this can be interpreted as $E_a \propto \eta_S$, as expected.

Some Electrophilic Reagents. Unfortunately there is not as much data available on electron affinities of other organic molecules. Still there are usually one or two examples known for each of the common classes, and these may sometimes be compared. Values of χ and η are known for a number of diverse carbonyl compounds and a few nitriles. The values of $\chi = 5.0$ eV for H_2CO and $\chi = 4.7$ for CH_3CN are indicative of weak electrophiles. The LUMO's of these molecules are on the unsaturated groups and concentrated on carbon.

Accordingly, values of ΔN have been calculated for a series of such molecules reacting with ammonia ($\chi = 2.6$, $\eta = 8.2$). The results are shown in Table VIII. The only reaction for which data is available for most of the entries[21] is the hydration reaction, e.g.

$$CH_2O(aq) + H_2O(l) = CH_2(OH)_2(aq) \qquad (7)$$

$$CH_3CN(aq) + H_2O(l) = CH_3CONH_2(aq) \qquad (8)$$

The equilibrium constant, K_h, for these reactions are also listed in Table VIII.

We cannot expect ΔN to correlate with these equilibrium constants. The values of K_h depend strongly on how easy

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[17] Some discretion is needed. The hydrogen atom, in particular, is usually much more protonic than indicated by its large χ value.

[18] Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401–410.

[19] Munger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1985**, *17*, 809–817.

[20] Krech, R. H.; McFadden, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 8402–8405.

[21] Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1–28.

Table V. Experimental Values for Radicals

radical	I^a	A^a	χ	η	radical	I^a	A^a	χ	η
F	17.42	3.40	10.41	7.01	C_6H_5S	8.63	2.47	5.50	3.08
OH	13.17	1.83	7.50	5.67	C_6H_5O	8.85	2.35	5.60	3.25
NH_2	11.40	0.74	6.07	5.33	C_2H_5	8.38	-0.39	4.00	4.39
CH_3	9.82	0.08	4.96	4.87	i-C_3H_7	7.57	-0.48	3.55	4.03
Cl	13.01	3.62	8.31	4.70	t-C_4H_9	6.93	-0.30	3.31	3.61
SH	10.41	2.30	6.40	4.10	C_6H_5	8.95	0.10	5.20	4.10
PH_2	9.83	1.25	5.54	4.29	C_2H_3	8.95	0.74	4.85	4.10
SiH_3	8.14	1.41	4.78	3.37	HCO	9.90	0.17	5.04	4.88
Br	11.84	3.36	7.60	4.24	CH_3CO	8.05	0.30	4.18	3.87
SeH	9.80	2.20	6.00	3.80	$C_6H_5CH_2$	7.63	0.88	4.26	3.38
I	10.45	3.06	6.76	3.70	CCl_3	8.78	1.90	5.35	3.45
H	13.59	0.74	7.17	6.42	CF_3	9.25	1.8^b	5.5	3.7
HO_2	11.53	1.19	6.36	5.17	$SiCl_3$	7.92	2.50	5.20	2.70
NO_2	>10.10	2.30	>6.20	>3.90	NO	9.25	0.02	4.63	4.61
CN	14.02	3.82	8.92	5.10					

[a] For sources see ref 27. [b] Reference 39.

Table VI. Values of ΔN for Reactions of $(CH_3)_3C$ with Olefins

reactant	χ,^{a} eV	η,^{a} eV	ΔN	k,^{b} M^{-1} s^{-1}
$(CH_3)_2C{=}C(CH_3)_2$	3.0	5.3	-0.017	32
cis-$CH_3CH{=}CHCH_3$	3.45	5.3	0.008	31
$CH_3CH{=}C(CH_3)_2$	3.3	5.5	0.000	80
$CH_2{=}C(CH_3)_2$	3.5	5.7	0.011	740
$CH_3CH{=}CH_2$	3.9	5.9	0.032	920
$CH_2{=}CH_2$	4.4	6.2	0.056	1250
cis-CHCl=CHCl	4.3	5.4	0.056	1350
trans-CHCl=CHCl	4.4	5.2	0.063	3650
$CH_2{=}CHOAc$	4.35	5.5	0.057	4200
$CH_2{=}CHCl$	4.4	5.6	0.060	16500
$CHCCl{=}CCl_2$	4.4	5.0	0.064	17000
$CH_2{=}CCl_2$	4.6	5.3	0.070	350000
$CH_2{=}CHCN$	5.4	5.6	0.114	1000000

[a] Values of *A* reported in ref 19. [b] At 300 K in 2-propanol, ref 19.

