Correspondence

Hard and Soft Acids and Bases?

AIC30830K

Sir:

Ahrland, Chatt, and Davies[1] are generally given credit for the concept of class a and class b acceptors, consisting of metals and metal ions. They stated that class a acceptors are those which form their most stable complexes with the first ligand atom of each group, *i.e.*, with N, O, and F, and class b acceptors are those which form their most stable complexes with the second or subsequent ligand atom. It appears that Schwarzenbach[2] invented the concept earlier, but the publication is so inaccessible as to be unavailable to most of the chemical community.

Ahrland, Chatt, and Davies did very little speculating concerning the underlying causes for the two different categories. They did suggest that class b character appears to depend on the availability of electrons from the lower d orbitals of the metal ion for dative π bonding. They also speculated on the effect of repulsion of nonbonding electron pairs on the donor and acceptor atoms.

Pearson[3-5] has tried to be more explicit about the phenomena underlying the difference between class a and class b, and in addition he has extended the classes so as to include all donor (base) and acceptor (acid) species. He states:[4] "If we examine the class (a) Lewis acids we find that the acceptor atoms are small in size, of high positive charge, and do not contain unshared pairs of electrons in their valence shell (not all of these properties need be possessed by any one acid). Now these are all properties which lead to high electronegativity and low polarizability. It seems appropriate to call such acids "hard". The class (b) Lewis acids, generally speaking, have acceptor atoms large in size, of low positive charge, and containing unshared pairs of electrons (p or d electrons) in their valence shell. These properties lead to high polarizability and low electronegativity. Again it seems reasonable to call these Lewis acids "soft"." The same type of definition and description applies to Lewis bases.

Pearson does not state this explicitly, but there can be little doubt that the terms "hard" and "soft" refer to polarizability, "hard" species having low polarizability and "soft" species high polarizability. In the abstract to ref 3 it is stated that; "class (a) acids prefer to bind to "hard" or nonpolarizable bases. Class (b) acids prefer to bind to "soft" or polarizable bases." This is the feature which comes through to other chemists.[6] He is careful to point out that polarizability is not the only property involved.[5] "It is just because so many phenomena can influence the strength of binding that it is not likely that one scale of intrinsic acid-base strength, or of hardness-softness can exist. It has been a great temptation to try to equate softness with some easily identified physical property, such as ionization potential, redox potential, or polarizability. All of these give roughly the same order, but not exactly the same."

Table I. Molar Polarizability of Ions and Some Neutral Ligands[a]

C^{4-}	5400	Ag^+	4.33	Nb^{5+}	0.66
N^{3-}	72.6	Ba^{2+}	3.94	Ga^{3+}	0.50
Se^{2-}	26	NH_4^+	3.8[b]	I^{7+}	0.49
S^{2-}	26.0	H_2O	3.66[b] ($\mu = 1.85$)	Mo^{6+}	0.48
H^-	25.65	Rb^+	3.57	Ti^{4+}	0.47
C_5H_5N	24.4 ($\mu = 2.2$)	Hg^{2+}	3.14	Na^+	0.46
I^-	18.07	Cd^{2+}	2.74	Ge^{4+}	0.36
CNS^-	17.0[b]	F^-	2.65	V^{5+}	0.31
SO_4^{2-}	14.44[b]	La^{3+}	2.64	As^{5+}	0.26
SO_3^{2-}	~14[c]	Tl^{3+}	2.19	Mg^{2+}	0.24
HS^-	12.5[b]	Sr^{2+}	2.18	Cr^{6+}	0.22
Br^-	12.14	K^+	2.12	Se^{6+}	0.19
Bi^{3+}	12[d]	Ce^{4+}	1.86	Mn^{7+}	0.16
CO_3^{2-}	11.7[b]	In^{3+}	1.84	Br^{7+}	0.15
NO_3^-	10.5[b]	Pb^{4+}	1.56	Al^{3+}	0.14
O^{2-}	9.88	Y^{3+}	1.41	Si^{4+}	0.084
Cl^-	9.30	Sn^{4+}	1.26	Li^+	0.074
Pb^{2+}	9.3[b]	Ca^{2+}	1.19	P^{5+}	0.054
Tl^+	9.2[b]	Bi^{5+}	1.15	S^{6+}	0.036
NO_2^-	8.6[b]	Cu^+	1.08	Cl^{7+}	0.025
CN^-	8.34[b]	Zr^{4+}	0.95	Be^{2+}	0.020
Cs^+	6.15	Sb^{5+}	0.91	B^{3+}	0.0076
NH_3	5.49[b] ($\mu = 1.47$)	Sc^{3+}	0.73	C^{4+}	0.0034
CO	5.0[e] ($\mu = 0.13$)	Zn^{2+}	0.72	N^{5+}	0.0018
Au^+	4.75	Te^{6+}	0.66	H^+	0
OH^-	4.6[b]				

