Electronegativity: Chemical Hardness II

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The identification of the absolute hardness of density functional theory with chemical hardness has proven to be problematic. A rather detailed examination of absolute hardness has revealed that it is in conflict with the commonly accepted interpretation of chemical hardness. To examine chemical hardness in detail, an operational definition has been proposed that gives rise to an interpretation of chemical hardness, which is consistent with that of absolute hardness.

Introduction

It is particularly desirable to be able to ascribe the strength of an acid or a base to one or more of the properties of that acid or base. Currently the two most popular models for doing this are the ionic−covalent model of Drago[1] and the hard−soft acid−base model of Pearson.[2] Both of these models are based on the Lewis definition of acids and bases, and both ascribe the strength or reactivity to only two properties or parameters for each acid and base.

In the ionic−covalent model, the measure of acid or base strength is taken to be the experimental enthalpy for the reaction of an acid−base pair. On this basis,each acid and each base is assigned a pair of parameters which together yield the strength and individually reflect the tendency of the acid or the base to form ionic versus covalent bonds. These have been generally determined for gas-phase reactions or reactions in poorly interacting solvents. They provide a means of acquiring quite reasonable reaction enthalpies for a very large number of acid−base reactions.

The hard−soft acid−base model partitions reactivity into an intrinsic component which is solely a property of the acid or the base, and an extrinsic part which, in the case of a base, is a property of the base, but reflects in some manner the influence of the acid on its strength. There is an analogous partitioning for an acid.[3,4] The experimental measures of strengths range from solubility data to gas-phase enthalpies. The media range from the gas phase to highly polar highly interacting solvents such as water. This is particularly significant since it has been shown that media effects play a dominant role in the extrinsic strength of an acid or a base.[5,6] Whereas the hard−soft acid−base model does not provide reaction enthalpies, it does permit the organizing of a very large number of reactions based on a knowledge of molecular structure and the properties of the constituent atoms.

It has been pointed out that one of the weaknesses of the hard−soft acid−base model is that it has remained largely qualitative, in that acids and bases are either hard or soft.[3] With the development of the absolute hardness of density functional theory, it had been concluded that a quantitative measure of chemical hardness had been found.[7] For a number of reasons it seems unlikely that the global absolute hardness of density functional theory is identical with chemical hardness.

In an attempt to explore the relationship between these two types of hardnesses, the absolute hardness has been examined in detail.[8] It has been shown that both the global and local absolute hardnesses arise from the electron−electron interactions within an acid or a base, rather than from the interaction of electrons with their own atomic cores or those of the molecules with which they are reacting. Furthermore, the global absolute hardness is associated with the response of the remaining electrons in the acid or base to the transfer of charge during an acid−base reaction, and not with the transferred charge itself. Absolute hardness does not appear to be associated with the difference in the energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) as suggested by the perturbation theory interpretation of chemical hardness.[4] Furthermore, it is not associated with the bond formed between the acid and the base as suggested by the ionic versus covalent and the charge versus frontier control interpretation. In addition to the hardness of the whole molecule, there are the hardnesses of the constituent atoms which may be little changed from those of isolated atoms. It would thus appear that the relationship between the absolute hardness of density functional theory and chemical hardness needs further investigation.

The association of acid−base strength with electronegativity is a natural one, since both seek to measure the tendency to transfer charge through a bond. In an investigation of the contributions of electronegativity and the associated properties of charge and charging energy to the base strength, it was determined that all of these significantly influence the proton affinity.[9] Both the global and local absolute hardnesses of the bases significantly influence the electronegativity, charge transferred and charging energy, and therefore the base strength. Of particular interest here is the role of electronegativity and its related properties in the chemical hardness of bases.

Computations

Operational Hardness. The operational chemical hardnesses were computed as the gas-phase enthalpies for the appropriate metathesis reactions using published heats of formation. The enthalpies were for the reactions at 25 °C.

Absolute Hardness and Electronegativity. The absolute hardnesses η and the electronegativities were obtained from the ionization data provided by Hinze and Jaffe.[10,11] The electronegativities used were those for the atoms in their appropriate valence states. The local hardness was taken to be that of the individual atoms, and to be approximately equal to that of the isolated gaseous atom in the appropriate valence state ($2\,\eta = b = \mathrm{IE} - \mathrm{EA}$). It was computed from the published valence state ionization energy and electron affinity.

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Although it has been common practice to use p orbital electronegativities for the halogens, it has been shown[10,11] that those of the tetrahedral valence state are more appropriate. Unfortunately, these are not available. It has been reported that the electronegativity of an atomic orbital decreases linearly as its p character increases. Thus the electronegativities of the tetrahedral valence states[12,13] can be estimated from the s and p orbital electronegativities of the halogens. These estimated values are 16.96, 11.84, 10.87, and 9.99 for fluorine, chlorine, bromine, and iodine, respectively. There is no such linear relationship for b, however. The b constant is related to the absolute electronegativity[3] a and the valence state ionization energy by

$$b = 2(\mathrm{IE_v} - a) = 2\eta \tag{1}$$

The valence state ionization energies for the halogens are also not available, but were estimated by a linear extrapolation of the ionization energies of the tetrahedral valence states of the corresponding group II−VI elements. This extrapolation represents the largest source of error in the estimated b. The correlation coefficients were 0.996, 0.985, 0.980, and 0.986 for fluorine, chlorine, bromine, and iodine, respectively, which resulted in an uncertainty of about 1 eV in the values of b. The b values are 22.04, 13.76, 14.33, and 16.58 for fluorine, chlorine, bromine, and iodine, respectively.

