J. Phys. Chem. A **1997,** *101,* 7396−7400

Electronegativity: Chemical Hardness I

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Received: March 28, 1997; In Final Form: July 23, 1997⊗

It has been suggested that the absolute hardness of density functional theory be identified with the chemical hardness of Pearson's principle of hard and soft acids and bases. It is unclear whether these two hardnesses are actually equivalent and if not how they are related. The problems arising from the identification of chemical hardness with absolute hardness are examined, as well as the problems associated with the evaluation of absolute hardnesses. The nature of absolute hardness is explored in some detail which has given rise to an interpretation which is in conflict with the commonly accepted interpretations of chemical hardness.

Introduction

The acid−base concept has been one of the oldest and most universally applied in all of chemistry. Although a number of definitions have been proposed, that of G. N. Lewis is probably the most universal as well as the most amenable to theoretical interpretation. Of particular interest has been the relative strengths of acids and bases. It seems clear to even the most casual observer that some bases (acids) are more reactive as bases (acids) than others. It is also clear that there is no universal ordering of this reactivity, and that the reactivity of a base is significantly influenced by both acid with which it reacts as well as the medium in which the reaction occurs. The same can be said for acids.

It is particularly desirable to be able to ascribe the reactivity or strength of an acid or a base to one or more properties of that acid or base. There are a number of models which have been formulated to ascribe acid−base strength to a one or more properties of the acid or of the base. Among them are the ionic−covalent model of Drago[1] and the hard−soft acid−base model of Pearson[2]. Both Drago's and Pearson's models assume that the strength of a particular acid or base can be described by a pair of parameters or properties.

The latter model, which is of interest here, partitions the strength of an acid or base into an intrinsic and an extrinsic part.[3,4] The intrinsic part is the inherent strength of the acid or base and is not influenced by the acid or base with which it reacts. The extrinsic part in some manner describes how the acid or base responds to the influence of the acid or base with which it is reacting. This latter property has been named the chemical hardness. The situation with the hard−soft acid−base model has been similar to that of electronegativity, in that it is clear that such a property exists, but no clear formulation has been forthcoming. There have been literally hundreds of reports which have substantiated the existence of "hardness", and the companion property, "softness", and they have been correlated with many atomic and molecular properties. Yet prior to the report of Parr and Pearson,[4] which identified chemical hardness with the absolute hardness of density functional theory, only these qualitative correlations had been examined.[1]

Whereas it does seem that the absolute hardness is and should be in some way strongly related to the chemical hardness, it does not seem clear that the absolute hardness can be automatically identified as being the same as chemical hardness. In this communication we wish to examine the hard−soft acid−base model of Pearson and to explore the identification of absolute hardness with chemical hardness in the hope of clarifying their relationship. To do so it will be necessary to examine and interpret in some detail the nature of absolute hardness.

Results and Discussion

The Identification of Absolute Hardness With Chemical Hardness. The absolute hardness η of density functional theory is defined as

$$\eta = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_v = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_v \qquad (1)$$

where μ is the electronic chemical potential, N the number of electrons, v the external potential, and E the energy. The companion property, softness, is the reciprocal of the hardness.

$$S = 1/\eta \qquad (2)$$

Although Pearson[3] has pointed out that, unlike the electronic chemical potential, the absolute hardnesses of the constituent atoms do not equalize in molecules, Chattaraj[5,6] has shown that they do in fact equalize. Whereas in the former case different regions in molecules may have different absolute hardnesses, the latter suggests a single hardness throughout the molecule. Thus of particular interest would be to what extent these local hardnesses will change upon chemical combination. In addition to these local hardnesses, there is also a global absolute hardness, η^*, which is associated with the whole atom or molecule. This global hardness should not be identified with the equalized local hardnesses.

