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Hard and Soft Acids and Bases

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A number of Lewis acids of diverse types are classified as (a) or (b) following the criterion of Ahrland, Chatt, and Davies. Other, auxiliary criteria are proposed. Class (a) acids prefer to bind to "hard" or nonpolarizable bases. Class (b) acids prefer to bind to "soft" or polarizable bases. Since class (a) acids are themselves "hard" and since class (b) acids are "soft" a simple, useful rule is proposed: hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. The explanations for such behavior include: (1) various degrees of ionic and covalent σ-binding; (2) π-bonding; (3) electron correlation phenomena; (4) solvation effects.

In a recent publication[1] the rate data for the generalized nucleophilic displacement reaction were reviewed and analyzed.

$$\mathrm{N} + \mathrm{S{-}X} \longrightarrow \mathrm{N{-}S} + \mathrm{X} \qquad (1)$$

Here N is a nucleophilic reagent (ligand, Lewis base) and S–X is a substrate containing a replaceable group X (also a base) and an electrophilic atom (Lewis acid) S. Other groups may also be bound to S. It was found that rates for certain substrates, S–X, were influenced chiefly by the basicity (toward the proton) of N, and other substrates had rates which depended chiefly on the polarizability (reducing power, degree of unsaturation) of N.

In this paper the equilibrium constants of eq. 1 will be considered, instead of the rates.

$$\mathrm{N\ (base)} + \underset{\text{complex)}}{\mathrm{S{-}X\ (acid{-}base}} \rightleftarrows \underset{\text{complex)}}{\mathrm{N{-}S\ (acid{-}base}} + \mathrm{X\ (base)} \qquad (2)$$

Thus the relative strengths of a series of bases, N, will be compared for various acids, S. The reference base X will be constant for each comparison. In solution X may simply be the solvent, and in the gas phase X may be completely absent. Thus the discussion of equilibrium constants is concerned only with the stability of acid–base adduct N–S and the stability of the free (or solvated) base N. The nature of N–S may be that of a stable organic or inorganic molecule, a complex ion, or a charge transfer complex. In all cases it will be assumed that N is acting in part as an electron donor and S as an electron acceptor so that a coordinate, covalent bond between N and S is formed. Other types of interaction, sometimes stronger, sometimes weaker, may occur. These will be discussed later.

In terms of equilibria, rather than rates, it again turns out that various substrate acids fall into two categories: those that bind strongly to bases which bind strongly to the proton, that is, basic in the usual sense; those that bind strongly to highly polarizable or unsaturated bases, which often have negligible proton basicity. Division into these two categories is not absolute and intermediate cases occur, but the classification is reasonably sharp and appears to be quite useful. It will be convenient to divide bases into two categories, those that are polarizable, or "soft," and those that are nonpolarizable, or "hard."[2] Now it is possible for a base to be both soft and strongly binding toward the proton, for example, sulfide ion. Still it will be true that hardness is associated with good proton binding. For example, for the bases in which the coordinating atom is from groups V, VI, and VII (the great majority of all bases), the atoms F, O, and N are the hardest in each group and also most basic to the proton. The reason for this has been discussed in reference 1. The atoms in each group become progressively softer with increasing atomic weight. They bind protons less effectively, but increase their ability to coordinate with certain other Lewis acids.

For the special case of metal ions as acids, Ahrland, Chatt, and Davies[3] made a very important and useful classification. All metal ions were divided into two classes depending on whether they formed their most stable complexes with the first ligand atom of each group, class (a), or whether they formed their most stable complexes with the second or a subsequent member of each group, class (b).[4] Thus the following sequences of complex ion stability are very often found

(a) $\mathrm{N \gg P > As > Sb > Bi}$
(b) $\mathrm{N \ll P > As > Sb > Bi}$
(a) $\mathrm{O \gg S > Se > Te}$
(b) $\mathrm{O \ll S \sim Se \sim Te}$
(a) $\mathrm{F \gg Cl > Br > I}$
(b) $\mathrm{F < Cl < Br \ll I}$

The classification is very consistent in that a metal ion of class (b) by its behavior to the halides, for example, will also be class (b) with respect to groups V and VI also.

Note that nothing is said concerning relative stabilities of group V ligands *vs.* group VI, for example, for a given metal ion. For a typical class (b) metal ion the order of decreasing stability of complexes for different ligand atoms is generally found to be $\mathrm{C \sim S >}$

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[1] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[2] The descriptive adjectives "hard" and "soft" were suggested by Professor D. H. Busch of Ohio State University.

[3] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[4] The terms (a) and (b) appear to have no significance except that most class (b) metal ions belong to B subgroups of the periodic table. Class (a) metal ions belong to both A and B subgroups.

$I > Br > Cl \sim N > O > F$, which is the same as that of increasing electronegativity and of increasing hardness. For a class (a) metal ion a strong, but not complete, inversion of this order occurs.[5] The inversion can be strong enough so that for some class (a) metal ions only O and F complexes can be obtained in aqueous solution. The failure to get complete inversion of the order is, as mentioned before, that some soft bases are still strong proton acceptors. The proton is, in fact, the most typical class (a) ion and other class (a) metals will bind strongly to ligands that are basic to the proton, whether they are hard or soft. Class (b) metal ions will bind to all soft bases whether they are good proton bases or not.

