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

$$\log K = S_{\mathrm{A}}S_{\mathrm{B}} + \sigma_{\mathrm{A}}\sigma_{\mathrm{B}} \qquad (1)$$

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]

$$\log K = \alpha E_{\mathrm{n}} + \beta H \qquad (2)$$

with $\alpha = \sigma_{\mathrm{A}}$, $E_{\mathrm{n}} = \sigma_{\mathrm{B}}$, $\beta = S_{\mathrm{A}}$, and $H = S_{\mathrm{B}}$. If we were to relate eq 1 to the Drago equation

$$-\Delta H = C_{\mathrm{A}}C_{\mathrm{B}} + E_{\mathrm{A}}E_{\mathrm{B}} \qquad (3)$$

then it is clear that the most consistent interpretation would be $C_{\mathrm{A}} = \sigma_{\mathrm{A}}$, $C_{\mathrm{B}} = \sigma_{\mathrm{B}}$, $E_{\mathrm{A}} = S_{\mathrm{A}}$, and $E_{\mathrm{B}} = S_{\mathrm{B}}$. 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).

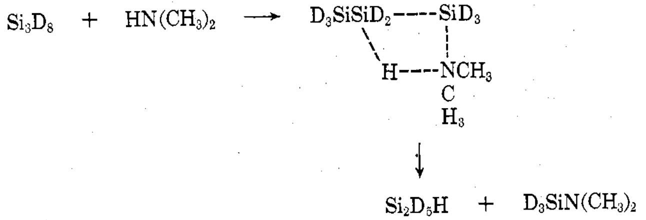
[6] A. J. Vanderwielen and M. A. Ring, *Inorg. Chem.*, **11**, 246 (1972).

the total pressure of this mixture was very close to that expected without an interaction between SiH_4 and $N(CH_3)_3$.

(2) **Si_2H_6–$N(CH_3)_3$, Si_3H_8–$N(CH_3)_3$.**—The vapor pressures of equimolar mixtures of $N(CH_3)_3$ and either Si_2H_6 or Si_3H_8 were below those calculated by Raoult's law. For Si_2H_6–$N(CH_3)_3$, the vapor pressures were 0.79, 0.71, and 0.57 of that calculated by Raoult's law at -63, -78, and $-95°$, respectively. For Si_3H_8–$N(CH_3)_3$, the vapor pressures were 0.54 and 0.29 of that calculated by Raoult's law at -63 and $-78°$, respectively. A Si_3H_8–$N(CH_3)_3$ mixture (0.55 mmol each) was maintained at $-78°$ and allowed to distil into a trap cooled to $-196°$. After 1 hr only 5% of the mixture remained while after 2 hr nothing remained in the $-78°$ trap.

These data demonstrate that weak complex formation does occur between $N(CH_3)_3$ and Si_2H_6 or Si_3H_8. Further, the data with all three silanes indicate an increase in the interaction between $N(CH_3)_3$ and the silanes in the order $SiH_4 < Si_2H_6 < Si_3H_8$. This order should be a measure of the relative Lewis acidities of the silanes with $N(CH_3)_3$ as the reference base.

(3) **Reaction of Si_3H_8 with $HN(CH_3)_2$.**—The above conclusion is also consistant with the following results. The vapor pressure of a $HN(CH_3)_2$–Si_2H_6 mixture was less than calculated by Raoult's law. While no reaction was observed between $HN(CH_3)_2$ and Si_2H_6, Si_2H_6 (0.44 mmol) was produced from the 1 hr reaction of Si_3H_8 with $HN(CH_3)_2$ at $-78°$. The other product (0.44 mmol) was $SiH_3N(CH_3)_2$ identified by its infrared,[7] nmr,[8] and mass spectrum. The above experiment was repeated with $HN(CH_3)_2$ and Si_3D_8 yielding Si_2D_5H[9] and $D_3SiN(CH_3)_2$. The infrared spectrum of $D_3SiN(CH_3)_2$ contained only Si–D stretching bands. The results from the reaction with Si_3D_8 suggest the mechanism



In the above mechanism the disilanyl group acts as a halogen.[10] The occurence of this reaction with

$$SiH_3Br + HN(CH_3)_2 \longrightarrow HBr + H_3SiN(CH_3)_2 \qquad (1)$$

Si_3H_8 but not with Si_2H_6 (under the same conditions) can be explained by an increased Lewis acidity of Si_3H_8 compared to Si_2H_6.