The idea that absolute hardness should be identical with the chemical hardness is problematic on several grounds. The chemical hardness is a quantity which determines or controls chemical reactivity. It would thus seem that chemical hardness should be an energy or at least a potential. The absolute hardness, on the other hand, is neither of these. It is, rather, the curvature of the energy charge relationship. In addition, it is unclear whether the local hardness or global hardness should be identified with the chemical hardness. Whereas the chemical hardness is significantly dependent on the charge carried by the acid or base, the absolute hardness appears to be virtually independent of charge. Finally, if the hardness is uniform throughout a molecule, differences in local hardness can no longer be considered to be responsible for differences in reactivity within the same molecule.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S1089-5639(97)01105-5 CCC: $14.00

Pearson has proposed[3] that an operational definition of the absolute hardness might be obtained using the finite difference approximation. If the derivative is approximated as a finite differences in the chemical potential and in the number of electrons then

$$\eta^* = \frac{1}{2}\frac{\partial\mu}{\partial \mathrm{N}} = \frac{1}{2}\frac{\Delta\mu}{\Delta N} \tag{3}$$

This, of course, yields the absolute global hardness rather than a local absolute hardness. Pearson's operational definition is

$$\eta^* = \frac{\mathrm{IE} - \mathrm{EA}}{2} \tag{4}$$

The use of the finite difference approximations (equation 3) is only appropriate, if the value of the derivative, $\partial\mu/\partial N$ does not vary appreciably over the interval ΔN (ΔN = 2). Thus the invocation of the finite difference approximation requires that the absolute hardness be essentially independent of charge over an interval of two units of charge. This does not appear to be the case for chemical hardness or the absolute hardness of atoms which are in fact significantly dependent on charge. A further difficulty with the operational definition is that the finite difference approximation eq 3 does not yield the eq 4.

These problems notwithstanding, eq 4 does yield a very excellent approximation to the absolute hardness provided certain conditions are met. Although Mulliken's formulation[7] of electronegativity

$$-\mu = \chi = \frac{\mathrm{IE} + \mathrm{EA}}{2} \tag{5}$$

has the form of a finite difference approximation to the Ickowski-Margrave formulation,[8]

$$\chi = -\frac{\partial E}{\partial N} = \frac{\Delta E}{\Delta N} = \frac{\mathrm{IE} + \mathrm{EA}}{2} \tag{6}$$

Mulliken had not suggested such. Furthermore, there is a very significant dependence of electronegativity on charge which makes the finite difference approximation inappropriate. Yet the Mulliken formulation does provide an excellent approximation for the absolute electronegativity, but only when the energy is a quadratic function of charge.

$$\mathrm{E} = aq + {}^{1}\!/_{2}bq^{2} \tag{7}$$

in which case the absolute hardness is equal to $b/2$. Only when this is the case do eqs 4 and 5 yield quite accurate values of the absolute electronegativity and the absolute hardness.[9] Furthermore, whereas the chemical hardness has a very significant dependence on charge, to suggest that absolute hardness derived from the operational definition is also charge dependent leads to an internal contradiction. This is because eq 4 only approximates the absolute hardness, if eq 7 is applicable, yet if the absolute hardness were not constant eq 7 would be inapplicable and the operational definition could not be used. To illustrate the reasonableness of eq 7 and the virtual constancy of the absolute hardness, consider the case of sodium for which E/q has been plotted against q, Figure 1. Where the plot is linear the relationship is quadratic, eq 7. There are two linear regions which correspond to the K and L shells. The slopes of these segments are equal to the absolute hardness. The deviation from linearity is imperceptible. Thus whereas Na^{1+} has the same absolute hardness as Na^{7+}, Na^{9+} and Na^{10+} are very much harder. The absolute hardness of sodium is virtually constant over nine units of charge.

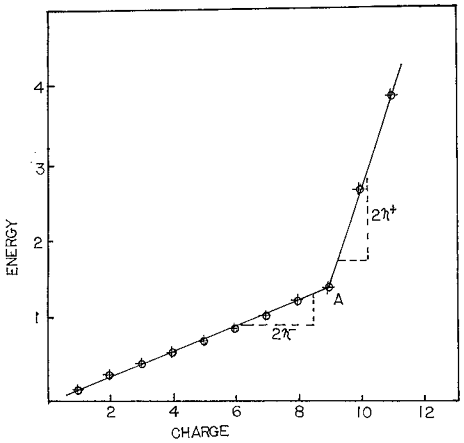

Figure 1. A plot of the sodium atom electronic energy versus the atomic charge: (o) experimental, (+) computed using Slater's model. Data taken from ref 10.

