11.11 Å. With the stronger Lewis base dimethyl sulfide, $B_9H_{13}CO$ can be converted into $B_9H_{13}SMe_2$ at temperatures above 40° with loss of CO as ligand. The reactions of $B_9H_{13}CO$ with amines are more complex and CO seems to be retained probably forming carbonic acid derivatives.[10,22]

(22) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 59, 780 (1937).

Registry No. $B_9H_{13}CO$, 40583-41-3; *i*-B_9H_{15}, 12447-79-9; KB_9H_{14}, 39296-28-1; $B_9H_{13}SMe_2$, 32357-02-1; CO, 630-08-0; dimethyl sulfide, 75-18-3.

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Correspondence

On Pearson's Quantitative Statement of HSAB

Sir:

A recent report[1] of a quantitative test of the HSAB concept was followed by an article taking exception to the test.[2] The issues raised have clouded the picture, made our criticisms appear semantic, and prompted this response. The hard–soft model has its basis in arguments which are related to the strength of bonding. It is then applied and offered as an explanation for observations on systems in which kinetic control, entropy of adduct formation, solvation effects (enthalpic and entropic), ion-pairing effects (enthalpic and entropic), or lattice energy effects (enthalpic and entropic) are large and could even dominate the observation. When HSAB considerations are employed on these systems, one is implying that the soft–soft or hard–hard interactions, which supposedly influence the bonding, dominate the chemistry. The *E* and *C* approach should not be viewed as an alternative to this kind of science. The *E* and *C* model does predict the strength of interaction quantitatively on systems in which the data employed are related to the strength of binding. If the HSAB ideas are correct models for the strength of bonding, it must be capable of being expressed in a mathematical form and do well on data related to the strength of interaction. If it does not, it should be discarded and replaced by a more correct interpretation of the strength of binding. This was the object of our previous note.

Knowledge of the factors influencing the strength of interaction is important in correlating trends in reactivity and in suggesting new syntheses or experiments. This has been amply demonstrated by the wide acceptance and utilization of the HSAB ideas. The more correct model should be even more powerful in this kind of application.

Pearson took issue with our quantitative statement of the rule that "hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases" with the equation[2a]

$$-\Delta H = H_A H_B + (K - H_A)(K' - H_B) \tag{1}$$

This rather obvious mathematical translation of the above rule was criticized because we failed to incorporate intrinsic strength. As mentioned in the note added in proof,[1] in a vast majority of the qualitative applications of HSAB, strength is not considered, so, apparently, the authors believe that just hard and soft work well most of the time. We felt that if the concept was correct and was being correctly applied (most of the time), eq 1 should work well most of the time on data related to the strength of bonding. It did not. Next, we shall examine whether or not the situation can be rectified with intrinsic strength as has been suggested.[2]

We shall refer to the addition of strength as the HSSAB (hardness, softness, strength) theory. The procedures to be employed for the introduction of strength have never been clearly elucidated.[3] The qualitative rationalization of results with HSAB can either work or not work. If it does not work, the failure can be attributed to strength. Thus, one can never miss, but, alas, the whole approach can never be tested. Since there is no chance ever to fail or to test the approach, there is no way to determine if any of this corresponds to reality. This apparent advantage for after the fact rationalization devastates the predictive power of the theory. Since we have not been provided with tables of strength, how can we predict anything? In qualitative use, how do we know the relative importance of hardness and softness *vs.* strength, *i.e.*, when do we know which one to use or ignore? Furthermore, if one reads all of the quantum mechanical explanations of hardness and softness, one wonders what is left over to give an enthalpy contribution for this term called strength. Since hardness and softness as employed in HSAB have a magnitude, there is some strength of bonding associated with these effects.

Again, since the matter has never been clearly defined, it is difficult to see how Pearson's quantitative statement[2] of HSAB can possibly work. Since we have not been told how this quantitative statement is to work, we must examine all possibilities to see if it will. If we substitute $-\Delta H$ for log *K* (these terms are used interchangeably in HSAB), we can write his equation as

$$-\Delta H = S_A S_B + \sigma_A \sigma_B \tag{2}$$

where "$\sigma_A \sigma_B$ is hardness or softness."[2] An equation of this form must fit the enthalpy data as well as our *E* and *C* equation

$$-\Delta H = C_A C_B + E_A E_B \tag{3}$$

However, can parameters be found for eq 2 which are *consistent with our qualitative intuition about hardness, softness, and strength*? The equalities recently made,[2] $C_A = \sigma_A$, $C_B = \sigma_B$, $E_A = S_A$, and $E_B = S_B$, are surely incorrect. The $(C_2H_5)_2S$-I_2 adduct would have a large softness contribution and work well, but everything we view as being mainly electrostatic, *e.g.*, $(C_2H_5)_2O$-C_6H_5OH, would have to

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(1) R. S. Drago and R. A. Kabler, *Inorg. Chem.*, 11, 3144 (1972).

(2) R. G. Pearson, *Inorg. Chem.*, 11, 3146 (1972).

(2a) Note Added in Proof. The equation

$$-\Delta H = H_A H_B + (K - H_A)H_B + (K' - H_B)H_A + (K - H_A)(K' - H_B)$$

reduces to $\Delta H = KK'$ and obviously will not work. The equation

$$-\Delta H = H_A H_B + H_A \frac{1}{H_B} + H_B \frac{1}{H_A} + \frac{1}{H_A}\,\frac{1}{H_B}$$

does not work significantly better than those reported in ref 1.