It seems clear that Chatt's (a) and (b) metal ions are the exact analogs of Edwards' and Pearson's substrates which are sensitive to proton basicity in the nucleophile (class (a)) and to polarizability in the nucleophile (class (b)).[1] Thus we could say that a substrate like a phosphate ester is a class (a) electrophilic reagent, or more properly that the phosphorus atom in the ester is a class (a) electrophilic center. The oxygen atom of peroxides is a class (b) electrophilic center. Nucleophiles also can be classified as hard (nonpolarizable) or soft (polarizable). Furthermore we can now examine equilibrium data for other Lewis acids than metal ions and classify them as (a) or (b) in type. Finally, the interesting question of why two contrasting kinds of behavior should exist will be examined.

Classification of Lewis Acids as Class (a) or (b).—Table I contains a listing of all generalized acids for which sufficient information could be found in the literture to enable a choice between class (a) or class (b) to be made. A few borderline cases are also given. The listing of reference 3 for the metal ions is left essentially unchanged. In classifying other Lewis acids, the criterion of Ahrland, Chatt, and Davies[3] was used whenever possible, that is, to compare the stabilities of F *vs.* I, O *vs.* S, and N *vs.* P type complexes. When this was not possible, two other criteria were used. One is that class (b) acids will complex readily with a variety of soft bases that are of negligible proton basicity. These include CO, olefins, aromatic hydrocarbons, and the like. The other auxiliary criterion is that if a given acid depends strongly on basicity and little on polarizability as far as *rates* of nucleophilic displacements are concerned, then it will depend even less on polarizability as far as equilibrium binding to bases is concerned. Such an acid will therefore be in class (a).

The justification of this rule comes partly from theory and partly from experimental facts. In a transition state there is an increased coordination number for displacement type reactions and an increased transfer of negative charge to the acid atom S in S–X. The theories to be described later all predict increased class (b) behavior for one or both of these reasons. For experimental proof we can cite data on tetrahedral carbon (see below) and metal ions such as platinum(II) or rhodium(III). For the metal ions, for example, hydroxide ion is a poor nucleophilic reagent but a strongly binding ligand at equilibrium.

Some other generalizations can serve both as precautionary remarks in the use of Table I, and as aids in the prediction of the class (a) or (b) character of new acids. As Chatt, *et al.*, observed[3] the class of a given element is not constant, but varies with oxidation state. A safe rule is that class (a) character increases with increasing positive oxidation state and *vice versa* for class (b) behavior. The acid class of a given element in a fixed oxidation state is also affected by the other groups attached to it, not counting the base to which it coordinates. Groups which transfer negative charge to the central atom will increase the class (b) character of that atom since such transfer of charge is equivalent to a reduction of the oxidation state. The groups which most easily transfer negative charge will be the soft bases, particularly if negatively charged. Thus, hydride ion, which is highly polarizable,[6] alkide ions, and sulfide ion will be very effective.

For bases which are ions, there will be a strong solvent dependence for their strength of binding. This will be of different magnitudes for hard and soft ions and hence inversions in the binding order of the halide ions, for example, can occur with changes in solvent. Conclusions as to class (a) or (b) character using as references ionic bases are hence a function of the environment. This topic will be discussed in more detail later. Fortunately for neutral bases the nature of the solvent, or even its complete absence, seems to have little effect on class (a) or (b) behavior.

The data from which Table I is constructed are of diverse kinds, most being true equilibrium data, some being heat data only, and, in a few cases, merely observations that certain reactions occur easily or that certain compounds are stable. Accordingly, the evidence for the new examples not listed in reference 3 will be given in some detail.

TABLE I

CLASSIFICATION OF LEWIS ACIDS

Class (a) or hard	Class (b) or soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	Tl^{3+}, $Tl(CH_3)_3$, BH_3
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	RS^+, RSe^+, RTe^+
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	I^+, Br^+, HO^+, RO^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I_2, Br_2, ICN, etc.
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	Trinitrobenzene, etc.
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Chloranil, quinones, etc.
RPO_2^+, $ROPO_2^+$	Tetracyanoethylene, etc.
RSO_2^+, $ROSO_2^+$, SO_3	O, Cl, Br, I, R_3C(?)
I^{7+}, I^{5+}, Cl^{7+}	M^0 (metal atoms)
R_3C^+, RCO^+, CO_2, NC^+	Bulk metals
HX (hydrogen bonding molecules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	

Use of Rate Data.—Assignments of class (a) character have been made on the basis of kinetic data for the acids RCO^+ (carbonyl carbon as in esters, acyl halides), RPO_2^+ and $ROPR_2^+$ (tetrahedral phosphorus), RSO_2^+ and $ROSO_2^+$ (tetrahedral sulfur), I (V) and Cl (VII) (tetrahedral halogen), and Si^{4+}. These substrates all react rapidly with strong bases and are little influenced by polarizability in the nucleophile.[7] Hence, as explained above, this strongly indicates that basicity will be the dominant factor to an even greater degree at equilibrium. This conclusion is certainly supported by the compounds formed by these acids in which oxygen atom donors are the most numerous by far.

Thermal data for SO_3, which is closely related to the sulfate and sulfonate esters, also support class (a) assignment. The heats of reaction, in the mixed liquids, are given as[8]

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(5) G. Schwarzenbach, *Advan. Inorg. Chem. Radiochem.*, **3** (1961).

(6) M. G. Veselov and L. N. Labzovskii, *Vestnik Leningrad Univ.*, **15**, 5 (1960); *Chem. Abstr.*, **55**, 1671 (1961).