Electronegativity and Base Strength. As has been repeatedly pointed out,[11−16] electronegativity and Lewis basicity are required to be closely related by virtue of their respective definitions. This relationship has been recently examined within the context of the reformulated electronegativity function and its attendant relationships.[11] One such relationship is

$$\eta^* = b^* = \sum_i \left[\frac{1}{b_i}\right]^{-1} \tag{8}$$

where b is defined by eq 7. This yields the relationship between the absolute hardness of individual atoms and the global absolute hardness. This hardness is not, as has been suggested,[9] the hardness to which all the atoms equalize. Of particular relevance is that quantities such as atomic charge, charge transferred, ionization energy and charging energy all correlate with the strength of a base toward a proton.[11] In all of these quantities the absolute electronegativity, the absolute hardness of the constituent atoms, and the global absolute hardness are significant components.

An Interpretation of Absolute Hardness. It would appear that both the operational definition (eq 4) and rigorous definition (eq 1) of absolute hardness identify it with the coefficient in the quadratic term in eq 7.

$$\eta = \frac{b}{2} \tag{9}$$

An interpretation of this coefficient has been provided by Klopman for atoms[17] and Reed for molecules.[18] Klopman has derived the following relationship for the electronic energy of an atom

$$E = qB_{\mathrm{x}} + \frac{q(q-1)}{2}A_{\mathrm{x}} \tag{10a}$$

which is also quadratic in charge, and thus

$$b = A_{\mathrm{x}}$$

and (eq 10b)

$$a = B_{\mathrm{x}} - \frac{A_{\mathrm{x}}}{2} \tag{10b}$$

Whereas B_{x} is derived from the integrals involving kinetic energy as well as nuclear-electron interactions, the A_{x} term is comprised only of integrals of the type

$$e^2\int\int\phi_i(1)\phi_j(2)\frac{1}{r_{12}}\phi_i(1)\phi_j(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{11a}$$

and

$$e^2\int\int\phi_i(1)\phi_j(2)\frac{1}{r_{12}}\phi_i(2)\phi_j(1)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{11b}$$

Thus for atoms it would appear that absolute hardness is directly related to the inverse of the mean electron−electron separation.

A similar quadratic relationship has been developed for molecules

$$E = a^*Z + {}^1\!/_2 b^*Z^2 \tag{12}$$

which is the molecular analogue to eq 7. Here Z is the charge on the molecule, and a^* is given by

$$a^* = \sum_i\left[\frac{a_i}{b_i}\right]b^* \tag{13}$$

and b^* given by eq 8. However, this relationship is only applicable when the charge being transferred involves an essentially nonbonding frontier orbital.[18−20] This is true for many Lewis bases. Thus where this condition holds the absolute hardness equals b*/2.

Whereas it is impossible to experimentally test the quadratic relationship suggested in eq 12, it has been possible to test the predictions of eq 12. Of course that there is a quadratic relationship between a molecule's energy and its charge (eq 12) is implicit in Pearson's operational definition of absolute hardness. In addition, the successful use of the model from which eq 12 is derived in estimating ionization energies, atomic charges, and charging energies, as well as in the correlations with Bronsted basicity, suggests that this is a very reasonable model and that eq 8 does provide very reasonable global hardnesses.[20]

