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Hard and Soft Acids and Bases: Small Molecules

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The operational chemical hardness has been determined for the hydride, chloride, and fluoride derivatives of the anionic atomic bases of the second period. Of interest is the identification of the structure and associated processes that give rise to hard—soft behavior in small molecules. The Pearson Principle of Hard and Soft Acids and Bases has been taken to be the defining statement about hard—soft behavior and as a definition of chemical hardness. Similar to the case for atoms, the molecule's responding electrons have been identified as the structure giving rise to hard—soft behavior, and a relaxation described by a modified Slater model has been identified as the associated process. The responding electrons are the molecule's valence electrons that are not undergoing electron transfer in an acid—base interaction. However, it has been demonstrated that chemical hardness is a local property, and only those responding electrons that are associated with the base's binding atom directly impact chemical hardness.

Introduction

The acid—base concept is one of the oldest and most enduring concepts in all of the chemical sciences. Yet understanding the strength of the acid—base interaction remains an ongoing challenge. Although there are a variety of ways to partition the contributions to the strengths of acids and bases,[1−10] it has proven particularly fruitful to partition the contributions into those derived solely from the properties of the acid or base itself (intrinsic strength) and those that are dependent on the acid or base, with which it reacts, as well as other things external to it (extrinsic strength). For example among the intrinsic contributions to acid and base strength is the energy associated with a change in spin multiplicity that might occur during an acid—base interaction. On the other hand the chemical hardness of an acid or base is one of the extrinsic properties of an acid or a base, and it determines how the acid or base, with which it interacts, influences the strength of the interaction Thus, an intrinsic contribution such as a change in multiplicity would not be part of an extrinsic contribution such as chemical hardness.

If hardness is a chemical property of an atom or molecule, then there should exist some structure and associated process within the molecule that gives rise to hard—soft behavior. Although there have been numerous investigations of the hard—soft model, the property itself has lacked a clear definition, and there has been no experimental measure of the property of hardness. In a recent communication, the structure and the process that gives rise to hard—soft behavior in atomic acids and bases have been identified.[10] Of interest in this communication is the eluciation of the structures and processes that give rise to hard—soft behavior in small molecules.

Background

Hardnesses: Definitions and Determinations. The property of acids and bases that has come to be called hardness is an extrinsic influence on the strengths of acids and bases, which is described by the Pearson Principle of Hard and Soft Acids and Bases.[5] In spite of the considerable body of literature dealing with hardness, hardness has lacked a formal definition, as well as a quantitative measure of its magnitude until quite recently.[10,11] This notwithstanding, in an effort to provide a quantitative measure of hardness, which at that time had been closely identified with polarizability, Pearson proposed the property, absolute hardness (η_{abs}), as a measure of hardness.[7]

$$\eta_{\mathrm{abs}} = \left[\frac{\partial^2 E}{\partial N^2}\right]_v \tag{1}$$

Here E is the energy of the system, v the external potential, and N is the number of electrons. Although Pearson was

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careful to name this new property the absolute hardness and thus distinguishing it from hardness itself; hardness and absolute hardness have been frequently taken to be synonymous.[7,12] This has occurred in part because the absolute hardness is a well-defined physical property of atoms and molecules that can in some cases be measured experimentally. Hardness on the other hand, which is a chemical property, has until recently lacked a formal definition and a quantitative means of measuring it.

Pearson also proposed that the formula

$$\eta_{\mathrm{abs}} = I - A \qquad (2)$$

in which I and A are the ionization energy and electron affinity, respectively, be used as an experimental measure of the absolute hardness. Prior to its association with the absolute hardness, η_{abs} had been shown to also be the charge coefficient in the electronegatvity function, $\chi(q)$,[13,14]

$$\chi(q) = a + bq = \chi_0 + \frac{1}{2}\eta_{\mathrm{abs}}q \qquad (3)$$

where a and χ_0 are symbols for the absolute electronegativity and b is the charge coefficient. Klopman showed that this charge coefficient and hence the absolute hardness is a combination of the coulomb and exchange integrals of the atom's electrons and thus derived from the Coulombic repulsions among the electrons.[13]

Using the Pearson principle, hardness can be defined as that property of acids and bases that causes hard acids to prefer to bind hard bases and soft acids to bind soft bases.[5] Hardness defined in this way has been called the chemical hardness to distinguish it from several other understandings of hardness.[5] In addition to providing a formal definition, the Principle also suggests a means of measuring chemical hardness quantitatively.