(7) Reference 1 and R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

(8) A. A. Woolf, *J. Inorg. Nucl. Chem.*, **14**, 21 (1960).

$$SO_2 + HF \longrightarrow HSO_3F \quad \Delta H = -20.9 \text{ kcal.}$$

$$SO_3 + HCl \longrightarrow HSO_3Cl \quad \Delta H = -6.0 \text{ kcal.}$$

$$SO_3 + HBr \longrightarrow \text{no reaction}$$

Equilibria in Solution.—Ir^{3+} is put in class (a) on the basis of equilibrium data[9] for the hydrolysis of $Ir(NH_3)_5X^{2+}$. The acid OH^+ is put in class (b) on the basis of the equilibria[10]

$$HOCl(aq) + Br^+(aq) \longrightarrow HOBr(aq) + Cl^-(aq) \quad \Delta G^\circ = -7.6 \text{ kcal.} \quad (3)$$

$$HOCl(aq) + I^-(aq) \longrightarrow HOI(aq) + Cl^-(aq) \quad \Delta G^\circ = -23.4 \text{ kcal.} \quad (4)$$

In a similar way the class (b) nature of the oxygen atom as a Lewis acid is shown by[10]

$$OCl^-(aq) + Br^-(aq) \longrightarrow OBr(aq) + Cl^-(aq) \quad \Delta G^\circ = -5.9 \text{ kcal.} \quad (5)$$

$$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq) \quad \Delta G^\circ = -18.6 \text{ kcal.} \quad (6)$$

This is supported by bond energy data in the gas phase[11]

$$(n\text{-}C_4H_9)_3PO(g) \longrightarrow (n\text{-}C_4H_9)_3P(g) + O(g) \quad \Delta E = 138 \text{ kcal.} \quad (7)$$

$$Cl_3PO(g) \longrightarrow PCl_3(g) + O(g) \quad \Delta E = 119 \text{ kcal.} \quad (8)$$

$$NH_3O(g) \longrightarrow NH_3(g) + O(g) \quad \Delta E < 44 \text{ kcal.} \quad (9)$$

The last figure comes from the fact that the heat of formation of the unknown NH_3O must be more positive than that of its stable isomer NH_2OH. The greater strength of the PO bond compared to NO is also shown by the ease of reactions of the following type from a preparative standpoint.[12]

$$R_3NO + R'_3P \longrightarrow R_3N + R'_3PO \quad (10)$$

The expected class (b) nature of CH_3Hg^+ is shown by equilibrium studies in water.[13] In similar studies $(CH_3)_2Sn^{2+}$ is found to be class (a).[14] It is somewhat surprising to note that Lindquist[15] reports that the neutral molecules $SnCl_4$ and $SbCl_5$ form thio-adducts which are sometimes more stable and sometimes less stable than the corresponding oxo-adducts. It is expected that Sn^{4+} and even $SnCl_2^{2+}$ would be definitely class (a).

Class (b) behavior for RS^+, RSe^+, and RTe^+ is indicated by the extensive surveys of Parker and Kharasch and Pryor.[16] These studies are only semiquantitative for the most part but they do indicate which bases are strong enough to cleave disulfides and related compounds in times long enough so that equilibrium may be assumed. The conclusion is that bases in which S or P is the active atom are much more effective than bases in which O or N donors are involved. The relatively slow reaction with hydroxide ion probably occurs chiefly because RSOH is unstable and disproportionates to RSO_3H and RSSR.

Parker has also discussed[17] the important case of basicity toward ordinary tetrahedral carbon compounds, that is, the acid strength of carbonium ions, R_3C^+. The point was made above that polarizability is much less important in the equilibrium situation than for rates. Conversely, basicity toward the proton becomes of much greater importance. For anionic bases, strong solvent effects exist as expected. In water solution the rate data for the forward and reverse reactions[18] can be used to calculate the equilibrium constant for

$$CH_3I(aq) + F^-(aq) \underset{k_3}{\overset{k_1}{\rightleftarrows}} CH_3F(aq) + I^-(aq) \quad (11)$$

At 70° the value of K_{eq} is 5, which is class (a) behavior, but just barely. The heat of reaction is 2.0 kcal. endothermic so that entropy effects account for the stability of CH_3F compared to CH_3I in this solvent. Data from the same source[18] show that CH_3I is slightly more stable than CH_3Br, which is class (b) behavior.

Bunnett, *et al.*,[19] have equilibrium data on the reaction

$$RSH + OH^- \longrightarrow ROH + SH^- \quad (12)$$

which show $K_{eq} > 10^3$. Here R^+ is a rather complex tertiary carbonium ion and a mixed solvent, acetone–water, was used. Conversely, Miller[20] has examples of reactions in ethanol which show the exactly opposite behavior for CH_3^+.

$$CH_3SP + OP^- \longrightarrow CH_3OP + SP^- \quad K_{eq} < 10^{-4} \quad (13)$$

Here SP^- is a complex thiophosphoric ester. The over-all conclusion from the limited data in solution is that R_3C^+ is a borderline case between (a) and (b). However, some data in the gas phase to be given next show more clearly class (a) behavior.

Gas Phase Equilibria.—Heats of formation and heats of evaporation allow the ΔH or ΔE of a number of gas phase reactions of interest to be calculated. These are of the type

$$CH_3I(g) + F^-(g) \longrightarrow CH_3F(g) + I^-(g) \quad (14)$$

for example. In such reactions the changes in entropy will be small and ΔH can be used to discuss equilibrium constants. Table II gives data for a number of reactions of interest. It can be seen that the acids shown, and all Lewis acids, would be class (a) if judged by their affinity for halide ions in the gas phase.[21] Such a classification would be of little value, however, since the reactions are purely hypothetical.