Table VII. Values of ΔN for Reaction of Free Radicals with Ethylene

radical	χ	η	ΔN	k,^{a} M^{-1} s^{-1}
Cl	8.3	4.7	0.179	4.5×10^{10}
OH	7.5	5.7	0.131	$5.0 \times 10^{9\,b}$
H	7.2	6.4	0.111	2.0×10^9
Br	7.6	4.2	0.154	1.0×10^8
CF_3	5.5	3.7	0.056	3.5×10^6
O_2H	6.4	5.2	0.086	$2.0 \times 10^{6\,c}$
CCl_3	5.4	3.0	0.049	4.5×10^4
CH_3	5.0	4.9	0.027	4.5×10^4
C_2H_5	4.0	4.4	-0.019	3.5×10^4
i-C_3H_7	3.6	4.0	-0.042	2.2×10^4
t-C_4H_9	3.3	3.6	-0.056	8.9×10^3

[a] At 437 K. Data from Tedder, J. M.; Walton, J. C. *Adv. Phys. Org. Chem.* **1978**, *16*, 51 except as indicated. [b] Klein, T.; et al. *J. Phys. Chem.* **1984**, *88*, 5020. [c] Kerr, J. A.; Parsonage, M. J. *Evaluated Kinetic Data on Gas Phase Addition Reactions*; Butterworth: London, 1972.

Table VIII. Values of ΔN for Reactions of Some Electrophiles with Ammonia

electrophile	χ	η	ΔN	K_{hyd},^{a} 25 °C
$CH_2{=}CHCHO$	5.25	4.85	0.102	
$CH_3COCOCH_3$	5.0	4.3	0.095	3.3
CH_2O	5.0	5.9	0.085	2×10^3
$ClCH_2COCH_3$	4.65^b	5.25^b	0.076	0.60
CH_3CHO	4.5	5.7	0.068	1.3
$(CH_3)_2CO$	4.1	5.6	0.056	2×10^{-3}
HCO_2CH_3	4.6	6.4	0.069	$4.7 \times 10^{-6\,c}$
$HCON(CH_3)_2$	3.4	5.8	0.029	$7.3 \times 10^{-15\,c}$
$CH_2{=}CHCN$	5.4	5.6	0.102	
HCN	5.7	8.0	0.096	$10^{12\,d}$
CH_3CN	4.7	7.5	0.067	$10^{6\,d}$

[a] For reaction 7 or 8 in H_2O. Data from ref 21, except as indicated. [b] Electron affinity from Modelli, A.; et al. *J. Chem. Soc., Perkin Trans.* **1984**, *2*, 1505. [c] From thermodynamic data on model compounds. Guthrie, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 3608. [d] From gas-phase free energies of formation and free energies of hydration.

it is to convert a multiple bond to a single bond, for each molecule. This is also what happens when a nucleophile adds to the molecule. It can be seen that the K_h values divide the entries in Table VIII into three groups: aldehydes and ketones, esters and amides, and nitriles. Only within each group can we expect ΔN to correlate with K_h.

There is fair agreement between ΔN and K_h for aldehydes and ketones, except for biacetyl. The results for the ester and the amide are consistent with the much greater reactivity of esters than of amides toward nucleophiles. The ordering for the nitriles is consistent with the experimental results that acrylonitrile and HCN are much more reactive toward nucleophiles than is acetonitrile.

Similarly acrolein has a large value of ΔN, consistent with its high reactivity. For acrolein and acrylonitrile, the values of K_h are not known, but they are irrelevant in any case. Addition in these two molecules is normally 1,4 and not 1,2.

Another important class of electrophiles is made up of alkyl halides and other RX molecules, where X is a displacable group. Applying eq 3 to the reaction of the methyl halides with $(CH_3)_3P$, we find the order

	CH_3I	CH_3Br	CH_3Cl	CH_3F
ΔN	0.099	0.097	0.037	0.013

These agree very well with relative reactivities toward nucleophiles.