If A and B denote the Lewis acid and base fragments in the metathesis reaction and the h and s superscripts denote the harder and softer fragments, respectively, the reaction free energy must be negative. If this is not true the Principle has been violated.

$$\mathrm{A^hB^s} + \mathrm{A^sB^h} \rightarrow \mathrm{A^sB^s} + \mathrm{A^hB^h} \qquad (4)$$

Thus the molar free energies for a series of such metathesis reactions can be used to assign relative chemical hardnesses. For experimental reasons it has proven more convenient to use molar enthalpies rather than free energies.[10,11]

As part of understanding the structure responsible for hard−soft behavior, the conjugate Lewis acid of a base has been defined as the Lewis acid that is generated when the donor electron pair is removed from the base. Similarly, the conjugate Lewis base is the Lewis base that is generated when an electron pair is added to the acceptor orbital of a Lewis acid. The conjugate Lewis radical is formed by adding an electron to the acid or removing one from the base.[10] The Lewis definition of acids and bases together with the properties of the metathesis reaction itself place several important requirements on the structures and accompanying processes that give rise to chemical hardness. The metathesis reaction itself requires that the hardness of a base be exactly equal to the softness of its conjugate Lewis acid, and similarly for an acid, its hardness must be exactly equal to the softness of its conjugate Lewis base. This requires that the same structure and process be responsible for the hardness of a base and its conjugate Lewis acid. Therefore the structure responsible for chemical hardness must be present in both the base and its conjugate Lewis acid.

Hardness: The Slater Model. In an effort to uncover the origins of chemical hardness, a number of theoretical models have been explored in many laboratories, each yielding important insights into the nature of chemical hardness. The simplest and perhaps the most intuitive model of atoms was developed by Slater nearly 80 years ago[15] and was recently revisited and revised in these laboratories.[16,17] In the Slater model the electron−electron interactions are approximated as shielding, s_{ij}, by the remaining electrons. As a consequence the one-electron energy of each electron, ε_i, is given by the expression for the hydrogen atom electron energy, in which the nuclear charge, Z, is replaced by an effective nuclear charge, Z_i*.

$$\varepsilon_i = -\left(1312\frac{\mathrm{kJ}}{\mathrm{mole}}\right)\left[\frac{Z_i^*}{Q_i}\right]^2 \qquad (5a)$$

Here Q_i is the principle quantum number and

$$Z_i^* = Z - \sum s_{ij} \qquad (5b)$$

where the summation is over the all of the remaining electrons and the s_{ij} are their shielding constants.[16] The atom's electronic energy, E, is now the sum of the one-electron energies of electrons of interest.

$$E = \sum_j^M \varepsilon_j \qquad (5c)$$

Hardness: The Responding Electrons. One of the advantages of the Slater model is that it provides for the facile partitioning of the atom's electrons. In Slater's model the atom's electron density naturally partitions into core and valence electrons. Subsequent work by Fukui and others has profitably further partitioned the valence electron density by identifying the relevant frontier orbitals as having a special role in determining chemical behavior.[6,18] The remaining valence electrons have since been designated the responding electrons. Whereas the responding electrons in atomic acids and

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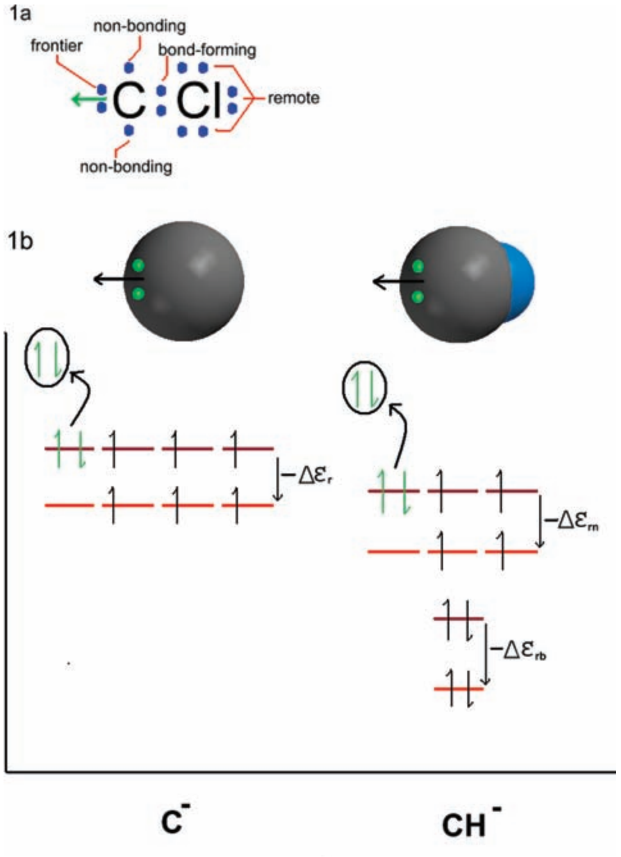

Figure 1. Schematics representing the (a) different types of responding electrons in CCl^- and (b) behavior of the responding electrons of C^- and HC^- as they relax during an electron transfer.

bases appear to require no additional partitioning,[10] it seems that the complexity of molecular systems might require partitioning of the responding electrons. Thus in molecules the responding electrons (subscript r) may be partitioned into non-bonding electrons on the binding atom (subscript rn), bond-forming electrons forming a bond to the binding atom (subscript rb), and electrons remote to the binding atom (subscript rr). The remote responding electrons are all responding electrons that are neither rn or rb. These types of responding electrons can be most clearly illustrated using the Lewis dot notation (Figure 1a).