As mentioned, the equilibria in aqueous solution are actually used as a basis. The great effect of water on reaction 14, which is 57 kcal. exothermic in the gas, is shown by returning to reaction 11 in water which is 2 kcal. endothermic. The difference is chiefly due to the heats of hydration of the ions. The negative hydration heats for the halide ions are 61, 74, 85, and 117 kcal./mole for I^-, Br^-, Cl^-, F^-, respectively.[22] The difference of 56 kcal. between I^- and F^- account almost exactly for the great change of the heat of reaction. The heats of hydration of neutral molecules are very much smaller, to begin with, and the difference between CH_3I and CH_3F would be even less, about 3 kcal. from the data.

The effect of water solvent is thus to lower the basicity of small (hard) anions with respect to related large (soft) anions. The same deactivation is found for OH^- compared to SH^-. For neutral bases, the influence of the solvent is small. The negative heats of hydration

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[9] A. B. Lamb and L. T. Fairhall, *J. Am. Chem. Soc.*, **45**, 378 (1923).

[10] National Bureau of Standards Circular No. 500 "Selected Values of Chemical Thermodynamic Properties," 1952; I. E. Flis, K. P. Mishchenko, and N. V. Pakhomova, *Zh. Neorgan. Khim.*, **3**, 1781 (1958).

[11] T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, pp. 192, 218, 253; C. L. Charwick and H. A. Skinner, *J. Chem. Soc.*, 1401 (1956).

[12] L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 480 (1956); E. Howard, Jr., and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959).

[13] M. Schellenberg and G. Schwarzenbach, Proc. of Seventh Intern. Conf. on Coord. Chem., Stockholm, June, 1962, paper 4A6.

[14] M. Yasuda and R. S. Tobias, *Inorg. Chem.*, **2**, 207 (1963).

[15] I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, Inc., New York, N. Y., 1963, p. 108.

[16] A. J. Parker and N. Kharasch, *J. Am. Chem. Soc.*, **82**, 3071 (1960); A. J. Parker, *Acta Chem. Scand.*, **16**, 855 (1962); see also W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 60.

[17] A. J. Parker, *Proc. Chem. Soc.*, 371 (1962).

[18] R. H. Bathgate and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 3642 (1959).

[19] J. F. Bunnett, C. F. Hauser, and K. V. Nahabedian, *Proc. Chem. Soc.*, 305 (1961).

[20] B. Miller, *ibid.*, 303 (1962).

[21] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 179.

[22] Reference 21, p. 67.

TABLE II

HEATS OF GAS PHASE REACTIONS

$MX(g) + Y^-(g) \longrightarrow MY(g) + X^-(g)$

Reactants	Products	ΔH, kcal./mole[a]	Reactants	Products	ΔH, kcal./mole[a]
HI/F^-	HF/I^-	−63	AlI_3/F^-	AlF_3/I^-	−72 × 3
LiI/F^-	LiF/I^-	−39	AsI_3/F^-	AsF_3/I^-	−68 × 3
CsI/F^-	CsF/F^-	−27	HI/Cl^-	HCl/I^-	−27
HgI/F^-	HgF/I^-	−12	LiI/Cl^-	$LiCl/I^-$	−18
I_2/F^-	IF/I^-	−23	AgI/Cl^-	$AgCl/I^-$	− 5
IBr/F^-	BrF/I^-	−11	I_2/Cl^-	ICl/I^-	− 2
CH_3I/F^-	CH_3F/I^-	−57	CH_3I/Cl^-	CH_3Cl/I^-	−25
CNI/F^-	CNF/I^-	−51	CH_3Br/F^-	CH_3F/Br^-	−45
NOI/F^-	NOF/I^-	−33	$COBr_2/F^-$	COF_2/Br^-	−61 × 2
HgI_2/F^-	HgF_2/I^-	−24 × 2			

[a] Thermodynamic data at 25° from Lewis and Randall, "Thermodynamics," 2nd Ed. revised by L. Brewer and K. S. Pitzer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp. 679–683; JANAF Interim Thermodynamic Tables, the Dow Chemical Co., ARPA Program, 1960; W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955). The heats of formation used for the gaseous halide ions were −65.1, −58.8, −59.3, and −58.0 kcal./mole for F^-, Cl^-, Br^-, and I^-, respectively.

for H_2O, H_2S, and H_2Se and 9.8, 4.6, and 9.3 kcal./mole, for example.

Solvents other than water would give effects in the same direction, but less in magnitude as a rule. Hydrogen-bonding solvents (protonic) would be most like water. Aprotic solvents, especially if highly polarizable, will produce a much smaller differentiation between fluoride ion and iodide ion, for example. The heats of reaction would resemble those in water more than in the gas phase, from the general rule that any solvent is much better than none as far as ions are concerned.[23] In summary, solvents tend to bring out class (b) character for acids compared to the gas phase. Water does this more than other common solvents. The effect is far greater for anionic bases.

Table II shows large negative values of ΔH for reactions of the type shown for class (a) acids and smaller values for typical class (b) acids. This enables us to classify As^{3+}, NC^+, and R_3C^+ as class (a), I^+, Br^+, and Cs^+ as class (b), and NO^+ as intermediate.

Hydrogen Bonding.—Considering the hydrogen-bonding interaction as acid–base in nature

$$Y + HX \longrightarrow Y{-}HX$$

then the acids HX shows all the expected behavior for class (a). The interaction is strong when Y is F and not I, O and not S, N and not P. Some earlier confusion in the literature has been removed by a recent study[24] in which it was found that hydrogen bonding of neutral bases to a reference phenol decreased in strength in the order $RF > RCl > RBr > RI$ and $R_2O > R_2S > R_2Se$. It is of interest to note that the theories of acid classes to be given in the Discussion state that the hydrogen bond is chiefly electrostatic in nature, if class (a) behavior is found.