Atomic Charges. The atomic charges were computed using a procedure developed from the reformulated electronegativity function.[10,12] The data were taken form the isolated atom electronegativities provided by Hinze and Jaffee.[12,13]

Results and Discussion

An Operational Definition. One of the difficulties with the concept of chemical hardness has been that it has lacked a clear formulation. In the absence of such a formulation it has been difficult to ascertain the adequacy of the hard−soft acid−base model as well as to determine if the proposal that chemical hardness be identified with the global absolute hardness is appropriate. It is proposed that the hard−soft acid−base principle of Pearson serve as an operational definition of chemical hardness. Thus, let chemical softness be defined as the inverse property of chemical hardness. Operational chemical hardness is a property of an acid or a base which influences its reactivity in such a way as to cause hard acids to prefer to bind hard bases and soft acids to prefer to bind to soft bases. This definition is operational and does not attempt to interpret chemical hardness, but rather assigns to it only those properties which are inherent in Pearson's principle of hard and soft acids and bases.

Operational Chemical Hardness. This definition also suggests a means of quantifying operational chemical hardness. Historically a wide range of properties have served to indicate acid and base strength. Many of these, however, are very much influenced by temperature and reaction medium. To minimized these influences, the gas-phase enthalpies have been selected as measures of reactivity.

Although generally there is no unique way to partition reactivity among reactants, partitioning the enthalpy linearly between the acid and the base is a particularly attractive though approximate model. Thus the change in enthalpy for the reaction of an acid, A, with a base, B:, would be given by

$$\Delta H_{\mathrm{AB}} = \Delta H_{\mathrm{A}} + \Delta H_{\mathrm{B}} \tag{2}$$

If the enthalpy change is further partitioned into the intrinsic contribution and the extrinsic contribution, we get

$$\Delta H_{\mathrm{AB}} = \Delta H_{\mathrm{A}}^{\mathrm{int}} + \Delta H_{\mathrm{A}}^{\mathrm{ext}}(\mathrm{B}) + \Delta H_{\mathrm{B}}^{\mathrm{int}} + \Delta H_{\mathrm{B}}^{\mathrm{ext}}(\mathrm{A}) \tag{3}$$

where $\Delta H_{\mathrm{A}}^{\mathrm{int}}$ is the enthalpy change arising from the intrinsic strength of A and $\Delta H_{\mathrm{A}}^{\mathrm{ext}}$ (B) is the enthalpy change arising from the extrinsic strength of A as influenced by the base B. Because in any reaction both intrinsic and extrinsic strengths are operative, the outcome is controlled by a combination of these.

Consider, however, the metathesis reaction below

$$\mathrm{AB} + \mathrm{A'B'} \rightarrow \mathrm{AB'} + \mathrm{A'B} \tag{4}$$

This reaction is in effect a restatement of the operational definition of chemical hardness, and it is the sum of of the following series of reactions. In this metathesis reaction the intrinsic strengths of the acids and bases make no contribution to the reaction enthalpy. Rather, the reaction enthalpy is determined by the extrinsic strengths of the acid and base fragments. In this model the operational chemical hardness may be identified with the extrinsic strengths. To further clarify the role(s) of extrinsic strength, and possibly the chemical hardness, consider a series of metathesis reactions in which the acids A and A′ are the same in all of the reactions. Furthermore, let A and A′ differ considerably in chemical hardness. Thus in a metathesis reaction the role of these acids is to discriminate between the bases B and B′ based on their relative hardnesses. These pairs of acids will be called the discriminating acids. Also let the base, B′, be the same in all of the reactions. In such a series the hardness of each base is compared to that of B′. Let it be called the reference base. Of course an analogous series can be developed to examine the chemical hardness for acids. Thus the reaction enthalpies in this series of reactions yield the chemical hardnesses in a context defined by the operational definition. Such metathesis reactions have been commonly used as definitive illustrations of the hard−soft acid−base Principle.

REACTIONS	ENTHALPY
$\mathrm{AB} \rightarrow \mathrm{A} + \mathrm{B}{:}$	$-\Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{int}} - \Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{ext}}(\mathrm{B}) - \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{int}} - \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{ext}}(\mathrm{A})$
$\mathrm{A'B'} \rightarrow \mathrm{A'} + \mathrm{B}{:}'$	$-\Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{int}} - \Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{ext}}(\mathrm{B'}) - \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{int}} - \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{ext}}(\mathrm{A'})$
$\mathrm{A} + \mathrm{B}{:}' \rightarrow \mathrm{AB'}$	$\Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{int}} + \Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{ext}}(\mathrm{B'}) + \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{int}} + \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{ext}}(\mathrm{A})$
$\mathrm{A'} + \mathrm{B}{:} \rightarrow \mathrm{A'B}$	$\Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{int}} + \Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{int}}(\mathrm{B}) + \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{int}} + \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{ext}}(\mathrm{A'})$
net: $\mathrm{AB} + \mathrm{A'B'} \rightarrow \mathrm{AB'} + \mathrm{A'B}$	
and	$\Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{ext}}(\mathrm{B'}) - \Delta \mathrm{H}_{\mathrm{A}}^{\mathrm{ext}}(\mathrm{B}) + \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{ext}}(\mathrm{A'}) - \Delta \mathrm{H}_{\mathrm{B}}^{\mathrm{ext}}(\mathrm{A}) + \Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{ext}}(\mathrm{B}) - \Delta \mathrm{H}_{\mathrm{A'}}^{\mathrm{ext}}(\mathrm{B'}) + \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{ext}}(\mathrm{A}) - \Delta \mathrm{H}_{\mathrm{B'}}^{\mathrm{ext}}(\mathrm{A'})$

In Table 1 are listed the enthalpies or operational chemical hardnesses for three series of metathesis reactions in which the discriminating acid pairs are $\mathrm{H^+}$−$\mathrm{Cl^+}$, $\mathrm{H^+}$−$\mathrm{F^+}$ and $\mathrm{H^+}$−$\mathrm{OH^+}$, and the reference base is the very soft hydride ion. In the case where $\mathrm{H^+}$ and $\mathrm{Cl^+}$ serve as discriminating acids, there is a 144 kcal/mol difference in the enthalpy for the hardest base and the softest base. Such a large range suggests that the extrinsic strength can have a very important role in and even control reactivity. Yet the very small enthalpies suggest that extrinsic strength may have little or no influence on the course of reactions which nonetheless involve very strong acids and bases.

