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Hard/soft-acid/base principle and the reaction $A_hB_s+A_sB_h \rightarrow A_hB_h+A_sB_s$

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The concept of hardness or softness of acids and bases, elucidated by Pearson[1,2,4] and Parr and Pearson,[3] has been very useful in discussing acid-base interactions.[5,6] The hard/soft-acid/base (HSAB) principle is that hard acids prefer binding with hard bases and soft with soft, and that the hard-hard bonds are generally more ionic and the soft-soft bonds generally more covalent. A mathematical derivation of the principle would be of great heuristic value. Recently Ayers[7] and Chattaraj and Ayers[8] have put forth such a proof, and concluded from it that the basis of the principle is electron transfer. It involves showing that the energy of $A_hB_h+A_sB_s$ is lower than the energy of $A_hB_s+A_sB_h$, where A_h is a hard acid, B_h is a hard base, A_s is a soft acid, and B_s is a soft base. In this note, we point out problems with the proof, some of which have been recognized in print.[9] (The conclusion about the importance of electron transfer has also been modified.[9]) We also emphasize that a proof or explanation of the HSAB principle based on an oversimplified model for bond energies is of doubtful utility.

The assumptions in the proof are first reviewed. The hardness of an atom, ion, or group is defined as the second derivative of the electronic energy with the number of electrons added δ at $\delta=0$ and the chemical potential as the first derivative.[3] Assuming that the dependence of the energy of the atom or group on δ is quadratic, one has

$$E(\delta) = E(0) + \mu\delta + \tfrac{1}{2}\eta\delta^2, \tag{1}$$

where μ is chemical potential and η is hardness. Considering that $E(1)=E(0)-A$ (A=electron affinity, $A \geqslant 0$) and $E(-1)=E(0)+I$ (I=ionization potential, $I>0$), it is easy to show that

$$\eta = -A + I, \tag{2}$$

$$\mu = -\frac{I+A}{2}. \tag{3}$$

It is further assumed[7] that the energy of the bond formed between the acid A and the base B is approximated by

$$\Delta E_{AB} = [E_A(\delta) + E_B(-\delta)] - [E_A(0) + E_B(0)] = (\mu_A - \mu_B)\delta + \tfrac{1}{2}(\eta_A + \eta_B)\delta^2. \tag{4}$$

Minimizing this expression with respect to δ, one obtains

$$\delta = (\mu_B - \mu_A)/(\eta_A + \eta_B), \tag{5}$$

which leads to

$$\Delta E_{AB} = -\frac{(\mu_A - \mu_B)^2}{2(\eta_A + \eta_B)}, \tag{6}$$

which is always negative.

The bond energy difference $\Delta\Delta E$ for the exchange reaction $A_hB_s+A_sB_h \rightarrow A_hB_h+A_sB_s$ is now calculated using Eq. (6) for each compound. Since both acid-base pairs are made from the same acids and bases, one has

$$\Delta\Delta E = E(A_hB_h + A_sB_s) - E(A_hB_s + A_sB_h), = \Delta E_{A_hB_h} + \Delta E_{A_sE_{B_s}} - \Delta E_{A_hB_s} - \Delta E_{A_sB_h}. \tag{7}$$

The HSAB principle will be demonstrated if it can be shown that $\Delta\Delta E$ is always negative. To simplify Eq. (7), it is assumed[7] that both acids have the same chemical potential μ_A, that both bases have the same chemical potential μ_B, that A_s and B_s have the same hardness η, and that A_h and B_h have the same hardness $\xi\eta(\xi>1)$. Then Eq. (7) can be simplified into a form which is negative definite thus proving[7] the theorem. However, there are several problems with this.

First, the above assumptions[7] about the chemical potentials and hardnesses may lead to an incorrect prediction of ionic character. With the assumption that $\mu_B-\mu_A$ is the same for all acid-base pairs, Eq. (5) predicts a smaller value of δ for hard acid-base bonds than for soft acid-base bonds. If A and B are electrically neutral, smaller δ means a lower ionic character, exactly the opposite of what the HSAB principle predicts. This points to an inconsistency in the assumptions used to simplify Eq. (7): one cannot make arbitrary assumptions about the values of μ and η because the two quantities are related, as shown in Eq. (2) and (3). Since I is usually large compared to A, a large (positive) value of η is generally associated with a large (negative) value of μ.