Charge Transfer Complexes.—The typical charge transfer complex is formed as a result of an acid–base reaction.[25] The electron donor is a base and the acceptor is a Lewis acid. A number of acceptors are listed in Table I as class (b) acids. The list includes I_2, Br_2, ICN, tetracyanoethylene, trinitrobenzene, chloranil, quinone. Obviously a number of similar molecules could be added. There is a large body of equilibrium data for such acids.[26] The behavior is strongly class (b) in type. Thioethers are preferred as bases to ethers, alkyl iodides to alkyl fluorides; aromatic hydrocarbons form quite stable complexes, as do other molecules with negligible proton basicities.

Halogen Atoms and Free Radicals.—A number of reports have appeared in the literature which indicate that free halogen atoms are stabilized by aromatic solvents and not by solvents containing oxygen or nitrogen atoms.[27] The data on recombination of iodine atoms requiring a third body is now interpreted[28] as involving the sequence

$$I + M \longrightarrow IM \qquad (15)$$

$$IM + I \longrightarrow I_2 + M \qquad (16)$$

The efficiency of M, the third body, increases with the critical temperature of M. The critical temperature depends largely on London forces which, in turn, depend on polarizability. Furthermore, aromatic molecules and alkyl iodides are unusually effective. It has been suggested[29] that the ready reaction of free radicals with sulfur- and phosphorus-bearing molecules involves complex formation prior to reaction. A complex between the isooctyl radical and methyl bromide appears to be formed.[29] All of this shows class (b) behavior certainly for electrophilic radicals such as Cl, Br, and I, and possibly for simple aliphatic radicals as well.

Metal Atoms and Metal Surfaces.—From the effect of changing the positive oxidation state of metals, it can be predicted that metal atoms at zero oxidation state will always be class (b) acids.[3] Complexes with neutral metal atoms typically contain the soft bases characteristic of class (b). These include CO, P, and As ligands, olefins, aromatics, isonitriles, and heterocyclic chelate amines.[30] It seems reasonable that metal atoms at the surface of a bulk metal would have the same properties. Certainly CO and unsaturated molecules are strongly adsorbed. The strong absorption of basic molecules on a metal surface is usually considered an electron donation process from the base to the metal, *i.e.*, an acid–base reaction.[31] Bases containing P, As, Sb, S, Se, and Te in low oxidation states are poisons in heterogeneous catalysis involving metallic catalysts. Strong oxygen- and nitrogen-containing bases are not poisons.[32] This agrees with the expectation if the metal is a class (b) acid since poisons are bases held so firmly that the active sites are blocked off to weaker bases, according to the usual view.

Discussion

The common features of the two classes of Lewis acids are easily discernible from Table I. The features which bring out class (a) behavior are small size and high positive oxidation state. Class (b) behavior is associated with a low or zero oxidation state and/or with large size. Both metals and nonmetals can be either (a) or (b) type acids depending on their charge and size. Since the features which promote class (a) behavior are those which lead to low polarizability, and those which create type (b) behavior lead to high polarizability, it is convenient to call class (a) acids "hard" acids and class (b) acids "soft" acids. We

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(23) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

(24) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von. R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(25) See R. S. Mulliken: (a) *J. Phys. Chem.*, **56**, 801 (1952); (b) *J. Am. Chem. Soc.*, **74**, 811 (1952).

(26) See G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; J. D. McCullough and I. C. Zimmerman, *J. Phys. Chem.*, **65**, 888 (1961).

(27) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); S. J. Rand and R. L. Strong, *ibid.*, **82**, 5 (1960); T. A. Gover and G. Porter, *Proc. Roy. Soc.* (London), **A262**, 476 (1961).

(28) G. Porter and J. A. Smith, *ibid.*, **A261**, 28 (1961); M. I. Christie, *J. Am. Chem. Soc.*, **84**, 4066 (1962).

(29) M. Szwarc in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 103.

(30) J. Chatt, *J. Inorg. Nucl. Chem.*, **8**, 515 (1958).

(31) See R. L. Burwell, Jr., in "Actes au Deuxieme Congres International de Catalyze," Paris, 1960, p. 1005.

(32) G. C. Bond, "Catalysis by Metals," Academic Press, Inc., New York, N. Y., 1962.

then have the useful generalization that hard acids prefer to associate with hard bases, and soft acids prefer soft bases.

Polarizability is simply a convenient property to use as a classification. It may well be that other properties which are roughly proportional to polarizability are more responsible for the typical behavior of the two classes of acids. For example, a low ionization potential is usually linked to a large polarizability and a high ionization potential to a low polarizability. Hence ionization potential, or the related electronegativity, might be the important property. Unsaturation, with the possibility of acceptor π-bonding in the acid-base complex, and ease of reduction, favoring strong electron transfer to the acid, are also associated with high polarizability. For example, Edwards[33] has developed a fairly successful equation for predicting nucleophilic reactivity using proton basicity and oxidation-reduction potential as the two parameters on which reactivity depends. Later it was shown that a polarizability term could take the place of the oxidation-reduction term with about equal success.[34] To help in deciding which properties are of importance, it is necessary to examine the theories which have been advanced to account for the facts on which Table I is based. Different investigators, looking at different aspects, have come up with several explanations. These may be called: (1) the ionic-covalent theory; (2) the π-bonding theory; (3) electron correlation theory; (4) solvation theory.

To anticipate the analysis of these different views, there seems to be no reason to doubt that all of the factors involved in the above theories are of importance in explaining the behavior of acids. Different examples will depend more or less strongly on the several factors.