It is even more informative to compare the enthalpies obtained using different pairs of discriminating acids. These comparisons are plotted in Figure 1. If the extrinsic strength of a base is in fact the response of a base to a single property of the acid, the choice of discriminating acids should not affect the relative magnitudes of the chemical hardnesses within a series of bases such as these. There should be a perfect linear correlation between any two sets of enthalpies. If, on the other hand, there

TABLE 1: Operational Chemical Hardness for a Series of Bases in Which the Reference Base Is Hydride and the Discrimainating Acids are the Proton with the Chlorine, Fluorine, and Hydroxide Cations

species	$\Delta H(\mathrm{H}^+{-}\mathrm{Cl}^+)$	ref	$\Delta H(\mathrm{H}^+{-}\mathrm{F}^+)$	ref	$\Delta H(\mathrm{H}^+{-}\mathrm{OH}^+)$	ref
F^0		*a*	171.54	*b*		
F^-	75.06	*b*	131.28	*a*	100.94	*b*
$\mathit{O}\mathrm{Cl}^-$	65.06	*b*				
$\mathit{O}\mathrm{NO_2}^-$	59.64	*b,c*	99.63	*b*		
$\mathit{O}\mathrm{H}^-$	57.86	*b*	100.94	*b*	83.07	*b*
Cl^0	54.465	*a*	74.240	*a*		
$\mathit{O}\mathrm{NO}^-$	54.23	*b,c*	99.99	*c*		
I^0	53.649	*a*	38.140	*a*		
Cl^-	44.14	*b*	75.06	*b*	57.86	*b*
OO^-	40.37	*b,c*	66.38	*c*		
O^-	36.82	*b*	81.75	*c*	53.37	*b*
Br^-	34.27	*b*	59.88	*b*	47.39	*d*
N^-			55.18	*d*		
$\mathit{C}\mathrm{Cl_3}^-$	23.8	*c*	20.829	*b*		
$\mathit{C}\mathrm{N}^-$	22.73	*b*	41.44	*a*		
Br^0	22.06	*b,d*		*b*		
I^-	21.95	*b*	38.192		32.498	*d*
$\mathit{C}\mathrm{FClCF_2Cl}^-$	21.396	*c*	16.981	*c*		
$\mathit{C}\mathrm{Cl_2F}^-$	20.765	*c*	15.340	*b*		
$\mathit{C}\mathrm{H_2CF_2Cl}^-$	20.44	*c*				
$\mathit{C}\mathrm{HCl_2}^-$	20.206	*b,c*	20.270	*c*		
$\mathit{C}\mathrm{H_2Cl}^-$	19.895	*b*	23.200	*b*		
$\mathit{C}\mathrm{ClF_2}^-$	19.665	*b*	11.040	*c*		
$\mathit{C}\mathrm{F_3}^-$	19.465	*b*	8.826	*b*		
$\mathit{C}\mathrm{H_3}^-$	19.03	*b*	27.04	*b*	27.52	*d*
$\mathit{C}\mathrm{H{=}CH_2}^-$	18.065	*b,c*				
$\mathit{C}\mathrm{H_2CH_2Cl}^-$	17.837	*d*			13.990	*e*
$\mathit{C}\mathrm{HClF}^-$	16.965	*b*	12.64	*b*		
$\mathit{C}\mathrm{HCl}^-$	16.448	*c*				
$\mathit{C}\mathrm{H_2}^-$	16.355	*c*	22.72	*c*	16.788	*c*
$\mathit{C}\mathrm{Cl_2}^-$	15.564	*c*	20.351	*c*		
$\mathit{C}\mathrm{H_2F}^-$	15.465	*b*	13.430	*c*		
$\mathit{C}\mathrm{H_2CH_3}^-$	15.349	*d*	22.359	*c*	21.757	*c*
$\mathit{C}\mathrm{HF_2}^-$	14.675	*b*	6.250	*c*		
$\mathit{N}\mathrm{O}^-$	10.62	*b*	25.64	*b*	15.16	*e*
$\mathit{C}\mathrm{HFCH_3}^-$	10.019	*c*				
CO^-	9.11	*b,c*				
$\mathit{C}\mathrm{H_2CH_2OH}^-$	7.582	*c*				
$\mathit{C}\mathrm{(O)CH_3}^-$	3.491	*c*			−5.833	*c*
P^-	1.065	*a*	−2.947	*e*		
H^-	0.00	*b*	0.00	*b*	0.00	*b*
$\mathit{B}\mathrm{Cl_2}^-$	−14.945	*b*				
$\mathit{B}\mathrm{F_2}^-$	−14.135	*b*	−30.880	*b*		
B^0	−15.93	*b,d*				
Hg^-	−16.185	*b*	8.64	*b*		
$\mathit{B}\mathrm{Br_2}^-$	−17.935	*b*				
Si^-	−18.825	*e*	−19.440	*e*		
Mg^-	−18.645	*a*	−28.57	*c*		
$\mathit{B}\mathrm{O}^-$	−33.53	*b*	−58.95	*b*	−56.20	*b*
Be^-	−40.20	*b*	−61.31	*b*	−43.97	*a*
B^-	−49.935	*b*	−68.360	*b*		
Na^-	−50.99	*b*	−33.98	*b*	−22.30	*e*
Al^-	−52.23	*b*	−60.26	*b*	−47.2	*b*
Ca^-	−56.035	*c*	−54.560	*e*		
Li^-	−58.32	*b*	−49.92	*a*	−34.65	*b*
K^-	−58.66	*b*	−42.36	*a*	−27.04	*a*
Cs^-	−63.035	*b,c*	−47.760	*b*	−28.902	*e*