From Table I we can conclude that molecules such as CH_3NH_2 will have negative values of ΔN and will react slowly. Thus NH_2^-, CH_3O^-, CH_3S^-, $As(CH_3)_2^-$, $P(CH_3)_2^-$, CH_3^-, and H^- will be poor leaving groups.[22] However it does not follow that methyl derivatives, which are above CH_3Cl in Table I, will have good leaving groups. Examples would be CH_3NO_2, CH_3O_2CH, and CH_3CN.

The reason is that in these molecules the LUMO is concentrated on the unsaturated part of the molecule. To correlate with nucleophilic displacement, the LUMO must be the antibonding orbital of the C–X bond. For the same reason, the (unknown) values of χ and η for methyl tosylate would not tell us that tosylate is a good leaving group. The LUMO is an empty π-ortibal of the benzene ring. Thus χ and η would be indicative of the reactivity of a substituted benzene, as in Table II.

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[22] For a listing of thermodynamic leaving group abilities, see: Pearson, R. G. *J. Org. Chem.* **1987**, *52*, 2131–2136.

Table IX. Values of ΔN for Reaction of Nucleophiles with Methyl Iodide

reactant	I, eV	A, eV	ΔN	n^b (pK_a)^c
$(CH_3)_3N$	7.8	−4.8	0.15	6.66
$(CH_3)_2O$	10.0	−6.0	0.11	
$(CH_3)_2S$	8.7	−3.3	0.10	5.54
$(CH_3)_3P$	8.6	−3.1	0.10	8.72
CH_3OH	10.9	−6.2^d	0.10	0.00
NH_3	10.7	−5.6	0.09	5.50
$(CH_3)_3As$	8.7	−2.7	0.09	6.90
$C_6H_5NH_2$	7.7	−1.1	0.09	5.70
$HCON(CH_3)_2$	9.1	−2.4	0.07	
C_6H_5SH	8.3	−0.8	0.06	
C_6H_5OH	0.5	−1.0	0.06	
CH_3COCH_3	9.7	−1.5	0.04	
$HCOOCH_3$	11.0	−1.8	0.015	
CH_3CN	12.2	−2.8	0.01	
$C_6H_5NO_2$	9.9	1.1	−0.03	
4-aminopyridine	8.76^a	−1.05^a	0.054	(9.17)
4-methylpyridine	9.50^a	−0.65^a	0.024	(6.02)
pyridine	9.60^a	−0.72^a	0.023	5.23 (5.17)
4-acetylpyridine	9.75^a	0.82^a	0.021	(4.2)^e
4-chloropyridine	10.1^a	−0.22^a	−0.002	(3.81)

[a] Modelli, A.; Burrow, P. D. *J. Electron Spectros. Relat. Phenom.* **1983**, *31*, 63. [b] log k/k_0 in methanol at 25 °C. [c] Numbers in parentheses are pK_a values in water at 25 °C. [d] Taken as mean of H_2O and $(CH_3)_2O$. [e] Estimated from gas-phase proton affinity. See: Aue, D. H.; et al. *J. Am. Chem. Soc.* **1976**, *98*, 854.

Even when the LUMO is the correct antibonding orbital, it does not follow that X^- will be displaced. Instead reaction can occur by the nucleophile attacking the X atom, rather than carbon. This is the case for CCl_4, for example, where it is sterically difficult to react at the carbon atom.

Nucleophilic Reactivity. If a wide range of nucleophiles is considered, it has proven to be difficult to predict their relative reactivities toward a given substrate.[22,23] Only when the donor atom is held constant, and steric factors avoided, have good correlations been found between log k and such properties as basicity and redox potentials.[24]

Equation 3 fares no better in this respect. Table IX shows the values of ΔN calculated for a number of potential nucleophiles reacting with CH_3I. Poor nucleophiles are characterized by larger χ values, and small values of ΔN. Molecules with χ greater than that of CH_3I are all very poor nucleophiles. The better nucleophiles have small values of χ and large values of ΔN.

Also included in Table IX are the nucleophilic reactivity parameters n, when known.[25] Agreement with ΔN is seen to be poor. Molecules that have small values of χ because of large negative values of A are poorer nucleophiles than predicted by ΔN. Small negative values of A enhance reactivity, as in $(CH_3)_3P$ compared to $(CH_3)_3N$, or $(CH_3)_2S$ compared to $(CH_3)_2O$.