[a] L. Pauling, *Proc. Roy. Soc., Ser. A*, 114 198 (1927), except as noted. [b] S. S. Batsanov, "Refractometry and Chemical Structure," Van Nostrand, Princeton, N. J., 1966. [c] Calculation from mole refraction of Na_2SO_3, subtracting polarizability of $2Na^+ = 0.92$. The crystal is not isotropic, but refraction along the axes is nearly the same, D line of sodium. [d] Calculated from molar refraction of SbF_3, subtracting $3F = 7.95$. [e] Molar refraction, D line of sodium.

However, it is clear from the last sentence above that polarizability is a sufficient criterion for setting up a scale of "hardness" and "softness" and for distinguishing large differences in "hardness" and "softness."

Let us now consider in fact whether polarizability is a criterion for classifying species as "hard" and "soft." Table I gives the molar polarizability of a large number of chemical species. Changing the environment will change the absolute value of the molar polarization, but such changes will not be large and will make only minor changes in the order of the ions. The quoted values for Cl^- range from 8.17 to 9.30. In aqueous solution the values are changed slightly, but the order of ions is the same, with a couple of minor inversions (Batsanov; see footnote *b* to Table I). Also some of the data are for the D line of sodium and some at infinite wavelength. This also makes little change in the value of the molar refraction. There have been continuing efforts to determine polarizability of individual ions. These have given *relative* values essentially in agreement with Table I, but with some inversions. For example Tessman, Kahn, and Shockley[7] suggest that Cu^+ is slightly more polarizable than K^+ but still *much* less than Cs^+ and Pb^{2+}.

Consider, for example, the molar polarizability of Cs^+, which Pearson classifies among the "hardest" of acids. Its polarizability is distinctly greater than that of Ag^+, Hg^{2+}, Tl^{3+}, Pb^{4+}, and Cu^+, all of which are classified as "soft" or

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(1) S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev., Chem. Soc.*, 12, 265 (1958).

(2) G. Schwarzenbach, *Experientia, Suppl.*, 5, 162 (1956).

(3) R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 3533 (1963).

(4) R. G. Pearson, *J. Chem. Educ.*, 45, 581 (1968).

(5) R. G. Pearson, *J. Chem. Educ.*, 45, 643 (1968).

(6) J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York, N. Y., 1972, p 226.

(7) J. R. Tessman, A. H. Kahn, and W. S. Shockley, *Phys. Rev.*, 92, 890 (1953).

borderline by Pearson. What about the effect of oxidation number? Pearson[5] argues that Tl^{3+} is softer than Tl^+, yet the opposite conclusion will be drawn from the polarizabilities. The same is true[5] for Pb^{4+} and Pb^{2+}. In fact, using the polarizability criterion we would conclude that Pb^{2+} is nearly the softest of the cation acids. This is not true. If CN^- is added to a solution of Pb^{2+} one can identify $Pb(OH)_3^-$ in the solution, but there is little evidence[8] for coordination of CN^-, although the latter is one of the "softest" of bases. Pearson also assumes that the presence of unshared pairs of electrons (p or d electrons) in the valence shell leads to high polarizability.[5] This is untrue as shown in Table I, where for example, the polarizability of K^+ is greater than that of either Cu^+ or Zn^{2+}, the latter two having ten d electrons. Yet Pearson classifies Cu^+ as soft and Zn^{2+} as borderline.

One other bit of information can be obtained from Table I. In general the polarizabilities of the cations are so small as compared to the anions that the polarizability of the former can be neglected. An example might be the species ZnI_4^{2-}. This is especially true when we consider that Zn^{2+} has a much greater polarizing effect on I^- than I^- has on Zn^{2+}.

There is a case in which more detailed numerical testing is possible. Pearson[4] proposes an equation of the form

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

to represent acid-base combination. The product $S_A S_B$ is equated with the strength of ionic bonding, the product $\sigma_A \sigma_B$ with covalent bonding. For the combination of "soft" acids with "soft" bases the product $\sigma_A \sigma_B$ is high, the contribution of covalent bonding is high, and the polarizabilities are high. He compares this general equation with the Edwards equation

$$\log (K/K_0) = \alpha E_n + \beta H \qquad (2)$$

and concludes[4] that the product αE_n is to be identified with $\sigma_A \sigma_B$. Edwards gives the values of α for several cations. If polarizability is indeed related to σ_A (or α) then a graph of α *vs.* molar polarizability should show it. Such a graph shows scattered points, with no correlation between α and polarizability.