These interpretations of the absolute hardness are consistent with a number of properties which have been found to correlate with chemical hardness. Although A_x is a collection of integrals, each yields the expectation value of the inverse electron−electron separation for pairs of orbitals. Thus for cases in which the orbitals are small and compact, A and thus b is large and the atom is hard. When the orbitals are large, A is small and the atom is soft. For molecules the canonical molecular orbitals are delocalized and hence large and dispersed. Thus molecules are always softer than their component atoms, as is evident from eq 8 where b* is smaller than any individual b, and metals are extremely soft. Soft bases have been characterized as polarizable and easily ionized and conversely for hard species. The polarizability is expected to correlate with the compactness or dispersness of the orbitals of which A is a measure. Rearrangement of eqs 7 and 12 yields

$$\mathrm{IE} = a + {}^1\!/_2 b \tag{14a}$$

$$\mathrm{IE} = a^* + {}^1\!/_2 b^* \tag{14b}$$

which illustrates the importance of the contribution of the absolute hardness to the magnitude of ionization energy and why soft atoms and molecules are easily ionized. These correlations notwithstanding, the absolute hardness is not so easily reconciled with some of the other characteristics of chemical hardness.

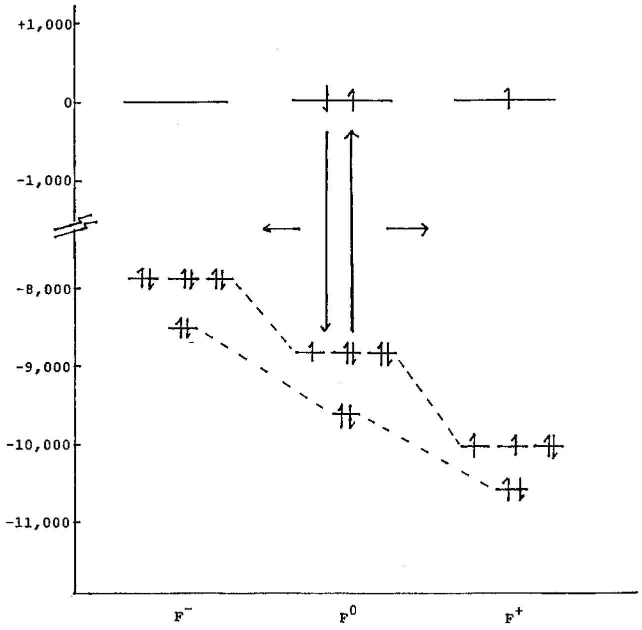

Figure 2. The one-electron energies for the valence electrons of fluorine, its anion, and its cation.

Absolute Hardness and Charge Transfer. Lewis's definition of acids and bases identifies an acid−base reaction with a charge-transfer process. Although a detailed interpretation of absolute hardness has been presented, its role in the charge-transfer process is not yet clear. A very simple but informative model was developed by Slater over half a century ago.[21]

Slater determined one-electron energies rather than the more common orbital energies. In this model, the energy acquired by an ionized electron during an ionization is equal in magnitude, but opposite in sign to that lost by an acquired electron in an electron affinity process. In the operational definition of absolute hardness (eq 4) these energies cancel and are thus not part of the absolute hardness. Rather the absolute hardness arises from the relaxation of the remaining electrons during both ionization and electron affinity processes. This is illustrated for the ionization energy and electron affinity of fluorine in Figure 2. It would thus appear that the absolute hardness does not so much describe the electrons being accepted or the orbital into which they are being accepted in an acid−base reaction, but rather the energetics of the response of the remaining electrons to this process.

Absolute Hardness and Frontier Orbitals. Arising from the operational definition of absolute hardness,[22] eq 4, as well as the use of perturbation theory to interpret chemical hardness, the absolute hardness has been interpreted as arising primarily from the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of each of the reacting species.[23] This understanding of absolute hardness arises as the result of invoking Koopmans theorem to equate LUMO and HOMO energies to electron affinities and ionization energies, respectively.[20] Because the justification of eq 4 derives from the validity of eq 7 rather from than an application finite difference approximation, this frontier orbital interpretation would seem to be in error. Because this energy gap in molecules arises primarily from the resonance integrals, the absolute hardness is primarily the result of the bonding interactions within the acid or base. This requires that absolute hardness in atoms be fundamentally different from the same property in molecules. This is also problematic.