The Ionic-Covalent Theory.—This is the oldest and usually the most obvious explanation.[35] The class (a) acids are assumed to bind bases with primarily ionic forces and the class (b) acids hold bases by covalent bonds. High positive charge and small size would favor strong ionic bonding and bases of large negative charge and small size would be held most strongly. Mulliken[25] has developed a theory of covalent bonding suitable for discussing soft bases and soft acids. Bonding will be strong if the electron affinity of the acid is large and the ionization potential of the base is low.[36] Softness in both the acid and base means that the repulsive part of the potential energy curve rises less sharply than for hard acids and bases. Thus closer approach is possible and better overlap of the wave functions used in covalent bonding.

Mulliken's treatment is intended chiefly for charge transfer complexes which involve type (b) acids. It is not applicable to type (a) acids where, as we have seen, the base of *highest* ionization potential, for example F^-, is bound most strongly. In the theory of covalent bonding, it is generally considered necessary that both bonded atoms be of similar electronegativity to have strong covalent bonding.[37] That is, the coulomb integrals on both bonded atoms should be similar, and the sizes of the bonding atomic orbitals should be similar to get good overlap. These considerations show that hard acids will prefer hard bases even when considerable covalency exists. Soft bases will mismatch with hard acids for good covalency, and ionic bonding will also be weak because of the small charge or large size of the base.

The π-Bonding Theory.—Chatt[38] has made important contributions to the theory of Lewis acids, applied chiefly to metallic complexes. The important feature of class (b) acids in his view is considered to be the presence of loosely held outer d-orbital electrons which can form π-bonds by donation to suitable ligands. Such ligands would be those in which empty d-orbitals are available on the basic atom, such as P, As, S, I. Also unsaturated ligands such as CO and isonitriles would also be able to accept metal electrons by the use of empty, but not too unstable, molecular orbitals. Class (a) acids would have tightly held outer electrons, but also there would be empty orbitals available, not too high in energy, on the metal ion. Basic atoms such as O and F particularly could form π-bonds in the opposite sense, by donating electrons from the ligand to the empty orbitals of the metal. With class (b) acids, there would be a repulsive interaction between the two sets of filled orbitals on metal and O and F ligands.

With some imagination, this model can be generalized to fit most of the entries in Table I. The soft acids are potential d- or p-electron donors *via* π-bonds. The hard acids are potential π-bond acceptors. Such effects are, of course, in addition to σ-bonding interactions. The hydrogen-bonding molecules and carbonium ions, R_3C^+, in class (a) do not seem to fit in with π-bonding ideas. At least one class (b) acid, Tl^{3+}, has such a high ionization potential that it is hard to imagine it as an electron donor.

Electron Correlation Effects.—Pitzer[39] has suggested that London, or van der Waals, dispersion forces between atoms or groups in the same molecule may lead to an appreciable stabilization of the molecule. Such London forces depend on the product of the polarizabilities of the interacting groups and vary inversely with the sixth power of the distance between them.[40] They are large when both groups are highly polarizable. Similarly, Bunnett[41] has noted that reaction rates are usually fast when a nucleophile of high polarizability reacts with a substrate carrying a highly polarizable substituent near the reaction site. This was attributed to stabilization of the transition state by London forces.

Even for bonded atoms it may be argued that the electron correlations responsible for London forces will operate for the nonbonding electrons.[39] It has been calculated that some 11 kcal. of the bromine-bromine bond energy may be due to London forces.[42] It then seems plausible to generalize and state that additional stability due to London forces will always exist in a complex formed between a polarizable acid and a polarizable base. In this way the affinity of soft acids for soft bases can be accounted for.

Mulliken[43] has given a different explanation for the extra stability of the bromine-bromine and iodine-iodine bonds. It is assumed that d_π-p_π orbital hybridization occurs so that both the π_u bonding molecular orbitals and π_g antibonding orbitals contain some admixed d-character. This has the twofold effect of strengthening the bonding orbital by increasing overlap and weakening the antibonding orbital by decreasing

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[33] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

[34] J. O. Edwards, *ibid.*, **78**, 1819 (1956).

[35] See A. A. Grinberg, "An Introduction to the Chemistry of Complex Compounds," translated by J. R. Leach, Pergamon Press, London, 1962, Chapter 7; G. Schwarzenbach, ref. 5; R. J. P. Williams, *Proc. Chem. Soc.*, 20 (1960).

[36] J. Weiss, *J. Chem. Soc.*, 245 (1942).

[37] C. A. Coulson, *Proc. Phil. Soc.*, **33**, 111 (1937).

[38] References 3 and 28; *Nature*, **165**, 859 (1950); **177**, 852 (1956); J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

[39] K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955); K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).

[40] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

[41] J. F. Bunnett, *J. Am. Chem. Soc.*, **79**, 5969 (1957); J. F. Bunnett and J. D. Reinheimer, *ibid.*, **84**, 3284 (1962).

[42] G. L. Caldow and C. A. Coulson, *Trans. Faraday Soc.*, **58**, 633 (1962).

[43] R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955).