[a] Data taken from ref 14. [b] Data taken from ref 15. [c] Data taken from ref 16. [d] Data taken from ref 17. [e] Data taken from ref 18.

is no extrinsic strength or if extrinsic strength consists of a number of unrelated properties, there should be a scatter of points with perhaps little or no correlation. What is observed in all cases is a less than perfect linear correlation. The correlation coefficient between the $\mathrm{H}^+{-}\mathrm{Cl}^+$ and $\mathrm{H}^+{-}\mathrm{F}^+$ is 0.945, between $\mathrm{H}^+{-}\mathrm{Cl}^+$ and $\mathrm{H}^+{-}\mathrm{OH}^+$ is 0.953, and between $\mathrm{H}^+{-}\mathrm{F}^+$ and $\mathrm{H}^+{-}\mathrm{OH}^+$ is 0.928.

That there is a correlation is significant, because it confirms the existence of the property operationally defined as chemical hardness. That the correlation is not perfect suggests that extrinsic strength consists of more than one property of the base.

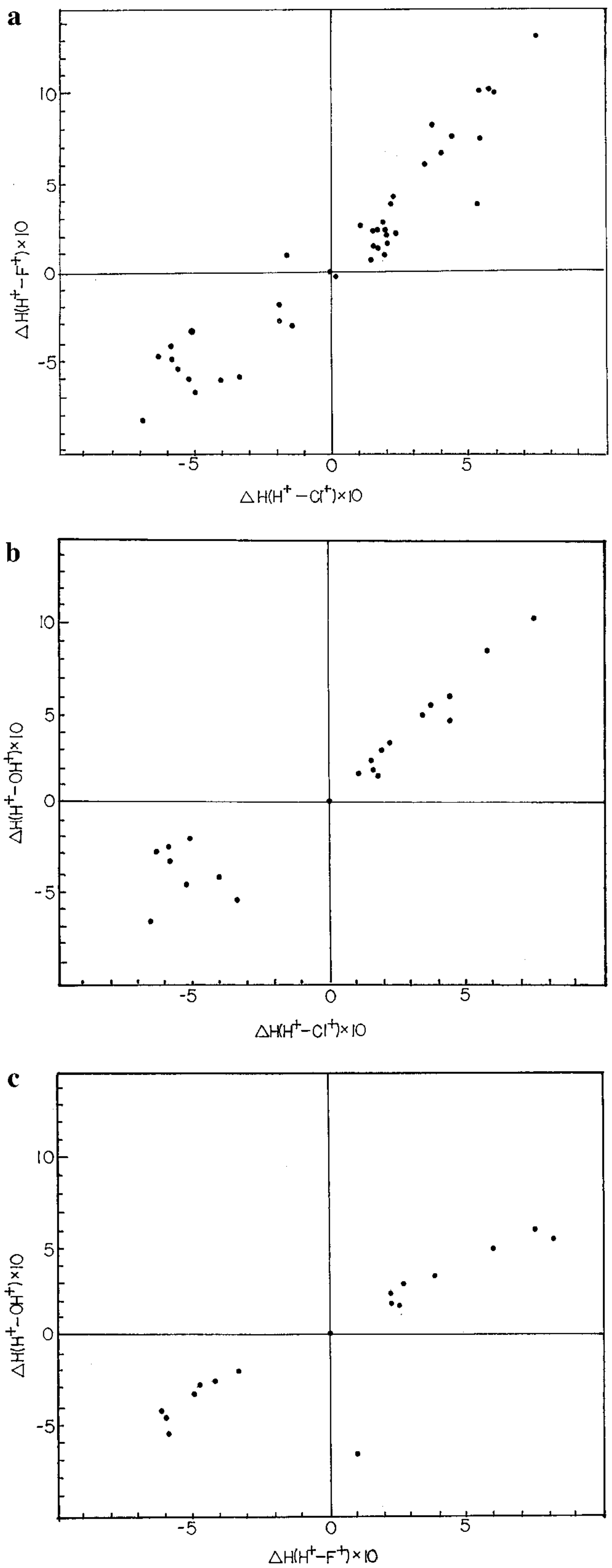

Figure 1. Plot of the operational chemical hardnesses of a series of bases: (a) using H^+ and Cl^+ as discriminating acids versus using H^+ and F^+ as discriminating acids, (b) using H^+ and Cl^+ as discriminating acids versus using H^+ and OH^+ as discriminating acids, (c) using H^+ and F^+ as discriminating acids versus using H^+ and OH^+ as discriminating acids.

However, such strong correlations suggest that among these properties chemical hardness is dominant. That the degree of correlation among the pairs of discriminating acids is virtually the same supports this interpretation. A particularly poor correlation is observed for the metal anions. Metal anions are known to be very soft, and this is born out by the data in table one. Therefore, for these metals the chemical hardness would be especially small, and it is likely that the other components of extrinsic strength would dominate and reduce the correlation. Since the hydrogen−chlorine cation data set is most extensive, these operational hardesses will be used from here on. Finally, should the actual chemical hardness be identified, it should have a weaker correlation with the operational chemical hardness than the correlations among these enthalpies.