The partitioning of the valence shell and the requirements imposed by the nature of the metathesis reaction itself suggest that hard−soft behavior in atomic acids and bases finds its origins in the atom's responding electrons. Although Slater's model is rather simplistic, it has proven to be very helpful in unraveling hard−soft behavior in atoms[10] and holds promise in understanding hard−soft behavior in molecules. A number of investigators, using a variety of approaches, have concluded that there is a close association of hardness with changes the electron−electron interactions in the valence shell.[13] According to the Slater model during an acid−base interaction the change in the occupancy of the relevant frontier orbitals alters the shielding experienced by each responding electron. The change in energy experienced by a responding electron resulting from an addition of one unit of charge to a frontier orbital shall be called the single-electron relaxation energy ($\Delta\varepsilon_{\rm r}$). The net change in energy for all of the responding electrons is referred to as the relaxation energy ($\Delta E_{\rm r}$) and it is the sum of the single-electron relaxation energies.

For atoms the single-electron relaxation energies can be computed using the revised Slater's rules[17] and eqs 5a to obtain

$$\Delta\varepsilon_{\rm r}^{\rm slr} = \left(1312\,\frac{\rm kJ}{\rm mole}\right)\left[\frac{2Z_{\rm r}^{*} + s_{\rm rf}}{Q_{\rm r}^{2}}\right]S_{\rm rf} \qquad (6)$$

where $s_{\rm rf}$ are the shielding constants of the responding electrons being shielded by the frontier electrons and $Q_{\rm r}$ is its principle quantum number. The superscript, slr, is used to denote quantities computed using eqs 5a. The primary influences on an atom's single-electron relaxation energy would appear to be the effective nuclear charge and the shielding constant for the relaxing electron being shielded by the frontier electrons. These relaxation processes in an atomic anion and its anionic hydride are illustrated in Figure 1b. This being the case and considering the partitioning of the valence shell the relaxation energy in molecules can be written as

$$\Delta E_{\rm r} = n_{\rm rn}\Delta\varepsilon_{\rm rn} + n_{\rm rb}\Delta\varepsilon_{\rm rb} + n_{\rm rr}\Delta\varepsilon_{\rm rr} \qquad (7)$$

where the n's are the numbers of each type of responding electron in the acid's or base's conjugate Lewis radical.

It is the goal of this communication to identify the structures and accompanying processes that give rise to hard−soft behavior and in so doing provide for more informed assignments of chemical hardness to molecules. The specific tasks therefore are to determine which of these types of responding electrons impact the hardness of molecules, as well as the magnitude of their impact.

Computations

To measure the operational chemical hardness, $\Delta H_\eta(\mathrm{Cl}^+ - \mathrm{H}^+)$ of a base X^-, the molar enthalpy of a reaction of the form

$$\mathrm{H^hX + Cl^sH^{ref} \rightarrow H^hH^{ref} + Cl^sX}\,\Delta H_\eta(\mathrm{Cl}^+ - \mathrm{H}^+) \qquad (8)$$

was determined. Here H^- is the reference base fragment and the fragments, H^+ and Cl^+, are the discriminating acids of which H^+ is taken to be the harder acid.[10] The operational chemical hardnesses were computed as the gas phase enthalpies using the published heats of formation at 25 °C.[19−24] The absolute electronegativities and absolute hardnesses

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Table 1. Operational Chemical Hardnesses, Computed Relaxation Energies and Single-Electron Relaxation Energies, and the Electronegativities (χ) of the Second Row Anionic Atomic Bases

base	$\Delta H_\eta{}^a$ (kcal/mol)	n_{rn}	$\Delta E_{rn}{}^{slr}$ (kJ/mol)	$\Delta \varepsilon_{rn}{}^{slr}$ (kJ/mol)	χ (eV)
Li^-	−58.3	0	0	0	−1.47
Be^-	−40.2	1	442	442	−2.81
B^-	−49.9	2	1160	580	−3.58
C^-	0.063	3	2385	720	−5.29
N^-	16.0	4	3456	864	−3.24
O^-	36.8	5	5035	1007	−3.03
F^-	75.1	6	6900	1150	−5.18

[a] Data take form reference 9.

were taken from Bratsch's compilations.[25] Atomic charges were computed using the electronegativity equalization method.[26,27] The electronegativities of the atomic ions were determined using eq 3. The one-electron energies, ε, one-electron relaxation energies, $\Delta\varepsilon_r{}^{slr}$, and the relaxation energies, $\Delta E_r{}^{slr}$, were computed using the expanded Slater's rules.[16,17]

Results and Discussion

The responding electrons have been identified as the structure in an atom that gives rise to hard−soft behavior through the relaxation of its electrons.[10] Whereas the identification and evaluation of n_r and $\Delta\varepsilon_r$ for atomic bases is rather straightforward using the Slater model, this in not necessarily the case for molecules. There are several issues that arise in expanding this interpretation for atoms to more complex systems. Principal among them is whether or not all of the molecule's responding electrons impact chemical hardness and whether or not they all impact hardness in the same manner.

The relationship between the chemical hardness, ΔH_η(Cl^+-H^+), and the absolute hardness, η_{abs}, has been examined and ΔH_η(Cl^+-H^+) has in fact been found to correlate with η_{abs}.[10] However, the relationship between the chemical hardness and relaxation energy has not yet been explored. The absolute hardness, the single-electron relaxation energy, and the relaxation energy may be found in Table 1.