(3) R. G. Pearson, *J. Chem. Educ.*, 45, 585 (1968).

be attributed to what Pearson calls strength. We would then have a softness–strength equation which is simply a way of relabeling our parameters. However, if one accepts this, hardness would be an unnecessary concept for it could not be factored out from strength.

In the same short article in which the above equalities are made, the statement is made[2] that "hardness or softness is σ_A or σ_B." We can also show that this statement must be incorrect. If σ_A were a large number for a hard acid and σ_B a large number for a soft base, the product would be large in violation of the hard prefers hard and soft prefers soft rule. The only way around this problem is to call one positive and the other negative. If hardness were negative, stabilization would result from a hard acid and hard base, but now a destabilization as large as the soft–soft or hard–hard stabilization would result when a hard acid and a soft base are brought together. Physically, this does not make much sense in the current framework of the theoretical explanations of HSAB or HSSAB in the literature. Furthermore, Pearson's claim that even hard substances have some soft character and vice versa cannot be accommodated with the one term $\sigma_A\sigma_B$. In fact, if hardness is negative and softness positive, intermediate acids and bases must be near zero, so $\sigma_A\sigma_B$ would be near zero and there would be practically no hard–hard or soft–soft contribution to adducts with intermediate acids (or bases) reacting with hard or soft bases (or acids). The only remaining possibility that can be considered for eq 2 is that σ is zero for a hard substance and appreciable for a soft substance. If σ is zero for a hard acid or base, for hardness to be an important effect (*i.e.*, something other than zero), it would then have to all be in the other term which is our eq 1. Clearly, no simple transformation of our current set of E and C parameters exists which allows eq 2 to produce a set of parameters *whose interpretation* is consistent with the HSSAB equation proposed by Pearson.[2,3] It may be possible to modify drastically the HSAB approach and eq 2 or its interpretation to be consistent with eq 3, but this seems like wasted effort, since the qualitative ionic-covalent model (E property or C property) works so well.

It is possible to be consistent with our E and C equation and view intermolecular interactions in terms of concepts *we could call* hardness, softness, and strength. However, in doing this, we will have to modify the qualitative ideas presented by Pearson about what hardness and softness mean *vide infra*. The approach involves converting[4] the E and C equation to polar coordinates. Our acids and bases are represented as vectors in E and C space in Figure 1. The dot product of these two vectors is given as $\mathbf{A}\cdot\mathbf{B} = \mathbf{AB}\cos\theta$ where $\theta = \theta_A - \theta_B$. With the enthalpy a scalar, taken as the dot product, we obtain eq 4. Now if we call a large

$$-\Delta H = \mathbf{A}\cdot\mathbf{B}\cos(\theta_A - \theta_B) \qquad (4)$$

number for θ softness and a small number hardness, we can obtain a linear scale for θ consistent with these names.

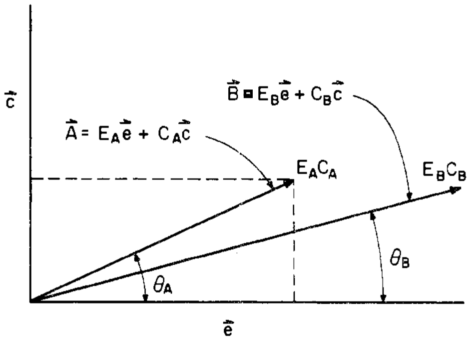

Figure 1. A vector representation of eq 3.

Furthermore, the cosine of the difference is close to 1 whenever θ_A and θ_B are both large or both small (*i.e.*, soft–soft or hard–hard, respectively). Whenever $\theta_A \gg \theta_B$ or $\theta_B \gg \theta_A$, the $\cos(\theta_A - \theta_B)$ is small. The length of the vector (**A** or **B**) can be equated to what Pearson calls intrinsic strength. Thus, eq 4 could be a hardness, softness, and strength equation. With this equation, softness or hardness is given by θ which is the arctan of C/E. The magnitudes (or intrinsic strengths) of the vectors **A** and **B** are given by $\mathbf{A} = \sqrt{E_A{}^2 + C_A{}^2}$ and $\mathbf{B} = \sqrt{E_B{}^2 + C_B{}^2}$. Thus, this result is consistent with our earlier claim[5] that the concept of hardness and softness is a function of the C/E ratio which by itself is meaningless as far as $-\Delta H$ is concerned because the **AB** multiplier, *i.e.*, the length of the vector, is left out. Only when $\mathbf{A}\cdot\mathbf{B}$ is constant in a series can one ascribe differences in the magnitudes of interaction to the nature of the interaction, *i.e.*, hardness and softness. Even then it must be realized that the hardness and softness term as we are using it describes the kind of interaction (*i.e.*, the direction of the vectors) and does not have energy units ($\mathbf{A}\cdot\mathbf{B}$ has units of kcal mol^{-1}).

Since ionic and covalent bonding can have both magnitude and strength and since their relative importance in bonding has been discussed and predicted in a qualitative way for years, we prefer this approach. It appears to be more meaningful, at least to a novice, than always talking about inherent strength and using hard–soft terms that have no magnitude but determine the magnitude of ΔH; *i.e.*, eq 4 is not as simple as the sum of two product terms.

We do not discount the possibility that a two-term, four-parameter equation could be found using trigonometric or other functions which can produce an energy term that becomes large for soft–soft or hard–hard combinations but not for others. Clearly, none has been reported to date and, even if one can be proposed, the objections outlined in the first and fourth paragraphs still pertain.

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[4] This transformation was suggested by Eric Johnson of my research group.

[5] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971).