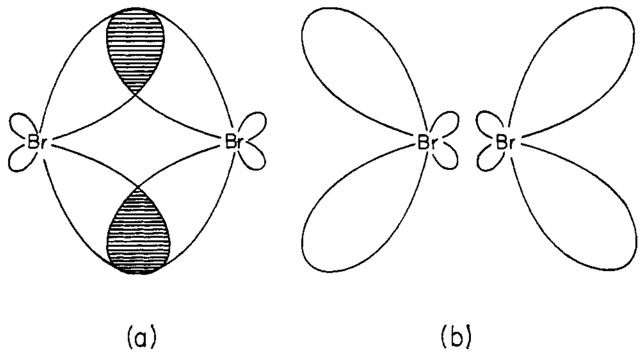

Fig. 1.—Atomic orbital hybrids for (a) bonding and (b) antibonding molecular orbitals.

overlap. Figure 1 shows schematically and exaggeratedly the d_π–p_π hybrids for both situations. Pearson and Edwards[1] proposed essentially the same mechanism to account for the high rate of reaction of polarizable nucleophiles with polarizable substrates.[44]

There is considerable similarity to the proposals of London forces and of orbital hybridization. They both represent electron correlation phenomena. The basic cause is different in the two cases, however. London correlation occurs because of the electrostatic repulsion of electrons for each other. The proposed π-orbital hybridization occurs largely because of nonbonded repulsion effects arising from the Pauli exclusion principle. It would appear that the latter would be more important for interactions between bonded atoms and the former for more remote interactions. Thus for the interaction of a soft acid and a soft base, orbital hybridization should usually be more important than stabilization due to van der Waals forces.

Mulliken's theory is the same as Chatt's π-bonding theory as far as the π_u bonding orbital is concerned. The new feature is the stabilization due to the π_g molecular orbital. As Mulliken points out[43] this effect can be more important than the more usual π-bonding. The reason is that the antibonding orbital is more antibonding than the bonding orbital is bonding, if overlap is included. For soft–soft systems, where there is considerable mutual penetration of charge clouds, this amelioration of repulsion due to the Pauli principle would be great. Unshared pairs of π-electrons would be affected more than electrons used for bonding purposes (compare I^- and $(C_2H_5)_3P$). An MO calculation, necessarily very approximate, gives some idea of the energies involved.

Consider the π-interactions of a system consisting of p_π and d_π atomic orbitals on an atom such as iodine and a p'_π atomic orbital on an atom such as oxygen. For simplicity let the p_π coulomb integrals be equal on both atoms, say q. The coulomb integral of the d_π orbital will be much nearer zero and may be set equal to zero for simplicity. The p_π–p'_π exchange integral will be β and assume the d_π–p'_π integral between the two atoms is also β, though it might be $\beta/2$, for example, without changing the argument. The d_π–p_π exchange for the same atom will be zero in the one-electron approximation.

The MO's found on solving the secular equation

$$\begin{array}{c|ccc|} & p & p' & d \\ p & q - E & \beta & 0 \\ p' & \beta & q - E & \beta \\ d & 0 & \beta & -E \end{array} = 0$$

are

$$\phi_1 = \frac{(\psi_p + \lambda\psi_d) + (1 + \lambda)\psi_p'}{2 + 2\lambda} \qquad (17)$$

$$\phi_2 = \frac{(\psi_p - \lambda\psi_d) - (1 - \lambda)\psi_p'}{2 - 2\lambda} \qquad (18)$$

$$\phi_3 = (\psi_d - \lambda\psi_p') \qquad (19)$$

The mixing parameter λ is equal to β/q which is small, say 0.10, and terms in λ^2 have been omitted; ϕ_1 and ϕ_2 resemble the bonding and antibonding orbitals, respectively, shown in Fig. 1. The corresponding energies, omitting terms in λ^2, are

$$E_1 = q + \beta + \beta^2/q \qquad (20)$$

$$E_2 = q - \beta + \beta^2/q \qquad (21)$$

$$E_3 = -2\beta^2/q \qquad (22)$$

The net stabilization for four electrons, two in the ϕ_1, or π_u, orbital and two in the ϕ_2, or π_g, orbital will be $4\beta^2/q$.

If only the usual π-bonding had been considered, the net stabilization would have been equal to $2\beta^2/q$, so in this case the two effects are equal in magnitude. Putting in the overlap integral does not change the above calculations in the first approximation, and the uncertainties involved prevent a more detailed calculation. Mulliken has made some further estimates.[43]

It will be noted that the effect of π-bonding depends directly on the square of the exchange integral β^2 and inversely on the excitation energy q, between the stable p-orbital and the unstable d-orbital. This explains why the first row elements cannot benefit from such π-bonding, even though empty d- and p-orbitals exist also at an energy near zero.[45] It also explains why the lowest empty d-orbital is most suitable for π-bonding even though many other states of near equal energy exist. It is expected that the overlap, and hence β, would be best for this d-orbital.

Polarizability also depends inversely on the excitation energy, q, to the excited levels.[46] This phenomenon is not restricted to the first empty d-orbital but includes all excited states. It can be seen that, generally speaking, the metallic cations of class (b) are of high polarizability, not only because of large size, but also because of easily excited outer d-orbital electrons. While some class (b) acids, such as the oxygen atom, do not appear polarizable compared to some class (a) acids such as $Al(CH_3)_3$, one must bear in mind that the acid site in the latter case is really a modified Al^{3+} ion. Furthermore, the unshared electron pairs on the oxygen atom will benefit more from correlation effects than the shared pairs of electrons in the Al–C bonds.

The Solvation Theory.—Parker[47] in particular has stressed the effect of solvents on reducing the basicity of small anions and hence causing large anions to appear abnormally strong. The implication that such solvation is the common explanation for the strong binding, or high rates of reaction, of polarizable bases seems to be incorrect. As was pointed out above, differences in solvation energies between neutral molecules such as ROH and RSH are very much smaller than the differences for the corresponding anions. Furthermore, much of the data on which Table I is based comes from the gas phase or from nonpolar solvents. Also solvation effects alone would not cause a division into two distinct classes of acids as are found.

What solvation does do is to generally destroy class (a) character and enhance class (b) character. The

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(44) Other explanations[1] for such high reactivity in terms of polarization of the σ-electrons seem to be equivalent to the covalent bonding discussed above.