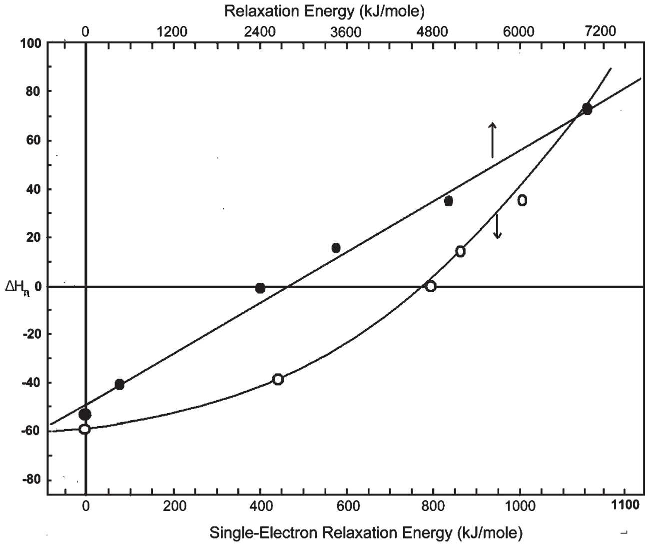

Figure 2. Plot of relaxations energy, ΔE_r, (upper scale) and the single-electron relaxation energy, $\Delta\varepsilon_r{}^{slr}$, (lower scale) versus the operational chemical hardness of the anionic bases, lithium through fluorine.

When the ΔH_η(Cl^+-H^+) for the anionic bases, lithium through fluorine, is plotted against the single electron relaxation energy, which has been computed using Slater's Model (eq 6), the plot has significant positive curvature (Figure 2).[28] The linear correlation coefficient for this curve is only 0.951. This observed positive curvature suggests that the increase in the single-electron relaxation energy, $\Delta\varepsilon_r{}^{slr}$, across the period is insufficient to account for the observed increase in the chemical hardness, ΔH_η(Cl^+-H^+). If, however, ΔH_η(Cl^+-H^+) is plotted against the relaxation energy, ΔE_r, the plot is essentially linear with a correlation coefficient of 0.991 (Figure 2). These observations suggest that both the number of responding electrons, n_r, and the single-electron relaxation energy, $\Delta\varepsilon_r$, are both major determinants of the chemical hardness in atomic bases and by extension atomic acids. This degree of linearity also provides a useful and reasonably reliable functional relationship between an experimental measure of hardness, ΔH_η(Cl^+-H^+), and the relaxation energy in atoms, ΔE_r.

$$\Delta H_\eta(Cl^+ - H^+) = \left(0.0182\frac{\text{kcal}}{\text{kJ}}\right)\Delta E_r^{\text{eff}} - 49.76\ \text{kcal/mole} \qquad (9)$$

Such a relationship will permit the determination of experimental or effective relaxation energies, $\Delta E_r{}^{eff}$, as well as in some cases experimentally determined single-electron relaxation energies, $\Delta\varepsilon_r{}^{eff}$ using eq 7 and 9.

Global Versus Local Hardness. The responding electrons have been defined as all of the valence electrons that are not frontier electrons. However, whether chemical hardness is a local or global property is determined by whether all or only part of the responding electrons are relevant to the determination of chemical hardness. The definition of the absolute hardness, which has historically been identified closely with chemical hardness, suggests that absolute hardness must be a global property.[29−31] On the other hand there is considerable chemical evidence that chemical hardness is a property local to the binding atom.[6,28−34] The relaxation energy, as formulated in eq 7, can accommodate chemical hardness as a local or as a global quantity. If it is global, n_r's must be equal to the actual numbers of responding electrons and all of the $\Delta\varepsilon_r$'s must be actual single-electron relaxation energies. If on the other hand it is local, there will be responding electrons that are not relevant to hard−soft behavior and their n_r's in eq 7 will be less than the actual numbers of

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Table 2. Operational Chemical Hardnesses, Numbers of Responding Electrons, Effective Relaxation Energy, and Local and Global Mean Single-Electron Relaxation Energies of the Hydrides and Halides Derived from the Second Period Anionic Bases

base	$\Delta H_\eta{}^a$ (kcal/mol)	n_{rn}	n_{rb}	n_{rr}	$\Delta E_r{}^{eff}$ (kJ/mol)	$\Delta\varepsilon_r{}^{loc}$ (kJ/mol)	$\Delta\varepsilon_r{}^{glb}$ (kJ/mol)
BeH^-	−30.9	0	2	0	1030	518	518
$BeCl^-$	−41.0	0	2	6	482	241	60
BH^-	−20	1	2	0	1635	545	545
BCl^-	−22.4	1	2	6	1503	501	167
$BH_2{}^-$	−18.4	0	4	0	1723	431	431
$BHCl^-$	−22.3	0	4	6	1509	377	151
$BCl_2{}^-$	−14.9	0	4	12	1915	479	120
CH^-	9.7	2	2	0	3268	817	817
CCl^-	−0.937	2	2	6	2682	671	268
$CH_2{}^-$	16.3	1	4	0	3630	726	726
$CH_3{}^-$	19.0	0	6	0	3778	630	630
CH_2Cl^-	18.8	0	6	6	3762	629	314
$CHCl_2{}^-$	19.9	0	6	12	3827	638	213
$CCl_3{}^-$	23.8	0	6	18	4042	674	168
CH_2F^-	15.5	0	6	6	3586	598	299
$CHF_2{}^-$	14.7	0	6	12	3542	590	197
$CF_3{}^-$	19.5	0	6	18	3805	634	159
NH^-	31	3	2	0	4437	887	887
NCl^-	23.5	3	2	6	4025	805	366
$NH_2{}^-$	39.0	2	4	0	4877	813	813
NHF^-	52.1	2	4	6	5596	933	466
$NF_2{}^-$	48.0	2	4	12	5371	895	298
OH^-	57.9	4	2	0	5916	986	986
OCl^-	60.9	4	2	6	6079	1013	506
$O_2{}^-$	40.4	0	5.5	5.5	4954	901	450
CO^-	9.11	0	5.5	3.5	3235	588	359
CN^-	22.7	0	6	2	3981	664	498