Equation 7 can only yield the absolute hardness for charges where the energy-charge function is continuous. This is not the case for filled orbitals which are not degenerate with one or more vacant or partially vacant orbitals. Furthermore this is not the case when the HOMO and the LUMO are nondegenerate or for filled shells or subshells in atoms. At these points of discontinuity two absolute hardnesses are appropriate, for electron donors η^{-1} and for electron acceptors η^{+}. This is also the case for the Fukui functions.[5] Thus for electron donors the absolute hardness equals the $b/2$ which is characteristic of the HOMO, and for electron acceptors it is still $b/2$, but in this case it is characteristic of the LUMO (see point A in Figure 1). Furthermore, in neither case does the absolute hardness derive from the energy gap between the HOMO and the LUMO, but rather from the Coulombic interactions within the HOMO or within the LUMO. This is very much consistent with the conclusion of the previous section which does not ascribe absolute hardness to the donor electrons or to the acceptor orbital, but to remaining electrons in the atom.

Global and Local Absolute Hardness. It has been suggested that the absolute hardnesses of atoms do not equalize upon the formation of molecules. Thus each molecular species will have a number of absolute hardnesses associated with it. There are those which are associated with each atom and a global hardness associated with the entire molecule. Equation 4 yields only experimental values for the global absolute hardness. The value of the hardness of an atom in a molecule is not experimentally obtainable, and they cannot be computed without considerable difficulty and some controversy.

The association of the absolute hardness with the expectation value of the electron−electron separation (eq 11), thus associates it with size, eq 11. The size of a molecule is dominated by the size of the largest atom. Similarly the global hardness is dominated by that of the softest atom, eq 12.

The global absolute hardness and the atomic absolute hardness both arise naturally as part of the reformulation of the electronegativity function.[18] Using these results the atomic charge, q, which may be evaluated using

$$q = \frac{\chi^* - a - {}^1/_2 r}{b} \qquad (15)$$

where the global electronegativity, χ^* is given by

$$\chi^* = a^* + {}^1/_2 r^* + b^* Z \qquad (16)$$

and is the electronegativity to which all atoms equalize. The r terms are the parts of the electronegativity function which reflect the bonding in the molecule. These and the other terms are discussed in detail elsewhere.[18] If an amount of charge Z is transferred during an acid−based interaction, and the HOMO or LUMO is essentially nonbonding, eqs 15 and 16 can be combined to yield

$$\Delta q_i = \frac{b^*}{b_i}\Delta Z \qquad (17)$$

where Δq_i is the change in the atomic charge on the ith atom. Komorowski has arrived at the same result using electrodynamic principles.[13] This suggests that one of the roles of absolute hardness is to determine how the charge acquired or lost is distributed in the acid or base fragment during an acid−base interaction. This is supported by the qualitative interpretations of hardness which have suggested that it is the softest atom(s) which experiences the greatest change during reaction.

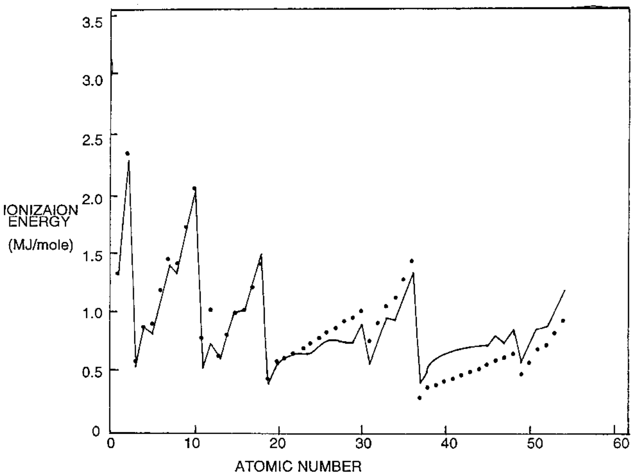

Figure 3. A plot of the first ionization energy versus the atomic number for elements 1 thru 54: (—) experimental, (○) computed.