Operational Chemical Hardness and Global Absolute Hardness. The absolute hardness of density functional theory is defined as[7]

$$\eta = \frac{1}{2}\frac{\partial\mu}{\partial N} = \frac{1}{2}\frac{\partial^2 E}{\partial N^2} \tag{5}$$

where μ is the electronic chemical potential, N the number of electrons, and E the energy. As an operational definition of absolute hardness, Pearson has proposed[7]

$$\eta^* = \frac{\mathrm{IE} - \mathrm{EA}}{2} \tag{6}$$

where IE and EA are the ionization energy and electron affinity, respectively. This is necessarily a property of the entire molecule, and is hence a global absolute hardness.[3,7,8] However, it has been pointed out that eq 6 yields the absolute hardness only when the ionization energy and electron affinity are those of the neutral species and when a quadratic relationship exists between the energy and the charge.[8,13] It was further pointed out that for charges where the energy−charge relationship is discontinuous, two different absolute hardnesses are appropriate at this discontinuity. Thus a further restriction on eq 6 is that the energy function not be discontinuous over the range of charge from −1 to +1. Unfortunately, this has not been true for the absolute hardnesses computed for some molecules using ionization data. This is also the case for many of the bases in Table 1. On the other hand, even for bases having charges for which the energy−charge relationship is discontinuous, eq 5 can yield the absolute hardness provided the energy−charge relationship is quadratic. This has been shown to be the case for atomic species,[8,19] but the same has not been possible for molecules.

An alternative method for determining the global absolute hardness for molecules is to compute it from the hardnesses of the constituent atoms. Whereas upon bond formation the electronegativities of atoms equalize, their absolute hardnesses may not. In the process of developing the molecular electronegativity function, the global absolute hardness arises naturally as part of that function.[10] Furthermore, it has been shown that it has a very significant role in a variety of processes involving charge transfer. These include gas-phase ionizations, aqueous oxidation−reduction reactions, and the strengths of acids and bases. The global absolute hardness is related to the hardnesses of the individual atoms via

$$2\eta^* = b^* = \sum_i \left[\frac{1}{b_i}\right]^{-1} \tag{7}$$

TABLE 2: Donor Atom Absolute Electronegativities a_D, Absolute Hardnesses η_D, the Global Absolute Hardness η_D^*, Absolute Hardness to Which the Atoms Equalize Mb^*, and Atomic Charges g_D

species	a_D[a]	$2\eta_D = b_D$[a]	$2\eta_D^* = b_D^*$[a]	Mb_D^*	q_D
F^0	16.96	22.04	22.04	22.04	0.00
F^-	16.96	22.04	22.04	22.04	−1.00
$\mathit{O}\mathrm{Cl}^-$	15.25	18.28	7.85	15.74	−0.54
$\mathit{O}\mathrm{NO_2}^-$	15.25	18.28	4.31	18.46	−0.47
$\mathit{O}\mathrm{H}^-$	15.25	18.28	7.55	15.09	−0.91
Cl^0	11.84	13.76	13.76	13.76	0.00
$\mathit{O}\mathrm{NO}^-$	15.25	18.28	5.65	16.94	−0.56
I^0	9.99	13.58	16.58	16.58	0.00
Cl^-	11.84	13.76	13.76	13.76	−1.00
OO^-	15.25	18.28	9.14	18.28	−0.50
O^-	15.25	18.28	18.28	18.28	−1.00
Br^-	10.87	14.33	14.33	14.33	−1.00
N^-	11.54	14.78	14.78	14.78	−1.00
$\mathit{C}\mathrm{Cl_3}^-$	7.98	13.27	3.41	13.64	−0.54
$\mathit{C}\mathrm{N}^-$	7.98	13.27	6.99	13.99	−0.40
Br^0	10.87	14.33	14.33	14.33	0.00
I^-	8.10	9.15	16.58	16.58	−1.00
$\mathit{C}\mathrm{FClCF_2Cl}^-$	7.98	13.27	2.31	16.20	+0.38
$\mathit{C}\mathrm{Cl_2F}^-$	7.98	13.27	3.76	15.04	+0.29
$\mathit{C}\mathrm{H_2CF_2Cl}^-$	7.98	13.27	2.13	15.33	+0.013
$\mathit{C}\mathrm{HCl_2}^-$	7.98	13.27	3.35	13.40	+0.0010
$\mathit{C}\mathrm{H_2Cl}^-$	7.98	13.27	3.29	13.18	−0.19
$\mathit{C}\mathrm{ClF_2}^-$	7.98	13.27	4.19	16.75	+0.41
$\mathit{C}\mathrm{F_3}^-$	7.98	13.27	4.73	18.92	+0.54
$\mathit{C}\mathrm{H_3}^-$	7.98	13.27	3.24	12.96	−0.38
$\mathit{C}\mathrm{H{=}CH_2}^-$	7.98	13.27	2.60	13.05	−0.33
$\mathit{C}\mathrm{H_2CH_2Cl}^-$	7.98	13.27	1.87	13.10	−0.19
$\mathit{C}\mathrm{HClF}^-$	7.98	13.27	3.69	14.75	+0.089
$\mathit{C}\mathrm{HCl}^-$	7.98	13.27	4.43	13.28	−0.29
$\mathit{C}\mathrm{H_2}^-$	7.98	13.27	4.33	12.99	−0.54
$\mathit{C}\mathrm{Cl_2}^-$	7.98	13.27	4.53	13.54	−0.045
$\mathit{C}\mathrm{H_2F}^-$	7.98	13.27	3.62	14.47	−0.12
$\mathit{C}\mathrm{H_2CH_3}^-$	7.98	13.27	1.85	12.96	−0.29
$\mathit{C}\mathrm{HF_2}^-$	7.98	13.27	4.10	16.40	−0.12
$\mathit{N}\mathrm{O}^-$	11.54	14.78	8.17	16.34	−0.44
$\mathit{C}\mathrm{HFCH_3}^-$	7.98	13.27	1.97	13.80	−0.089
CO^-	7.98	13.27	7.69	15.38	−0.349
$\mathit{C}\mathrm{H_2CH_2OH}^-$	7.98	13.27	1.68	13.46	−0.25
$\mathit{C}\mathrm{(O)CH_3}^-$	7.98	13.27	2.28	13.67	−0.11
P^-	8.90	11.33	11.33	11.33	−1.00
H^-	7.17	12.85	12.85	12.28	−1.00
$\mathit{B}\mathrm{Cl_2}^-$	6.33	9.91	4.06	12.18	+0.12
$\mathit{B}\mathrm{F_2}^-$	6.33	9.91	5.22	15.65	+0.38
B^0	6.33	9.91	9.91	9.91	0.00
Hg^-					+1.00
$\mathit{B}\mathrm{Br_2}^-$	6.33	9.91	4.51	13.54	−0.35
Si^-	7.30	9.04	9.04	9.04	−1.00
Mg^-	4.09	6.02	6.02	6.02	−1.00
$\mathit{B}\mathrm{O}^-$	6.33	9.91	6.43	12.85	−0.33
Be^-	4.78	7.59	7.59	7.59	−1.00
B^-	6.33	9.91	9.91	9.91	−1.00
Na^-	2.80	4.67	4.67	4.67	−1.00
Al^-	5.47	6.72	6.72	6.72	−1.00
Ca^-	3.30	4.74	4.74	4.74	−1.00
Li+	3.10	4.57	4.57	4.57	−1.00
K^-	2.90	2.88	2.88	2.88	−1.00
Cs^-					−1.00