Ahrland[9] has come to a similar conclusion. He states that ". . .high polarizability alone, without the presence of a well-filled d-shell, does not confer (b)-properties on a metal ion."

Polarizability will, however, enter into bond strength. There is an inherent electrical attraction between a metal ion and the ligand. This attraction will be enhanced by the polarizing effect of the cation on the ligand, such polarization increasing the electrical charge near the metal ion and increasing the force of attraction. But this is an increase in ionic bonding rather than covalent bonding.

Underlying much of the difficulty is an error in a basic assumption: the strength of covalent bonding increases as the polarizability of the atoms increases. As polarizability increases we find that size increases (in general). And as size increases the bond strength decreases (both ionic and covalent). If the polarizability criterion were correct then CsBr would be a very covalent compound (*cf.* data in Table I). The truth is that covalent character increases as electronegativities of the two atoms approach each other.

In summary the following can be said. Pearson has introduced the terms "soft" and "hard" for class b and class a behavior of acids and bases, respectively. He has suggested that "soft" implies high polarizability and "hard" implies low polarizability. The data in this paper show that there is essentially no relation between class a and class b behavior and polarizability, at least for metal ion acceptors. These constitute the major part of the so-called "hard" acids. Consequently the terms "hard" and "soft" should be dropped from our vocabulary, and we should seek an explanation of class a and class b behavior using other concepts. Pearson himself has described some of these briefly in one of his papers.[5]

Drago and Kabler[10] have also suggested, on other grounds, that the designations "hard" and "soft" be given up.

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(8) "Gmelins Handbuch der anorganischen Chemie," Vol. 47, Part C, No. 2, pp 715-716.

(9) St. Ahrland, *Struct. Bonding (Berlin)*, 1, 207 (1966).

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

Kinetics of the Reactions of Sodium Dithionite with Dioxygen and Hydrogen Peroxide

AIC400635

Sir:

The reaction of dioxygen with sodium dithionite was reported by Rinker, *et al.*, to obey the rate law

$$-d[S_2O_4^{2-}]/dt = k_1 [O_2][S_2O_4^{2-}]^{1/2} \qquad (1)$$

with $k_1 = 0.15\ M^{-1/2}\ \mathrm{sec}^{-1}$ at 30° in 0.10 *M* sodium hydroxide.[1] They invoked the following scheme, with eq 3 being rate determining, to rationalize this rate law

$$S_2O_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2SO_2^- \qquad (2)$$

$$SO_2^- + O_2 \xrightarrow{k_3} \text{products} \qquad (3)$$

This scheme, together with $K_2 = 1.4 \times 10^{-9}\ M$,[2] leads to $k_3 = 4.0 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ at 30°.

For some years sodium dithionite has been used to destroy O_2 in studies of oxyhemoglobin dissociation kinetics. In these studies the dithionite-dioxygen reaction is assumed to be very rapid. Concerned by the incompatibility of the results of Rinker, *et al.*, with this assumption, Morello, *et al.*, reinvestigated the reaction of dithionite with dioxygen at 37° in the above medium and found the rate of disappearance of dioxygen to be zero order in dioxygen and first order with respect to dithionite, with the "initial" rate constant $42.5\ \mathrm{sec}^{-1}$.[3] This result is inconsistent with eq 1. It is, however, consistent with the above kinetic scheme (eq 2 and 3) if the rate of production of SO_2^- radicals, $2k_2[S_2O_4^{2-}]$, is rate determining. Most recently Lambeth and Palmer[2] studied the reaction at excess dioxygen in 0.1 *M* sodium hydroxide. They found $k_2 = 1.7\ \mathrm{sec}^{-1}$ at 25° and $8.6\ \mathrm{sec}^{-1}$ at 37°. From analysis of the lag period in the dithio-

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(1) R. G. Rinker, T. P. Gordon, D. M. Mason, R. R. Sakaida, and W. H. Corcoran, *J. Phys. Chem.*, 64, 573 (1960).

(2) D. O. Lambeth and G. Palmer, *J. Biol. Chem.*, 248, 6095 (1973).

(3) J. A. Morello, M. R. Craw, H. P. Constantine, and R. E. Forster, *J. Appl. Physiol.*, 19, 522 (1964).