As was pointed out earlier the hard−soft acid−base model ascribed to chemical hardness the ability to control or direct reactivity, and as such it should be an energy or at least a potential. The absolute hardness is associated with the response of the remaining electrons to the transfer of charge, but it is not that energy itself. Equations 7 and 11 suggests that the energy associated with the absolute hardness derives from b^*Z^2 and $b_i q_i$ type terms.

Computations. In Slater's model the one-electron energies for each of the electrons in an atom is determined using

$$-1312\ \text{kJ/mol}\,\frac{Z^{*2}}{n^2} \qquad (18)$$

where n is the principle quantum number and the effective nuclear charge Z is the difference between the nuclear charge and the shielding by each of the other electrons. The total electronic energy is simply the sum of these one-electron energies. Using these one-electron energies the ionization energies can be computed and compared to the experimental ionization energies. Although Slater's original rules did not reproduced the experimental ionization energies very well, a set of modified rules has been developed which reproduce with surprising accuracy not only the first ionization energies (Figure 3), but also the second, third, and sequential ionization energies of the same atom. In addition they provide very good estimations for X-ray photoelectron spectra as well as atomic optical spectra and promotion energies. Furthermore it faithfully yields the quadratic energy charge relationship and reproduces the data in Figure 1. The rules for computing the shielding are given below.

The Rules. Rule 1. An electron is not shielded by any electron in a larger shell, and s and p electrons are not shielded by d electrons in the same shell.

Rule 2. An electron is completely shielded by electrons in shells which are smaller than the next smallest shell, and d electrons are also completely shielded by electrons in the next smallest shell.

Rule 3. An s electron is shielded by an s or p electron in the next smallest shell by 0.8366, and for a p electron the same shielding is 0.9155. Both s and p electrons are shielded by d electrons in the next smallest shell by 0.9143.

Rule 4. Both s and p electrons in the same shell shield each other 0.3228, and d electrons in the same shell also shield each other 0.3228 but are shielded by s and p electrons in the same shell 0.8933.

Rule 5. The pairing energy for a pair of p electrons is

$$\frac{1360.1}{n^2}(\text{kJ/mol}).$$

Rule 6. The pairing energy for a pair of d electrons is

$$\frac{9610.7}{n^2}(\text{kJ mol}).$$

These results suggest that this model and these shielding constants yield a representation of the energetics of an atom which is sufficiently faithful to be used in interpreting absolute hardness. To illustrate, the computed energies are virtually superimposable on the experimental energies in Figure 1.

In Conclusion

The hard−soft acid−base model partitions the strength of acids and bases into intrinsic and extrinsic components. The latter which is the chemical hardness has been identified with the absolute hardness of density functional theory. Examination of these two hardnesses suggests that, whereas the absolute hardnesses may be important in determining the strength of acids and bases, the chemical and absolute hardnesses are not identical. Thus a more careful description of both absolute hardness and chemical hardness is desirable.

In addition to the rigorous definition of absolute hardness, an operational definition has been proposed. Because this operational absolute hardness is a property of the entire molecule, it is the global absolute hardness. This not withstanding, there are some rather severe restrictions on the applicability of this definition. An alternative route to the global absolute hardness derives from the molecular electronegativity function, which provides for its computation from the absolute hardnesses of the constituent atoms.

Both the global and local absolute hardnesses appear to arise from the electron−electron interactions within the acid or base and most directly with the relaxation which occurs upon charge transfer. Moreover, they are not directly associated with the electron density being transferred during an acid−base interaction and, hence, not with the bond that is being formed. This being the case, it would appear that the absolute hardness cannot be easily reconciled with the ioniccovalent interpretation of chemical hardness. Similarly, absolute hardness does appear to be consistent with the frontier versus charge control interpretation of chemical hardness.

Acknowledgment. The author wishes to acknowledge the support of the Army Research Office, contract DAAA15-94-K0004.

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