While orbital effects between the donor atom and the accepting orbital of CH_3I may play a role, it appears that the ability of the donor molecule to *accept* electron density from CH_3I is also important. This corresponds to π-back-bonding, or stabilization of the transition state by mutual polarization.[21]

An alternative explanation is that molecules with large negative electron affinities should be considered as electron donors only, and I should be weighted more heavily in estimating χ.[7] This would increase χ and decrease ΔN, consistent with the lower reactivity.

We can expect better correlation between reactivity and ΔN, if we restrict comparisons to a set of closely related molecules. Table IX includes some data for 4-substituted pyridines. The ΔN results are to be compared with the pK_a data in parentheses. Since it has been shown that there is a Brønsted relationship between log k and pK_a when pyridines react with other substrates,[26] this is equivalent to using relative n values. The agreement is seen to be good, but even the 3-substituted pyridines would require a somewhat different correlation.

Anions and Cations. Local Properties. Anions and polyatomic cations cannot be treated in the same way as neutral species. For anions the approximate definitions of eq 2 are no longer valid. For polyatomic cations it is not feasible to measure the needed second ionization potentials. For these charged species, however, other methods have been developed to give rank orders of hardness.[27] These methods are based on bond dissociation energies and give values related to the local hardness, $\tilde{\eta}$.

The local hardness is not easily given an absolute value,[28] but a closely related parameter, the local softness, $\tilde{\sigma}$, is.[29]

$$\tilde{\sigma} = \sigma\rho_{\mathrm{HOMO}} \quad \text{electron acceptor} \tag{9}$$

$$\tilde{\sigma} = \sigma\rho_{\mathrm{LUMO}} \quad \text{electron donor} \tag{10}$$

Here π_{HOMO} and π_{LUMO} are the normalized densities of the frontier orbitals. These densities are simply the square of the orbital and are a function of position. Furthermore it can be shown that

$$\tilde{\sigma} = \left[\frac{\partial\rho}{\partial\mu}\right]_v \tag{11}$$

This means that the softest sites of a molecule are those where the electron density can be changed most easily, and attack by reagents will occur at these sites. This is completely consistent with frontier orbital theory, but the reasons are rather different in density functional theory.

For highly delocalized systems, whether ions or neutrals, the local hardness or softness is critical in determining the preferred reaction site. This is true, at least, if electron transfer between reactants is important. For ionic bonding, the net charges at each atom are more important. The predictions are necessarily the same as in frontier orbital theory.[30]

There are other effects in delocalized systems to consider. As Figure 1 suggests, and other arguments confirm,[7,28] hardness results from a combination of electron–electron repulsions and the energy spacing between frontier orbitals. As the positive charge on an atom increases, both of these terms become larger and the atom becomes harder. The same may be expected for the local hardness of an atom in a molecule.

In a delocalized system we can expect electron–electron repulsions to be less and energy spacing to be reduced. Thus the global softness of such systems is increased. But there is an opposing effect, as expressed in eq 9 and 10, so that the local softness at a selected site may actually decrease. This is closely related to the resonance energy of the delocalized ion or molecule, which may be lost if

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[23] *Nucleophilicity*; Advanced Chemistry Series 215; Harris, J. M., McManus, S. P., Eds.; American Chemical Society: Washington, 1985.

[24] See article by Bordwell, F. G.; Cripe, A. T.; Hughes, D. L. in Ref 23. Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1985–1988.

[25] Defined as log k/k_0, where k is for the nucleophile and k_0 is for the solvent methanol. Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319–326.

[26] Hudson, R. F.; Loveday, G. W. *J. Chem. Soc.* **1962**, 1068–1073.

[27] Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684–7690.

[28] Berkowitz, M.; Parr, R. G. *J. Chem. Phys.* **1988**, *88*, 2554–2558.

[29] Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6223–6227. Note that $\tilde{\eta}$ is not the reciprocal of $\tilde{\sigma}$.

[30] See: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976, for examples.