Acknowledgment.—The authors are indebted to the Army Research Office for financial support.

(7) M. J. Butler and D. C. McKean, *Spectrochim. Acta*, **21**, 485 (1965).

(8) E. A. V. Ebsworth and N. Sheppard, *J. Inorg. Nucl. Chem.*, **9**, 95 (1959).

(9) M. A. Ring, G. D. Beverly, F. H. Koester, and R. P. Hollandsworth, *Inorg. Chem.*, **8**, 2033 (1969).

(10) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, **76**, 4631 (1954).

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Acid-Catalyzed Substitution of OH^- in the Hydrogen Chromate(VI) Anion by Various Ligands. Free Energy Relationships and Mechanistic Considerations[1]

Sir:

Oxidation–reduction reactions involving the chromium(III)–chromium(VI) couple have been extensively investigated.[2] In many instances, the initial step in the reduction of the hydrogen chromate anion involves the formation of a chromium(VI)–substrate complex. In recent years, mostly through the work of Haight, Beattie, and coworkers, kinetic and thermodynamic information about these chromium(VI)–substrate complexes has become available.[3,4] It is the purpose of this note to point out the existence of a linear free energy relationship between the kinetic and the equilibrium data for the formation and dissociation of the complexes, and to make some comments about the mechanism of substitution at the chromium(VI) center.

All of the reactions under consideration can be represented by eq 1 or 2. A stoichiometric distinction be-

$$X^{n-} + HCrO_4^- + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + CrO_3X^{n-} \quad Q \qquad (1)$$

$$HX^{n-} + HCrO_4^- + H^+ \underset{k_r'}{\overset{k_f}{\rightleftharpoons}} H_2O + CrO_3X^{(n+1)-} + H^+ \quad Q' \qquad (2)$$

tween these two types of reactions is made depending upon whether hydrogen ions are consumed (forward reaction in eq 1) or act as catalytic agents (eq 2). However, there is no kinetic difference between the two classes, the rate law for the forward reactions being given in all cases by eq 3. When the substrate Su is

$$\text{rate} = k_f[HCrO_4^-][H^+][Su] \qquad (3)$$

basic, the reported rate law has the form ($HSu^+ = HCrO_4^-, HS_2O_3^-$)[3,5]

$$\text{rate} = k_f'[HCrO^-][HSu^+] \qquad (4)$$

However, using the known ionization constants of the weak acids HSu^+, we have chosen to recast these rate laws in the form of eq 3. In this manner, the reactions of the chromate and thiosulfate ions can be compared directly with the reactions of the remaining substrates.

The available values of k_f, k_r, and Q[6] are presented in Table I. It will be seen that the chromium(VI) center exhibits a strong equilibrium discrimination toward the various substrates (*ca.* 10^7), but only a modest (a factor of 10) kinetic discrimination toward addition of the substrate. These trends are entirely analogous to those observed previously for the anation reactions of aquopentaamminecobalt(III).[7,8] The wide variation

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(2) For a classic review see F. Westheimer, *Chem. Rev.*, **45**, 419 (1949). For an account of more recent developments, see J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

(3) K. A. Muirhead, G. P. Haight, Jr., and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3006 (1972).

(4) C. Lin and J. K. Beattie, *ibid.*, **94**, 3011 (1972).

(5) J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964).

(6) Unless the equilibrium quotient Q was determined independently, the values of Q are k_f/k_r.

(7) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

(8) A. Haim, *ibid.*, **9**, 426 (1970).