[a] Data taken from references 18−23

responding electrons. Furthermore, $\Delta\varepsilon_r$'s need not be actual single-electron relaxation energies as described by eq 6, but may represent some other response.

The single-electron relaxation energy in atomic bases arises from a simple deshielding of the responding electrons, but it need not be so simply formulated for all of the responding electrons in a molecule. However, the requirement, imposed by the nature of the metathesis reaction (eq 4), that the same structure must give rise to hard−soft behavior in both a base and its conjugate Lewis acid,[10] would seem to limit the types of the changes that the responding electrons may undergo. In addition, in a non-orbital model such as Density Functional Theory, where the frontier electron density is taken to be the difference in the electron density of the molecule or ion and that of the species generated by the addition of an electron (for the lowest unoccupied molecular orbital (LUMO)) or the removal of an electron (for the highest occupied molecular orbital (HOMO)), restrictions are imposed on the changes that the responding electrons undergo. Inherent in this procedure is the assumption that the responding electrons are not transferred among the atoms in a charge transfer process. The restrictions imposed on the behaviors of the responding electrons suggest that the simple partitioning and parametrization of the relaxation energy in molecules (eq 7) should be adequate.

Non-Bonding and Bond-Forming Responding Electrons. The anionic hydrides can be thought of as being formed by combining the parent anionic atomic base with one or more hydrogen atoms. The Mulliken−Jaffe electronegativities of the parent bases can be determined using eq 3 and these are also found in Table 1. In all cases the electronegativity of the parent base is significantly less than 7.17, the electronegativity of the hydrogen atom. This means that electron density is lost from the parent base when it binds hydrogen. Additionally, symmetry restricts the number and type of interactions among the orbitals of the responding electrons, which results in the responding electrons for the hydrides at least being either non-bonding localized on the binding atom or being bond-forming. This being the case, for the hydride bases eq 7 reduces to:

$$\Delta E_r = n_{rn}\Delta\varepsilon_{rn} + n_{rb}\Delta\varepsilon_{rb} \tag{10}$$

The number of non-bonding responding electrons, n_{rn}, should then equal the number of responding electrons in the parent base less the number of hydrogen atoms, and the bond-forming responding electrons, n_{rb}, equals twice the number of hydrogen atoms (Table 2). The orbitals of the non-bonding responding electrons of the hydrides are expected to be very similar as those of the parent atomic bases. They differ in one important respect, however. Because all of the parent atomic bases are less electronegative than hydrogen, all of the hydrogens in the anionic hydrides are expected to be hydridic, having acquired electron density from the parent atomic base. This being the case the non-bonding responding electrons are expected to be less shielded than they are in the parent atomic bases and, should according to eq 6 give rise to $\Delta\varepsilon_{rn}$'s that are greater than the $\Delta\varepsilon_{rn}$'s of the parent bases.

The impact of bond-forming electrons on the relaxation energy is more difficult to both predict and interpret. Whereas for localized non-bonding electrons the meaning of $\Delta\varepsilon_{rn}$ is reasonably well understood, this is not as true for the $\Delta\varepsilon_{rb}$. Although there are restrictions on the behaviors of the responding electrons, this does not require that these electrons respond in a manner identical

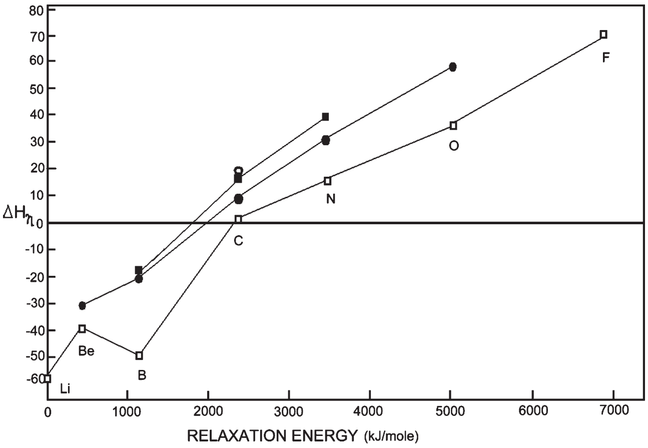

Figure 3. Plot of the computed relaxation energy (ΔE_r^{slr}) versus the operational chemical hardness (ΔH_η) for the series XH_n^-, where □, $n = 0$; ●, $n = 1$; ■, $n = 2$; ○, $n = 3$. X represents the elements lithium through fluorine.

to that of the non-bonding responding electrons. Furthermore, rather than a single effective nuclear charge (eq 6), these electrons are under the influence of at least two effective nuclear charges and the shielding by the frontier electrons of such electrons may be quite different from that occurring in the parent atomic base.