[a] Data taken from refs 12 and 13.

Using quite different assumptions and models, other investigators have arrived at this same or very similar result.[19−21] It should be kept in mind that the hardness of a molecule is distinct from the hardness to which its atoms equalize, η_{eq}. Ghosh and co-workers[21] have examined the relationship between the absolute hardness of individual atoms and the hardness to which they equalize, and found that

$$\frac{1}{\eta_{eq}} = \frac{1}{M}\sum_i^M \frac{1}{\eta_i} = \frac{1}{Mb^*} \tag{8}$$

where M is the number of atoms in the molecule.

The global absolute hardnesses determined using eq 7, may be found in Table 2. The correlation between the operational chemical hardness and the global absolute hardness obtained from the electronegativity function (eq 7) is 0.326. It would thus appear that not only is it inappropriate to identify global absolute hardness with operational chemical hardness, but as importantly it does not appear to be a significant component of it. Given the very small correlation coefficient, even should more accurate absolute global hardnesses be determined, they would be unlikely to yield significant correlation. On the other hand, the hardness to which the atoms equalize does show a significant correlation ($r = 0.787$) with the operational chemical hardness. This data set, however, includes both monatomic and polyatomic bases. Thus the correlation coefficient reflects the correlation of both the local absolute hardness of the donor atom as well as the hardness to which all the atoms equalize. To more accurately assess the correlation of the latter with the operational chemical hardness, only polyatomic species were considered in the correlation, and the correlation coefficient dropped to 0.614. It would thus appear that there is a very poor correlation between the operational chemical hardness and the absolution hardness to which the atoms equalize. It cannot therefore, be equated with chemical hardness.

Operational Chemical Hardness and Ionic Character. The hard−soft acid−base model, the charge versus frontier control model, and the ionic−covalent model all cite the tendency of an acid or a base to form ionic versus covalent bonds as being determinant in its reactivity. In the hard−soft acid−base model, chemical hardness is associated with the preference to form ionic bonds, whereas softness is associated with a preference to bind covalently. Thus for these metathesis reactions, those which increase the ionicity of the bond to the harder base should be favored over those which decrease the ionicity of the bond to the harder base.

The difference in the charges carried by the atoms forming a bond is a measure of the ionicity of that bond. The atomic charges have been computed for the donor atoms of the bases and the discriminating acids to which they are bonded, Table 3. It is interesting to note that the donor atoms carry a very large range of charges, Table 2. It has been shown that donor atom charge correlates strongly with the overall strength of acids and bases,[9−11] but there is virtually no correlation with the operational hardness of these bases ($r = 0.263$). There is a very large range in the ionicities of the bonds formed between the base and the discriminating acid. Yet the bond ionicity correlates very poorly with the operational chemical hardness ($r = -0.632$ for the hydrides and $r = -0.783$ for the chlorides).

This notwithstanding, in the ionic-covalent and the frontier versus charge control interpretation of chemical hardness, it is not the bond ionicity which is determinant, but rather the preference to form predominantly ionic or predominantly covalent bonds. Thus the changes in ionicity which occur during the metathesis reactions are listed in Table 3. Although there is a very large range in operational chemical hardnesses, a very large range in charge transferred and a very large range in bond ionicities, the change in the bond ionicity in the metathesis reactions is surprisingly constant. The average change in bond ionicity is 0.768 with a standard deviation of 0.065. There also appears to be little if any correlation between the operational chemical hardness and the change in the bond ionicity ($r = 0.221$). The group IA metals were not included.

These results would seem to suggest that chemical hardness is not significantly associated with a preference for forming ionic or a preference for forming covalent bonds. This is in stark contrast to the prevalent interpretations, but is consistent with the nature of absolute hardness, which has less to do with the bond formed and more to do with the energetics of the remaining electrons of the base.