Table X. Empirical Hardness Parameters for Cationic Lewis Acids

acid	Δ,[a,b] kcal	acid	Δ,[a,b] kcal
SiF_3^+	~80	$C_2H_5^+$	54
CF_3^+	76	n-$C_3H_7^+$	54
SiH_3^+	76	cyclohexyl$^+$	54
CH_3CO^+	70	CH_3^+	53
HCO^+	70	cyclopropyl$^+$	52
$C_6H_5CO^+$	66	cyclobutyl$^+$	52
H^+	65	cyclopentyl$^+$	52
$C_6H_5^+$	60	Li^+	55
t-$C_4H_9^+$	58	CN^+	39
$C_2H_3^+$	56	I^+	31
$C_6H_5CH_2^+$	56	Ag^+	23
i-$C_3H_7^+$	54	Br^+	18
allyl$^+$	54	HO^+	-4

[a] These numbers give the rank order for local hardness at the bonding atom. [b] For sources, see ref 27. Also: Bochkov, A. F. *Zhur. Org. Khim.* **1986**, *22*, 2041.

covalent bond formation occurs.

To illustrate these points, Table X contains a number of cations of interest to organic chemists together with an empirical rank ordering parameter, Δ.[27] This parameter is defined by the equation

$$AF(g) + I(g) = AI(g) + F(g) \qquad \Delta H = \Delta \tag{12}$$

A large value of Δ means that the cation, A^+, has a large value of $\tilde{\eta}$ at the bond forming atom.

Since the LUMO of both CH_3^+ and SiH_3^+ is simply the p_z orbital of the central atom, the greater hardness of the latter must be due to a much higher positive charge on silicon. The greater hardness of CF_3^+ compared to CH_3^+ is also due to a greater positive charge on carbon, in part. But there is also an orbital component. The LUMO is now delocalized over the fluorine atoms in an antibonding mode. Planar CF_3^+ is stabilized by π-bonding between C and F. Adding electrons to the LUMO will destroy this π-bonding.

The hardness of HCO^+ and CH_3CO^+ is also due in part to the greater positive charge on carbon, and in part to an orbital effect. The LUMO is an antibonding π-orbital over both C and O. The linear HCO^+ ion has a triple bond (compare to HCN).[31] Adding electrons to the LUMO destroys one π-bond.

As the table suggests, and as other bond energies confirm[27] the hardness sequence t-$C_4H_9^+$ > i-$C_3H_7^+$ > $C_2H_5^+$ > CH_3^+ is always found. This result appears anomalous because we usually regard the methyl group as electron donating. However the ambivalent behavior of alkyl groups is now well known.[32]

The reasons why t-$C_4H_9^+$ is harder than CH_3^+ are the same as for CF_3^+. The positive charge on carbon is greater in t-$C_4H_9^+$ than in CH_3^+.[33] Also the LUMO of the latter is delocalized over the methyl substituents. Adding electrons to the LUMO neutralizes hyperconjugation. The difference in hardness, while small, has important chemical consequences.[1]

Because of the interest in alkyl groups, it is worth reviewing the properties of the radicals, CH_3 to t-C_4H_9, as well as the cations. As Table V shows, χ for the radicals decreases steadily. The values may be compared with the Pauling electronegativities, χ_P.[34]

	H	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9
χ_M	7.17	4.96	4.00	3.55	3.31
χ_P	2.08	2.32	2.35	2.38	2.41

The ordering is quite different. The order given by the Mulliken, or absolute scale, has recently been confirmed by very accurate calculations of the charge distributions in hydrocarbons.[35]

The hardness of the alkyl radicals decreases on going from CH_3 to t-C_4H_9, the opposite behavior to that of CH_3^+ to t-$C_4H_9^+$. There is no inconsistency here; the hardness in the radicals is equal to the mean interelectronic repulsion of two electrons in the SOMO.[8] The size factor determines that this decreases from CH_3 to t-C_4H_9.

Consider CH_3Cl and t-C_4H_9Cl. These may be formed in two ways, by combining the constituent radicals or the constituent ions. The χ and η values for the radicals predict that the alkyl–halogen bond will be more polar in t-C_4H_9Cl than in CH_3Cl. This agrees with the experimental results, obtained by nuclear quadrupole resonance.[36] Considering the ions as progenitors, the greater hardness of t-$C_4H_9^+$ hinders transfer of electron density from Cl^- and keeps the bond ionic.

Further Applications of Hardness. The electronegativities of anions and polyatomic cations are not clearly defined or known. However much bonding information can be obtained from their relative hardness values alone. The HSAB Principle may be used in the following way:

$$hs + sh = hh + ss \qquad \Delta H < 0 \tag{13}$$

where hs means a combination of a hard acid with a soft base, and so on.