We attempted to find less stringent restrictions on the values of μ and η, consistent with Eqs. (2) and (3), which would force $\Delta\Delta E=E(A_hB_h+A_sB_s)-E(A_hB_s+A_sB_h)$ to be negative, proving the HSAB principle. Thus, we calculated μ and η for each species (A_h, B_h, A_s, and B_s) in terms of I and A for that species. Then we varied the four ionization potentials and the four electron affinities, imposing one or more of the restrictions mentioned below, to determine whether $\Delta\Delta E$ could become positive.

The first restriction tried was that both A_h and B_h had higher hardnesses than either A_s or B_s. The next was that the chemical potentials of both acids were lower (more negative) than the chemical potential of either base. Subsequently, we required that the chemical potentials of the acids be at least 1 eV more negative than the chemical potentials of the

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TABLE I. Values of ionization potentials and electron affinities making $\Delta\Delta E$ positive.

Species	I (eV)	A (eV)	μ (eV)	η (eV)
A_h	5.0	1.5	−3.25	3.5
B_h	4.0	0.0	−2.0	4.0
A_s	4.25	1.75	−3.0	2.5
B_s	2.5	1.0	−1.75	1.5

bases. Then a similar requirement was imposed on the hardnesses of A_h and B_h relative to the hardnesses of A_s and B_s. In all cases, $\Delta\Delta E$ could be made positive with reasonable values for ionization potentials and electron affinities. An example is shown in Table I.

Recently, Chattaraj and Ayers[8] have shown that if one requires that the two acids have the same "intrinsic strength" and that the two bases have the same intrinsic strength, $\Delta\Delta E$ is necessarily negative. [The intrinsic strength is the chemical potential, given by Eq. (3), so that one expects $\mu_A < \mu_B$; in fact, $\Delta\Delta E$ in this case is proportional to $(\mu_A - \mu_B)^2$, so the sign of $\mu_A - \mu_B$ is irrelevant.] Then for any values of acid and base hardnesses such that $\eta_{A_s} < \eta_{A_h}$ and $\eta_{B_s} < \eta_{B_h}$, it can be shown algebraically that $\Delta\Delta E < 0$. It is concluded[9] that the HSAB principle is valid when "the difference in the intrinsic strength of the acids and bases… is not too large," as has been recognized elsewhere.[5,10] This raises the question of what "not too large" means: in our table, the chemical potentials of B_h and B_s differ by 1/4 eV and those of A_h and A_s by 1/4 eV.

Although it is gratifying that Eq. (7), under the proper circumstances, can lead to results in accord with reality, simple considerations suggest that the HSAB principle should not be derived by consideration of $\Delta\Delta E$ if $\Delta\Delta E$ is calculated using an oversimplified formula such as Eq. (6) for the bond energy ΔE_{AB}. First, the HSAB principle is not simple.[5] Second, Eq. (6) is incomplete. While the energy of electron transfer certainly contributes to the bond energy in the context of atoms in molecules, there are other contributions[3] which are equally important. For instance, transfer of δ electrons from a neutral base to a neutral acid must result in an electrostatic contribution to the bond energy of the form $-C\delta^2$, where assuming the dielectric constant of vacuum and a bond length of 200 pm, $C = 7.2$ eV. [Including this term in the bond energy changes the denominator of Eq. (6) to $\{\eta_A + \eta_B - C\}$ but is of no help in repairing the problems with Eq. (7).] An exchange-correlation contribution to the bond energy must also be included. Third, one should really be calculating free energies of reaction ΔG_{AB} instead of ΔE_{AB}, and ΔG_{AB} has important contributions from nonelectronic energy, as well as from solvation energy when reactions are carried out in solution.

If Eq. (6) led to useful and general conclusions about bond energies and HSAB, it would be appropriate to justify the neglect of additional contributions and other terms, or to argue that they cancel. Unfortunately, it does not. Early on, Pearson[2] emphasized that "no one factor seems universally responsible" for HSAB behavior, an observation which seems[5] very *apropos*. Even when an oversimplified model can be made to give conclusions in accord with the principle, it should not be considered as a "proof" or used as a basis for other conclusions.

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