TABLE 3: Ionicities of the Donor Atom−Hydrogen Bond, the Donor Atom-Chlorine Bond and the Change in Ionicity During the Metathesis Reaction

species	bond ionicity (D−H)	bond ionicity (D−Cl)	change in ionicity
F^0	−1.278	−0.518	−0.760
F^-	−1.016	−0.289	−0.730
$O\mathrm{Cl}^-$	−0.853	−0.027	−0.826
$O\mathrm{NO_2}^-$	−0.858	−0.005	−0.853
$O\mathrm{H}^-$	−0.789	+0.022	−0.767
Cl^0	−0.854	+0.000	−0.854
$O\mathrm{NO}^-$	−0.839	+0.000	−0.839
I^0	−0.702	+0.030	−0.732
Cl^-	−0.820	+0.000	−0.820
OO^-	−0.614	+0.198	−0.812
O^-	−0.992	−0.268	−0.654
Br^-	−0.812	+0.078	−0.890
N^-	−0.760	+0.022	−0.782
$C\mathrm{Cl_3}^-$	−0.042	+0.775	−0.733
$C\mathrm{N}^-$	+0.044	−0.760	−0.716
Br^0	−0.728	+0.196	−0.924
I^-	−0.574	+0.122	−0.696
$C\mathrm{FClCF_2Cl}^-$	+0.050	+0.786	−0.736
$C\mathrm{Cl_2F}^-$	+0.083	+0.818	−0.735
$C\mathrm{H_2CF_2Cl}^-$	−0.063	+0.666	−0.723
$C\mathrm{HCl_2}^-$	+0.007	+0.732	−0.725
$C\mathrm{H_2Cl}^-$	−0.027	+0.688	−0.715
$C\mathrm{ClF_2}^-$	+0.125	+0.861	−0.736
$C\mathrm{F_3}^-$	+0.166	+0.904	−0.738
$C\mathrm{H_3}^-$	−0.061	+0.646	−0.707
$C\mathrm{H{=}CH_2}^-$	−0.048	+0.656	−0.704
$C\mathrm{H_2CH_2Cl}^-$	−0.057	+0.654	−0.711
$C\mathrm{HClF}^-$	+0.050	+0.774	−0.724
$C\mathrm{HCl}^-$	−0.154	+0.568	−0.722
$C\mathrm{H_2}^-$	−0.188	+0.523	−0.711
$C\mathrm{Cl_2}^-$	−0.120	+0.612	−0.732
$C\mathrm{H_2F}^-$	+0.016	_0.731	−0.715
$C\mathrm{H_2CH_3}^-$	−0.055	+0.650	−0.705
$C\mathrm{HF_2}^-$	+0.092	+0.817	−0.725
$N\mathrm{O}^-$	−0.360	+0.427	−0.787
$C\mathrm{HFCH_3}^-$	+0.024	+0.734	−0.710
CO^-	+0.136	+0.852	−0.716
$C\mathrm{H_2CH_2OH}^-$	−0.074	+0.634	−0.708
$C\mathrm{(O)CH_3}^-$	+0.076	+0.786	−0.710
P^-	−0.580	+0.234	−0.814
H^-	+0.000	+0.820	−0.820
$B\mathrm{Cl_2}^-$	+0.296	+1.055	−0.759
$B\mathrm{F_2}^-$	+0.443	+1.213	−0.770
B^0	−0.144	+0.684	−0.828
Hg^-			
$B\mathrm{Br_2}^-$	+0.189	+0.939	−0.750
Si^-	−0.446	+0.398	−0.844
Mg^-	+0.066	+0.960	−0.894
$B\mathrm{O}^-$	+0.341	+1.104	−0.763
Be^-	+0.022	+0.832	−0.810
B^-	+0.272	+0.522	−0.794
Na^-	+0.498	+1.502	−1.004
Al^-	−0.204	+0.684	−0.888
Ca^-	+0.180	+1.102	−0.922
Li^-	+0.468	+1.548	−1.05
K^-	+0.542	+1.653	+1.114
Cs^-			

Operational Chemical Hardness and Electronegativity. In the literature a number of molecular and atomic properties have been reported to correlate with chemical hardness. Pearson reports that bases with donor atoms of low polarizability and high electronegativity, and which are difficult to reduce and have only high-energy vacant orbitals, should be hard.[4] With the exception of the last, all of these properties are those of the donor atom, which is in contrast to the operational definition of absolute hardness which is a global property, eq 4.[4,7,8]

The correlation of chemical hardness with the absolute electronegativity of the donor atom has a long standing history. In most cases the Pauling or absolute electronegativities are considered. The absolute electronegativities of Hinze and Jaffe,[12,13] do in fact correlate ($r = 0.876$) with the operational chemical hardness as evidenced by the data in Table 2. Whereas the absolute electronegativity, χ_0 is by definition independent of charge

$$\chi_0 = \left[\frac{\partial E}{\partial q}\right]_{q=0} \tag{9}$$

the actual electronegativity is dependent on the charge carried by the donor atom

$$\chi = a + bq \tag{10}$$

Furthermore, the operational chemical hardness would seem to be charge dependent as evidenced by the fact that the neutral bases have larger operational chemical hardnesses than their corresponding anions. This notwithstanding, within a group of bases having the same donor atom there appears to be no correlation between the charge carried by the donor atom and operational chemical hardness, Table 2. In the case of oxygen bases, the correlation coefficient is 0.396 and for carbon bases it is 0.399. That there should be virtually no correlation between the operational chemical hardness and the charge on the donor atom is problematic and suggests that its correlation with the absolute electronegativity might in reality be coincidental.