(45) W. Klemperer, *J. Am. Chem. Soc.*, **83**, 3910 (1961); A. F. Saturno and J. F. Eastham, *ibid.*, **84**, 1313 (1962).

(46) See H. Eyring, G. E. Kimball, and J. Walter, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 121.

(47) A. J. Parker, *J. Chem. Soc.*, 1328 (1961); *Quart. Rev.* (London), **14**, 163 (1962); J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961).

magnitude of the class (a) character in the gas phase will determine if a solvent can cause inversion (compare Table II).[48] It is clear then that solvation effects, while of great importance, particularly for ions, do not explain why some acids prefer hard bases and some acids prefer soft bases. The explanation for this must come from interactions existing in the acid–base complex. Such interactions include ionic–covalent σ-bonding, π-bonding, and electron correlation effects, all of which seem to play a role in determining class (a) and (b), or hard and soft, character.

Some Consequences of Hard–Soft Classification of Acids and Bases.—The simple rule that hard acids prefer to bind hard bases and soft acids prefer soft bases permits a useful systematization of a large amount of chemical information. Some illustrations of the usefulness of the rule will now be given.

Stabilization of Metal–Metal Bonds.—It was shown above that zero-valent metals and bulk metals are class (b) acids. Metals can also act as Lewis bases, since donation of electrons is more characteristic of them than the acceptance of electrons. They will only be good bases in a zero or low valent state. Thus they will be soft bases. To form a compound with a stable metal to metal bond, then, requires that *both* metal atoms be in a low or zero oxidation state. Typical examples would be Hg_2^{2+} and $Mn_2(CO)_{10}$. To stabilize the metal–metal bond other ligands attached to the metal should be typical soft bases such as CO, R_3P, and alkide ions, R^-.[49] This has the dual effect of stabilizing each metal atom in the low valent condition and of increasing softness by increasing the electron density on the metal atoms.

Metal–metal bonding appears in an interesting way in heterogeneous catalysis. Metal ions of class (b) are poisons for metal surfaces, while metal ions of class (a) are not.[32] This can be explained by the softness of the metal considered as a base. The softness of the metal as an acid (Table I) explains why phosphines, sulfides, etc., are poisons.

Classification of Solvents as Hard or Soft.—Solute–solvent interactions may often be considered as acid–base interactions of varying degree. Considering solvents as acids, HF, H_2O, and hydroxylic solvents will be hard solvents. They will strongly solvate hard bases such as F^-, OH^-, and other oxygen anions. A variety of dipolar, aprotic solvents such as dimethyl sulfoxide, sulfolane, dimethylformamide, nitroparaffins, and acetone will be soft acid solvents. These solvents will have a mild preference for solvating large anions which function as soft bases.[50] The class (a), or hard, solvents will tend to level basicity while class (b) or soft, solvents will not. Hence the high reactivity of OH^- and OR^- noted in class (b) solvents.[50]

Solvents can be classified as hard or soft by virtue of their basic properties as well, and this will influence their interaction with cations. Even neutral solutes will be affected to a lesser degree. The obvious rule is that hard solvents dissolve hard solutes well and soft solvents dissolve soft solutes well.[51]

Stabilization of Valence States and Ligands.—It is well known in coordination chemistry that ligands of large size, low charge, and low electronegativity are good for stabilizing metal ions in low valence states.[52] For metal ions in high positive oxidation states, the fluoride ion and oxide ion are the best stabilizing groups.[52] Obviously these are examples of preferential soft–soft and hard–hard interactions. A somewhat less obvious corollary has to do with the preparation of certain classes of compounds containing unstable ligands such as H^- and R^-.

It has been found by Chatt[53] that such complexes for transition metals are stabilized by the presence of typical soft ligands. Chatt has emphasized the high ligand field strength of such ligands as a factor in their stabilizing ability. Equally important is the concept that such ligands keep the metal in the class (b) condition necessary for it to combine effectively with the highly polarizable hydride and alkide ions.

Formation of Unexpected Complexes.—The common use of water, a hard solvent, and of H^+, a hard acid, as a reference for basicity, justify the statement that soft acids form unexpected complexes, particularly in aqueous solutions. Since soft bases often do not bind the proton at all in water (H_3O^+ being formed instead), the fact that they are bases is often forgotten. The complexes formed with suitable soft acids, even in aqueous solutions, are then considered rather abnormal. Examples would be I_3^-, I_2SCN^-, $Ag(C_2H_4)^+$, $PtCl_3C_2H_4^{2-}$, and charge-transfer complexes in general. It is true that increasing familiarity with such complexes, and increasing sophistication, cause them to appear less surprising now than a few years ago. It is probable that the entire area of molecule–molecule and ion–molecule interactions can be examined with profit as examples of generalized acid–base phenomena. If so, the concept of hard and soft acids and bases should prove useful.

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[48] A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 1023 (1961).

[49] Compare R. S. Nyholm, E. Coffey, and J. Lewis, paper 1H3, Proc. of Seventh Conf. on Coord. Chem., Stockholm, June, 1962. Other factors influencing metal–metal bonds are discussed in this paper and in R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

[50] (a) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); (b) see also N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, **85**, 1141, 1148 (1963).

[51] Reference 50a gives a number of examples.

[52] Reference 28 and W. Klemm, *J. Inorg. Nucl. Chem.*, **8**, 532 (1958); also the succeeding papers by various authors.

[53] J. Chatt, Tilden Lecture, *Proc. Chem. Soc.*, 318 (1962); see also G. Calvin, G. E. Coates, and P. S. Dixon, *Chem. Ind.* (London), 1628 (1959).