For example, in the reaction

$$\begin{array}{lcccccc} & CH_3OH(g) & + & SiH_3CN(g) & = & CH_3CN(g) & + \ SiH_3OH(g) \\ D^\circ & 92\,\text{kcal} & & x & & 122 & 119 \end{array} \tag{14}$$

we can be quite sure that ΔH is a large negative number. This follows from the experimental result that CN^- is much softer than OH^-.[27] This puts limits on the unknown bond strength, D°, of silyl cyanide.

Since all chemical reactions require changes in electron distribution, and since η measures the resistance to change, we can expect a general correlation between the reactivity of molecles and their hardness values. We can see this in the η values in Table I for the various hydrocarbons, such as CH_4, C_2H_4, C_2H_2, and C_6H_6. Consider the series

	CH_4	CH_3OH	CH_2O	HCO_2CH_3	CO_2
η	10.3	8.6	5.9	6.4	8.8

a maximum in reactivity is indicated for the aldehyde stage of oxidation, which is a very reasonable result.

In a recent paper, Parr has shown that scales of aromaticity for cyclic, conjugated molecules are linear functions of $(I - A)$.[37] Since high aromaticity means high stability and low reactivity, this also means that large

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(31) For the MO's of HCO^+, see: Forsen, S.; Roos, B. *Chem. Phys. Lett.* **1970**, *6*, 128–130.

(32) Aitken, E. J.; Bahl, M. K.; Bomben, K. D.; Gimzewski, J. K.; Nolan, G. S.; Thomas, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 4873–4879.

(33) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935–5944.

(34) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271–7275.

(35) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001–1012. This paper uses the basin method ($\Delta\rho = 0$) to partition charge densities among atoms. This method is much superior to the Mulliken method.

(36) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 164.

(37) Zhou, S.; Parr, R. G.; Garst, J. F. *Tetrahedron Lett.* **1988**, *29*, 4843–4845.

(38) Luke, B. T.; Loew, G. H.; McLean, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 3396–3400.

(39) *Electron-Molecule Interactions and Their Applications*; Christophorous, L. G., Ed.; Academic Press: New York, 1984; Vol. II.

values of η produce low reactivity.

Since the lowest energy absorption band in the electronic spectrum is also related to $(I - A)$, we can also use the spectra of molecules as a guide to reactivity.[11] However care must be taken to show that the first band is indeed related to the appropriate frontier orbitals.

Judging by its spectrum, the hardest molecule appears to be CF_4. Its first adsorption band has a maximum at 110.5 kK, compared to 78.2 for CH_4.[11] Neither I nor A is accurately known, but I is about 15 eV and A about −8 eV. This makes $\eta \simeq 11.5$ eV, compared to 10.3 for CH_4.

Conclusion. In the preceding sections it has been shown that the concepts of absolute electronegativity and hardness have considerable predictive power for the reactions of typical organic molecules and radicals. The use of eq 3 seems particularly promising, even though only initial interactions are considered. However it must not be regarded as infallible, since it is no better than the results in the tables indicate.

Physical–organic chemistry over the years has explained most of the phenomena discussed in many different ways. It is not the intent of the present work to discredit any of these explanations. The intent is to show that χ and η can also be used in a novel and rational way.

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Notes

A Convenient Method for the Reduction of Ozonides to Alcohols with Borane–Dimethyl Sulfide Complex

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A versatile procedure for the direct conversion of ozonides to alcohols[1] would be a potentially valuable addition to the synthetic repertory. Several well-known reducing agents have been exploited for this purpose; however, all of these suffer from intrinsic limitations. Thus, lithium aluminum hydride efficiently reduces ozonides,[2,3] but it cannot be used in the presence of a variety of other functional groups. Sodium borohydride,[3d,4] while tolerant of a wider range of functionality than $LiAlH_4$, is generally limited to use in highly polar solvents—the usual requirement of an aqueous extraction step to remove these solvents in the workup stage of $NaBH_4$ reductions may render the procedures inconvenient for the preparation of water-soluble alcohols.[5,6] Complexes of borane with pyridine, triethylamine, and tetrahydrofuran have been carefully evaluated for direct reductions of 10-undecenoic