Operational Chemical Hardness and Local Absolute Hardness. In eq 10 the absolute electronegativity is identified with a, and the absolute hardness with $b/2$. Furthermore, there is a strong correlation between a and b. Thus, if the absolute electronegativity of the donor atom correlates with the operational chemical hardnesses, then the absolute hardness of the donor atom should also correlate with the operational chemical hardnesses. This is in fact the case ($r = 0.933$). It is significant that the absolute hardness of the donor atom should correlate more strongly than its absolute electronegativity. If the operational chemical hardness derives from the absolute electronegativity, and its correlation with the absolute hardness derives from the imperfect correlation of absolute hardness and electronegativity, the absolute hardness must correlate less strongly. It is not conclusive, but these results would suggest that the chemical hardness derives from the absolute hardness of the donor atom, rather than its absolute electronegativity. A correlation of 0.933 is comparable to the correlations observed among the operational chemical hardnesses derived from the various pairs of discriminating acids, thus it is unlikely that any stronger correlation might be found. Although it appears that the local absolute hardness is most closely associated with the operation chemical hardness, it is still the case that atoms having the same donor atom exhibit a range of operational hardnesses. One, but certainly not the only, interpretation is that the second component of the extrinsic strength is responsible for the weak correlation. The other is that the local absolute hardness of the donor atoms is perturbed by the molecular environment. It is curious, however, that although the hardness of atoms equalize upon chemical combination, the hardness of isolated atoms appear to influence reactivity.

The Operational Chemical Hardness of Acids. From an intuitive standpoint, more is understood about the relative chemical hardness of bases than about the relative chemical hardness of acids. The relative chemical hardnesses of the bases in Table 1 are, with few exceptions, in agreement with those reported by others. Consider the metathesis reaction in eq 4, but let A and A′ be Lewis bases and B and B′ be Lewis acids. For the data in Table 1, the hydrogen becomes the reference acid, and chloride and hydride become the discriminating bases. Hydride is of course the softer base. The species in Table 1 become their cations or dications, and are Lewis acids. The donor electron orbital becomes the acceptor orbital. The result is that the corresponding acids in table one are now listed in order of increasing hardness. This result is independent of any particular data set, and can be stated as a general result.

The removal of the two donor electrons from a Lewis base of high operational chemical hardness yields an acid of low operational chemical hardness. The removal of two donor electrons from a base of low operational chemical hardness yields an acid of high operational chemical hardness.

This result is somewhat surprising considering the properties originally ascribed by Pearson[4] to hard and soft acids and bases. Hard bases have donor atoms of low polarizability, and hard acids are nonpolarizable. Hard bases have donor atoms of low polarizability, and soft acids have acceptor atoms that are polarizable. The other properties lead to the same conclusion that hard bases should yield hard acids and soft bases should yield soft acids.

It is perhaps not surprising that the operational chemical hardness of acids and their derivative bases should be so closely related. As is the case for Lewis bases, the chemical hardness of acids derives not from the properties of the bond formed or from the frontier orbitals, but rather from the absolute hardness of the acceptor atom. Whereas the operational chemical hardness of bases correlates with the absolute hardness of the donor atom, there is a negative correlation with the absolute hardness of the acceptor atom. This behavior is consistent with the interpretation of absolute hardness which associates it with the response of the remaining (those not being transferred) electrons to those being transferred. In the case of Lewis bases these electrons are deshielded in an acid−base interaction which lowers their energy. This is favorable to the acid−base interaction. On the other hand, for acids the shielding of these electrons increases which raises their energy. This is unfavorable for an acid−base interaction.

Conclusion

Of general interest has been the role of electronegativity in the strengths of acids and bases. Lewis' concept of acids and bases, which identifies them with the transfer of charge, is intimately tied to electronegativity as it was defined by Pauling.[22] The energetics of the acid−base interaction are also intimately tied to electronegativity by the definition of Ickowski and Margrave.[23] It has been shown that the components of the electronegativity function, which are the global and local absolute electronegativities and hardnesses, have very significant roles in determining the Bronsted acid and base strength of molecules.[8−11]

The hard−soft acid−base model partitions the strength of acids and bases into intrinsic and extrinsic components.[4] The partitioning into intrinsic and extrinsic components does not appear to be an universally adopted practice in the application of the hard−soft acid−base model. The identification of this extrinsic component, which is called the chemical hardness, with the global absolute hardness of density functional theory has proven problematic.[8] This has prompted a detailed examination of both absolute and chemical hardnesses. The nature of chemical hardness has been examined in some detail. To do this it has been necessary to develop an operational definition of chemical hardness, and Pearson's Principle of hard and soft acids and bases has been taken as such an operational definition. The enthalpies of a series of metathesis reactions have provided a means of quantitatively determining the relative extrinsic strength. It appears that, although the extrinsic strength derives from at least two properties of both the acids and the bases, it is dominated by the chemical hardness.

Whereas the absolute hardness has been shown to arise from the response of electrons not directly involved in the bond formed between the acid and base,[8] the predominant interpretation of chemical hardness is that it arises from the nature of the bond formed during an acid−base interaction. It would thus appear that absolute hardness and chemical hardness, as commonly understood, are fundamentally different.

Yet the operational chemical hardness which is dominated by the chemical hardness appears to be unrelated to the polarity of the bond formed or to a preference to form ionic versus covalent bonds during an acid−base interaction. That there is a correlation between operational chemical hardness and the absolute the electronegativity of the donor atom would seem to suggest that bond polarity is a component of chemical hardness. This correlation may be coincidental, however. There exists an even stronger correlation between operational chemical hardness and the absolute hardness of the donor atom. This would suggest that, contrary to the common interpretation, both the absolute hardnesses and the chemical hardness derive from the electrons not involved in bond formation. Furthermore, this interpretation of chemical hardness requires that upon removal of the two donor electrons from a hard base a soft acid is formed. This is in fact what is observed. On the other hand the commonly accepted interpretations of chemical hardness would suggest that a hard base should yield a hard acid upon the removal of the donor electrons.

Finally, the operational absolute hardness, which is a global hardness associated with the response of all the other electrons in the molecule to the transfer of charge and is otherwise know as inductive stabilization, is determinant in the overall strength of acids and bases.[10,11] The global absolute hardness would appear to be a component of the intrinsic strength and is not determinant in chemical hardness. Rather, it is the response of only the electrons of the donor or acceptor atom which determines chemical hardness.

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