The experimental operational chemical hardnesses have been determined for a number of the anionic hydrides of the second period elements (Table 2) and in all cases these hydrides are significantly harder than their parent anionic atomic bases. The increased chemical hardness of the hydrides over their parent atomic bases is somewhat unexpected, given the close historic association of chemical hardness with both polarizability and absolute hardness. The polarizabilities of the hydrides are expected to be greater than those of the parent anionic atomic bases, and the absolute hardnesses of the hydrides are expected to be less than those of the parent atomic bases.[11] Both of these expectations suggest that the chemical hardness of the hydrides should be less than those of the parent atomic bases, which of course is not the case and thus must be explained by the current model.

The plots $\Delta H_\eta(Cl^+{-}H^+)$ versus the ΔE_r^{slr} for the parent atomic base for each of the XH_n^- series (X = Li through F and $n = 0-3$) are in general quite linear, and the series are nearly parallel (Figure 3). There is also a slight increase in slope as the number of hydrogen atoms increases. The linearity of these plots and that they are parallel and close to one another strongly support the proposition that the same process is effective in causing the hard−soft behavior in both the atomic bases and their hydrides. Furthermore, the parent atomic bases and not the hydrogens appear to be dominant in determining the resulting chemical hardnesses of the hydrides.

The consistent increase in hardness upon the addition of hydrogen atoms can be attributed to an increase in the number of responding electrons ($n_{rn} + n_{rb}$), an increase in single-electron relaxation energy, $\Delta\varepsilon_r$, for at least some of the responding electrons or possibly a combination of both of these. Among the hydrides, BeH^-, BH_2^-, and CH_3^- have no non-bonding responding electrons. Thus for these $n_{rn} = 0$. This being the case, eq 9 may be used to compute ΔE_r^{eff} for these bases, from which the single-electron relaxation energies for the bond-forming electrons, $\Delta\varepsilon_{rb}^{eff}$, may be estimated using eq 10. The estimated single-electron relaxation energies for these bond-forming electrons ($\Delta\varepsilon_{rb}^{eff}$'s) are 518, 431, and 630 kJ/mol for BeH^-, BH_2^-, and CH_3^-, respectively (Table 2). Though differing significantly from the single electron relaxation energies of their parent atomic bases, the average difference is only about 108 kJ/mol. It would thus seem that the relaxation of the bond-forming electrons is dominated by the parent atomic base rather than hydrogen and that the perturbation caused by hydrogen, though significant, is a comparatively small perturbation. The smallness of the sample and the uncertainty in the experimental data prohibits any attempt at a more detailed interpretation of the $\Delta\varepsilon_{rb}^{eff}$.

Because the non-bonding responding electrons are expected to be very similar to the responding electrons of the parent atomic base, they should be more readily described by Slater's model than are the bond-forming electrons, and eq 6 should provide reasonable estimates of their relaxation energies. Again the formation of the hydrides should deshield the non-bonding electrons and according to eq 6 increase their one-electron relaxation energies. Having determined $\Delta\varepsilon_{rb}^{eff}$ for B−H and C−H bond-forming electrons and assuming that they are to some degree transferrable, it is possible to estimate $\Delta\varepsilon_{rn}^{eff}$ for BH^-, CH^-, and CH_2^-, which have non-bonding and bond-forming responding electrons. The estimated $\Delta\varepsilon_{rn}^{eff}$'s are 773, 1004, and 1110 kJ/mol for BH^-, CH^-, and CH_2^-, respectively, which are increases of 193, 284, and 390 kJ/mol over the values for the parent bases. In spite of the large uncertainty in these values, the ordering is what one might have expected. Although boron is the least electronegative and should thus experience the greatest deshielding, it also has the smallest effective nuclear charge. For this reason it has the smallest increase in $\Delta\varepsilon_{rn}^{eff}$ (eq 6). The addition of a hydrogen atom to CH^- should further deshield the non-bonding responding electrons on the carbon and thus increase $\Delta\varepsilon_{rn}^{eff}$, which is what is observed. It would thus appear that electrons in bonds to the binding atom do impact chemical hardness and that the formation of bonds to an atom increases both the chemical hardness and the non-bonding single-electron relaxation energy.

Remote Responding Electrons. If chemical hardness is indeed a global property, as is the case for absolute hardness, the chemical hardness of a molecule should be impacted in the same manner by all of the atoms in the molecule. Thus all of the molecule's non-bonding responding electrons must be relevant to hard−soft behavior and they must undergo a single-electron relaxation in a manner described by eq 6. If on the other hand chemical hardness is a local property, electrons that are remote to the binding atom impact chemical hardness to a significantly lesser extent and perhaps in a manner quite different from the relaxation process described by eq 6.

