Correspondence

Reply to the Paper "A Quantitative Evaluation of the HSAB Concept," by Drago and Kabler

Sir:

The above-mentioned paper[1] is alleged to be a quantitative evaluation of the HSAB concept. However, it can hardly be that, since it starts with an erroneous interpretation of the concept. I quote from the article by Drago and Kabler: "the idea that some substances are just stronger acids or bases than others with regard to both covalent and electrostatic interaction invariably is ignored in HSAB."

On the contrary, I have stressed just the opposite in all my writings on the subject and in countless lectures on HSAB (including an American Chemical Society audio course on tape). I quote from two of my articles.[2,3]

"What has been suggested in the previous section is that two properties of an acid or a base are needed to make an estimate of the stability of the complex which they might form. One property is what we might call the intrinsic strength (S_A or S_B), the other is the hardness or softness (σ_A or σ_B)."[2]

"It is still quite possible for a compound formed from a hard acid and a soft base to be more stable than one made from a better matched pair. All that is needed is that the first acid and base both be quite strong."[3]

The equation I have proposed as a possible quantitative statement of HSAB is

$$\log K = S_A S_B + \sigma_A \sigma_B \qquad (1)$$

This is a typical four-parameter equation, two *independent* parameters for both the acid and base. It is most closely related to the Edwards equation[4]

$$\log K = \alpha E_n + \beta H \qquad (2)$$

with $\alpha = \sigma_A$, $E_n = \sigma_B$, $\beta = S_A$, and $H = S_B$. If we were to relate eq 1 to the Drago equation

$$-\Delta H = C_A C_B + E_A E_B \qquad (3)$$

then it is clear that the most consistent interpretation would be $C_A = \sigma_A$, $C_B = \sigma_B$, $E_A = S_A$, and $E_B = S_B$. This is quite different from Drago and Kabler's mysterious decision that C is softness and E is hardness.

This arbitrary decision, of course, reduces the number of independent parameters from 4 to 2. Drago and Kabler then go on to show that none of the two-parameter equations fits the data very well, a result that is hardly surprising.

It must be appreciated that empirical equations such as (3) do not possess unique solutions for the parameters.[5] At least four values must be set beforehand. Two of these simply set the scale. The other two are selected with some model in mind and automatically bias all other values to fit that model. For this reason I doubt that any of the published C values are good measures of hardness or softness.

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

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

(3) R. G. Pearson, *ibid.*, **45**, 645 (1968).

(4) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

(5) See W. L. Jolly, J. D. Illige, and M. H. Mendelsohn, *Inorg. Chem.*, **11**, 867 (1972), and D. R. McMillin and R. S. Drago, *ibid.*, **11**, 872 (1972), for two quite different sets of E and C values covering the same data.

Complex Formation of Trimethylamine with Silane, Disilane, and Trisilane

Sir:

It has been well established that the Lewis acidity of silanes depends on the substituents. While adduct formation was not observed between SiH_4 and pyridine or $(CH_3)_3N$,[1] stable complexes have been formed between $ClSiH_3$,[1,2] $ISiH_3$,[1,3] and many other halosilanes with pyridine and $(CH_3)_3N$.

There have been at least three rationalizations of experimental data based on the suggestion that, during nucleophilic attack, a disilane (or disilanyl group) is a stronger Lewis acid than a monosilane (or silyl group).[4-6]

In this correspondence we report evidence for such an order of Lewis acidities.

(1) **SiH_4-$N(CH_3)_3$.**—Evidence for an interaction between SiH_4 and $N(CH_3)_3$ arises from the following result. A mixture of SiH_4 and $N(CH_3)_3$ (0.76 mmol each) was condensed into a "U" trap at −196°. The −196° bath was removed and replaced with a −78° bath. The pressure rose rapidly to 131 mm after 26 sec, then dropped to 96 mm after a total of 33 sec, and then slowly rose to 142 mm. This sequence was repeated a number of times. The results can be explained by an initial vaporization of SiH_4, followed by complex formation with $N(CH_3)_3$, followed by decomposition of the complex as the temperature increased from −196 toward −78°. Further evidence for such an interaction between SiH_4 and $N(CH_3)_3$ can be derived from the following data. At −130 and −119°, where the vapor pressure of $N(CH_3)_3$ is essentially zero, the total pressure of a mixture of $N(CH_3)_3$ and SiH_4 (0.76 mmol each) was 25 and 56 mm, respectively. The total pressure of the same neat SiH_4 at these temperatures was 112 and 118 mm, respectively. At −78°

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(1) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1508 (1966).

(2) H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).

(3) B. J. Aylett, H. J. Emeleus, and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 187 (1955).

(4) C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 744 (1964).

(5) F. K. Cartledge, *J. Organometal. Chem.*, **13**, 516 (1968).

(6) A. J. Vanderwielen and M. A. Ring, *Inorg. Chem.*, **11**, 246 (1972).