Table I

$$\text{1-decene} \xrightarrow[\text{2. BH}_3\text{–DMS}]{\text{1. O}_3} \underset{\mathbf{1}}{\text{1-nonanol}} + \underset{\mathbf{2}}{\text{1-decene ozonide}} + \underset{\mathbf{3}}{\text{nonanal}}$$

entry	reaction conditions	product distribution[a]
1	2.0 equiv of BH_3–DMS, 22 °C, 24 h	**1** (47%) + **2** (52%) + **3** (≤1%)
2	4.0 equiv of BH_3–DMS, 22 °C, 24 h	**1** (100%)
3	2.0 equiv of BH_3–DMS, 40 °C, 3 h	**1** (64%) + **2** (36%)
4	3.0 equiv of BH_3–DMS, 40 °C, 3 h	**1** (95%) + **2** (4%) + **3** (1%)
5	4.0 equiv of BH_3–DMS, 40 °C, 1 h	**1** (100%)

[a] Product distributions were determined on the crude reaction mixtures by ^1H NMR spectroscopy (300 MHz; $CDCl_3$) with internal TMS as a reference.

Table II

$$\text{methyl 10-undecenoate} \xrightarrow[\text{2. BH}_3\text{–DMS}]{\text{1. O}_3}$$
$$\underset{\mathbf{4}}{\text{methyl 10-hydroxydecanoate}} + \underset{\mathbf{5}}{\text{methyl 10-undecenoate ozonide}} + \underset{\mathbf{6}}{\text{1,10-decanediol}} + \underset{\mathbf{7}}{\text{methyl 10-oxodecanoate}}$$

entry	reaction conditions	product distribution[a]
1	3.5 equiv of BH_3–DMS, 22 °C, 18 h	**4** (95%) + **5** (3%) + **7** (2%)
2	4.0 equiv of BH_3–DMS, 22 °C, 16 h	**4** (91%) + **5** (8%) + **7** (1%)
3	4.0 equiv of BH_3–DMS, 22 °C, 24 h	**4** (98%) + **5** (1%) + **7** (1%)
4	4.0 equiv of BH_3–DMS, 40 °C, 2 h	**4** (72%) + **6** (27%)
5	5.0 equiv of BH_3–DMS, 22 °C, 16 h	**4** (35%) + **6** (65%)

[a] Product distributions were determined from the crude reaction mixtures by ^1H NMR spectroscopy (300 MHz; $CDCl_3$) with internal TMS as the reference.

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(1) For an overview of currently available methods for this transformation, see: (a) Fischer, G. W.; Zimmerman, T. In *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Pergamon Press: New York, 1984; Vol. 6 p 879. (b) Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1, Chapter 8. (c) Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1982; Vol. 2.

(2) Maier, G.; Schneider, M.; Sayrac, T. *Chem. Ber.* **1978**, *111*, 3412.

(3) See also, (a) Carles, J.; Fliszár, S. *Can. J. Chem.* **1969**, *47*, 1113. (b) Bishop, C. E.; Story, P. R. *J. Am. Chem. Soc.* **1968**, *90*, 1905. (c) Story, P. R.; Bishop, C. E.; Burgess, J. R.; Murray, R. W.; Youssefyeh, R. D. *Ibid.* *1968*, *90*, 1907. (d) Sousa, J. O.; Bluhm, A. L. *J. Org. Chem.* **1960**, *25*, 108. (e) Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

(4) For representative procedures, see: (a) Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 1396. (b) Grieco, P. A.; Mishizama, M.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* **1976**, *98*, 1612. (c) Diaper, D. G. M.; Mitchell, D. L. *Can. J. Chem.* **1960**, *38*, 1976.

(5) For a summary of procedures and leading references concerning the general use and workup of sodium borohydride reduction mixtures, see: (a) *Reagents for Organic Synthesis*; Fieser, L., Fieser, M., Eds.; Wiley: New York, 1967; Vol. 1, p 1049. (b) Gaylord, N. *Reduction with Complex Metal Hydrides*; Interscience: New York, 1957; p 1013. (c) Hudlicky, M. *Reductions in Organic Chemistry*; Horwood: Chichester, 1984; p 21.

(6) For example, Sousa and Blum reported a preparation of water-soluble 1,6-hexanediol in 63% yield via $NaBH_4$ reduction of cyclohexene ozonide (ref 3d). In our hands the procedure afforded crude 1,6-hexanediol, mp 41–42.5 °C, in 56% yield.

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