The responding electrons of the atomic bases and the hydrides, which have been discussed thus far, have lacked remote responding electrons. The halogen containing derivatives of the anionic atomic bases do however contain remote responding electrons in the form of

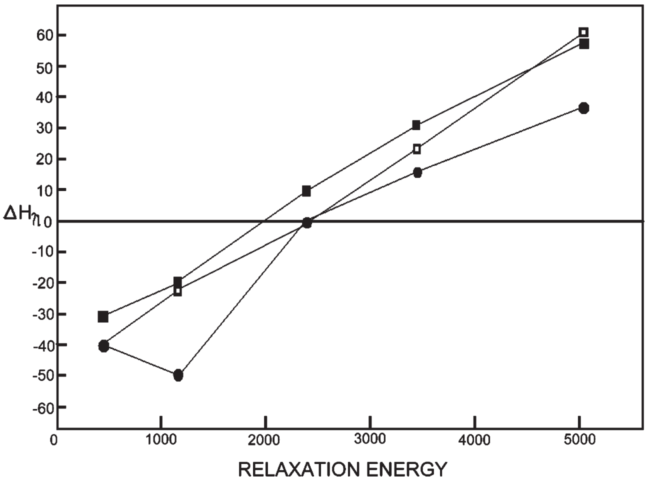

Figure 4. Plot of the relaxation energy (ΔE_r^{slr}) versus the operational chemical hardness (ΔH_η ($Cl^+ - H^+$) for the series BX^-, where: ●, atomic bases; ■, hydrides; □, chlorides, where B represents the elements beryllium through oxygen.

non-bonding electrons localized on the halogen atoms (Figure 1a). For these bases in principle at least all of the terms in eq 7 should be considered. In Table 2 may be found the series of the type $BH_nX_m^-$ where X is Cl or F and B is one of the parent atomic bases. Here *n* or *m* may be zero and $n + m$ is less than the characteristic valence of the parent atomic base. As with the hydrides, in all cases the molecular species are found to be harder than the parent atomic bases, which may be accounted for by the increase in the number of responding electrons. However, hydrogen and the halogens, although they contribute very different numbers of responding electrons, produce similar increases in chemical hardness. Furthermore, although hydrogen, chlorine, and fluorine have very different electronegativities and absolute hardnesses, they surprisingly produce quite similar changes in the hardness of the parent atomic bases. Finally, the chemical hardnesses of these molecular bases are most similar to the hardnesses of the parent atomic bases rather than the hydrogens or halogens that are bonded to the parent atomic bases.

The operational chemical hardnesses of the atomic anions, monohydrides, and monochlorides have been plotted against the relaxation energies (ΔE_r^{slr}, Figure 4). The $\Delta H_\eta(Cl^+ - H^+)$'s of the monochlorides generally lie between those of the atomic bases and the monohydrides. It would thus appear that the addition of chloride or the replacement of hydrogen by chlorine has a similar and only moderate effect on chemical hardness. This is in spite of the large differences in the number of responding electrons, electronegativity, and chemical hardnesses of chlorine, fluorine, and hydrogen. These observations very strongly suggest that the remote responding electrons on the halogen atoms do not impact chemical hardness in the same manner as either the non-bonding responding electrons or the bond-forming responding electrons, which are localized on the binding atom.

Unfortunately, unlike the hydrides there are no bases, in which all but one of the n_r's in eq 7 are zero. Therefore it is not possible to obtain $\Delta\varepsilon_r^{eff}$'s for any of the three types of responding electrons. As an alternative mean single-electron relaxation energies have been computed. The mean single-electron relaxation energies ($\Delta\varepsilon_r^{glb}$ and $\Delta\varepsilon_r^{loc}$) were computed making two different assumptions. For $\Delta\varepsilon_r^{glb}$ it was assumed that chemical hardness was a global property (eq 11a) and for $\Delta\varepsilon_r^{loc}$ it was assumed that chemical hardness was localized on the binding atom (eq 11b).

$$\Delta E_r^{eff} = (n_{rn} + n_{rb} + n_{rr})\,\Delta\varepsilon_r^{glb} \qquad (11a)$$

$$\Delta E_r^{eff} = (n_{rn} + n_{rb})\Delta\varepsilon_r^{loc} \qquad (11b)$$

Values for $\Delta\varepsilon_r^{loc}$ and $\Delta\varepsilon_r^{glb}$ may be also found in Table 2.

Because of deshielding single-electron relaxation energies for the non-bonding responding electrons have been greater in the molecules than in the parent atomic bases. Furthermore, the single-electron relaxation energies for bond-forming responding electrons are comparable usually within about 100 kcal/mol to the single-electron relaxation energies in the atomic bases. This means that, if $\Delta\varepsilon_r^{glb}$ is significantly smaller than the single-electron relaxation energy for the atomic bases, then $\Delta\varepsilon_{rr}^{eff}$ may be expected to be not only smaller than the single-electron relaxation energy for atomic bases, but smaller than $\Delta\varepsilon_r^{glb}$. In all cases the $\Delta\varepsilon_r^{glb}$'s are in fact much smaller than the single-electron relaxation energies of the parent atomic bases and therefore the effective relaxation energy of the remote electron, $\Delta\varepsilon_{rr}^{eff}$, must be smaller than $\Delta\varepsilon_r^{glb}$.

If chemical hardness is truly global, then all of the non-bonding electrons, including the remote electrons on the halogens, must undergo the same type of relaxation. However, it has just been shown that $\Delta\varepsilon_{rr}^{eff}$ is expected to be generally less than $\Delta\varepsilon_r^{glb}$. This being the case eq 6 can be used to estimate an upper limit for the effective nuclear charge experienced by the halogen's non-bonding electrons. The values of $\Delta\varepsilon_r^{glb}$ range from 60 for $BeCl^-$ to 506 for OCl^-, which are, respectively, only 15% and 50% of those of the parent atomic bases. Taking CCl_3^- to be a case, in which the more accurate thermodynamic data are available and in which $\Delta\varepsilon_r^{glb}$ is 21% of that of the parent atomic base, one would have to have an effective nuclear charge for the chlorine non-bonding electrons of less than 0.6. Such a small effective nuclear charge would require that the atomic charge on the chlorine in CCl_3^- be more negative than −10, which of course is not possible.

Consider the series $BH_nX_m^-$ where $n + m$ equals one less than the characteristic valence of the binding atom, B, and X is Cl or F. As *m* increases, because X is more electronegative than hydrogen, the atomic charge on X must become more positive and as a result X's electrons become increasingly deshielded. This would cause the single-electron relaxation energy for the halogen atom's remote responding electrons, $\Delta\varepsilon_{rr}^{eff}$, to increase. Since $\Delta\varepsilon_{rr}^{eff}$ is expected to be less than $\Delta\varepsilon_r^{glb}$, $\Delta\varepsilon_{rr}^{eff}$ appears to be actually decreasing. These results would seem to very strongly suggest that the remote responding electrons on halogen atoms do not impact chemical hardness in the same manner as non-bonding and bond-forming responding electrons, and that chemical hardness appears to be in fact a local property.

Additional Observations. The hydroxyl ion derives from the most electronegative of the parent atomic bases that form hydrides. Its oxygen carries a −0.91 atomic charge,[26] which is very near the charge on oxygen in the parent atomic base. As a result of the high polarity of the O−H bond, in simple molecular orbital terms the bond-forming orbital is very much dominated by the oxygen atomic orbitals. The net result is that all of the responding electrons of the hydroxyl ion are expected to be nearly identical to those of the parent atomic base and should thus have nearly the same single-electron relaxation energy. Although the hydroxyl ion is significantly harder than the parent atomic base ($\Delta H_\eta(\mathrm{Cl}^+-\mathrm{H}^+)$ equals 57.9 and 36.8 kcal/mol, respectively.), consistent with this prediction, its single-electron relaxation energy ($\Delta\varepsilon_r^{loc}$ = 985 kJ/mol) differs by only 2% from that of the parent atomic base ($\Delta\varepsilon_r^{slr}$ = 1007 kJ/mol).

In addition to bases containing atoms that are singly bonded to the parent atomic base, several containing multiple bonds have been examined. In the case of the cyanide ion, in which there are six bond-forming responding electrons and two remote responding electrons, $\Delta\varepsilon_{rb}^{eff}$ (which equal $\Delta\varepsilon_r^{loc}$) is 666, which is comparable to the other carbon bases, in which the carbon is bound to three other atoms via single bonds. In the case of O_2^- and CO^- determination of the number of responding electrons is not quite as straightforward. In both cases the bond order has been taken to be the average of the two dominant resonance forms, which has yielded a bond order of 1.5 for both and 5.5 and 3.5 remote responding electrons for O_2^- and CO^-, respectively. The resulting values of $\Delta\varepsilon_{rb}^{eff}$ were 901 and 588 for O_2^- and CO^-, respectively. These are also comparable to the other carbon and oxygen bases. It would thus appear that this model is also applicable to these bases containing multiple bonds.

Conclusion

It has been established that in the case of anionic atomic acids and bases, the structure responsible for chemical hardness is the atom's responding electrons, which during an acid−base interaction undergo relaxation as a result of a change in shielding. Chemical hardness consequently derives from both the number of electrons undergoing this relaxation as well as the change in energy experienced by each of these electrons. When small molecules are formed by binding atoms to a parent atomic base, the same structure, in this case the responding electrons of the molecule, and the same process should be responsible for hard−soft behavior. Consistent with the common practice of characterizing the hardness of molecules by the hardness of the binding atom in the acid−base interaction, in small molecules the structure giving rise to hard−soft behavior may be characterized as being the non-bonding responding electrons associated with the binding atom and the bond-forming responding electrons also associated with the binding atom. The remote responding electrons, which are those responding electrons not associated with the binding atom, appear to have no direct impact on chemical hardness. The increase in hardness resulting from bonding atoms to the parent atomic base results principally from the increase in the number of responding electrons and secondarily from changes in the single-electron relaxation energy. Whereas the examples cited in this report have been small molecular bases, because of the relationship between bases and their conjugate Lewis acids the same structure and processes are responsible for the hard−soft behavior of acids.

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