HSAB theory

The **HSAB concept** is an initialism for "hard and soft (Lewis) acids and bases". Also known as the **Pearson acid base concept**, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable.[1] The concept is a way of applying the notion of orbital overlap to specific chemical cases.

The theory is used in contexts where a qualitative, rather than quantitative, description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

HSAB theory is also useful in predicting the products of metathesis reactions. In 2005 it was shown that even the sensitivity and performance of explosive materials can be explained on basis of HSAB theory.[2]

Ralph Pearson introduced the HSAB principle in the early 1960s[3][4][5] as an attempt to unify inorganic and organic reaction chemistry.[6]

1 Theory

The gist of this theory is that *soft* acids react faster and form stronger bonds with *soft* bases, whereas *hard* acids react faster and form stronger bonds with *hard* bases, all other factors being equal.[7] The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

Hard acids and **hard bases** tend to have the following characteristics:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity (bases)
- hard bases have highest-occupied molecular orbitals (HOMO) of low energy, and hard acids have lowest-unoccupied molecular orbitals (LUMO) of high energy.[7][8]

Examples of hard acids are: H^+, light alkali ions (Li through K all have small ionic radius), Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3. Examples of hard bases are: OH^-, F^-, Cl^-, NH_3, CH_3COO^-, $CO_3{}^{2-}$. The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and **soft bases** tend to have the following characteristics:

- large atomic/ionic radius
- low or zero oxidation state bonding
- high polarizability
- low electronegativity
- soft bases have HOMO of higher energy than hard bases, and soft acids have LUMO of lower energy than hard acids. (However the soft-base HOMO energies are still lower than the soft-acid LUMO energies.)[7][8]

Examples of soft acids are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, $Hg_2{}^{2+}$, Cd^{2+}, BH_3. Examples of soft bases are: H^-, R_3P, SCN^-, I^-. The affinity of soft acids and bases for each other is mainly covalent in nature.

Borderline cases are also identified: **borderline acids** are trimethylborane, sulfur dioxide and ferrous Fe^{2+}, cobalt Co^{2+} caesium Cs^+ and lead Pb^{2+} cations. **Borderline bases** are: aniline, pyridine, nitrogen N_2 and the azide, chloride, bromide, nitrate and sulfate anions.

Generally speaking, acids and bases interact and the most stable interactions are hard-hard (ionogenic character) and soft-soft (covalent character).

An attempt to quantify the 'softness' of a base consists in determining the equilibrium constant for the following equilibrium:

$$BH + CH_3Hg^+ \leftrightarrow H^+ + CH_3HgB$$

Where CH_3Hg^+ (methylmercury ion) is a very soft acid and H^+ (proton) is a hard acid, which compete for B (the base to be classified).

Some examples illustrating the effectiveness of the theory:

- Bulk metals are soft acids and are poisoned by soft bases such as phosphines and sulfides.
- Hard solvents such as hydrogen fluoride, water and the protic solvents tend to solvate strong solute bases such as the fluorine anion and the oxygen anions. On the other hand, dipolar aprotic solvents such as dimethyl sulfoxide and acetone are soft solvents with a preference for solvating large anions and soft bases.
- In coordination chemistry soft-soft and hard-hard interactions exist between ligands and metal centers.

2 Chemical hardness

In 1983 Pearson together with Robert Parr extended the qualitative HSAB theory with a quantitative definition of the **chemical hardness** (η) as being proportional to the second derivative of the total energy of a chemical system with respect to changes in the number of electrons at a fixed nuclear environment:[9]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_Z .$$

The factor of one-half is arbitrary and often dropped as Pearson has noted.[10]

An operational definition for the chemical hardness is obtained by applying a three-point finite difference approximation to the second derivative:[11]

$$\begin{aligned}\eta &\approx \frac{E(N+1) - 2E(N) + E(N-1)}{2}, \\ &= \frac{(E(N-1) - E(N)) - (E(N) - E(N+1))}{2}, \\ &= \frac{1}{2}(I - A),\end{aligned}$$

where *I* is the ionization potential and *A* the electron affinity. This expression implies that the chemical hardness is proportional to the band gap of a chemical system, when a gap exists.

The first derivative of the energy with respect to the number of electrons is equal to the chemical potential, μ, of the system,

$$\mu = \left(\frac{\partial E}{\partial N}\right)_Z ,$$

from which an operational definition for the chemical potential is obtained from a finite difference approximation to the first order derivative as

$$\begin{aligned}\mu &\approx \frac{E(N+1) - E(N-1)}{2}, \\ &= \frac{-(E(N-1) - E(N)) - (E(N) - E(N+1))}{2}, \\ &= -\frac{1}{2}(I + A),\end{aligned}$$

which is equal to the negative of the electronegativity (χ) definition on the Mulliken scale: $\mu = -\chi$.

The hardness and Mulliken electronegativity are related as

$$2\eta = \left(\frac{\partial \mu}{\partial N}\right)_Z \approx -\left(\frac{\partial \chi}{\partial N}\right)_Z ,$$

and in this sense hardness is a measure for resistance to deformation or change. Likewise a value of zero denotes maximum **softness**, where softness is defined as the reciprocal of hardness.

In a compilation of hardness values only that of the hydride anion deviates. Another discrepancy noted in the original 1983 article are the apparent higher hardness of Tl^{3+} compared to Tl^{+}.

3 Modifications

If the interaction between acid and base in solution results in an equilibrium mixture the strength of the interaction can be quantified in terms of an equilibrium constant. An alternative quantitative measure is the standard heat (enthalpy) of formation of the adduct in a non-coordinating solvent. Drago and Wayland proposed a two-parameter equation which predicts the formation of a very large number of adducts quite accurately.

$$-\Delta H^{O}\ (A{-}B) = EAEB + CACB$$

Value of the *E* and *C* parameters can be found in Drago *et al.*[12] Hancock and Martell found that an E and C equation analogous to that of Drago gave an excellent quantitative prediction of formation constants for complexes of 34 metal ions plus the proton with a wide range of unidentate Lewis acids in aqueous solution, and also offered insights into factors governing HSAB behavior in solution.[13]

Another quantitative system has been proposed, in which Lewis acid strength is based on gas-phase affinity for fluoride. [14]

4 Kornblum's rule

An application of HSAB theory is the so-called **Kornblum's rule** which states that in reactions with ambident

nucleophiles (nucleophiles that can attack from two or more places), the more electronegative atom reacts when the reaction mechanism is SN1 and the less electronegative one in a SN2 reaction. This rule (established in 1954) [15] actually predates HSAB theory but in HSAB terms its explanation is that in a SN1 reaction the carbocation (a hard acid) reacts with a hard base (high electronegativity) and that in a SN2 reaction tetravalent carbon (a soft acid) reacts with soft bases.

According to recent findings electrophilic alkylations at free CN^- occur preferentially at carbon, regardless of whether the SN1 or SN2 mechanism is involved and whether hard or soft electrophiles are employed. Preferred N attack, as postulated for hard electrophiles by the HSAB principle, could not be observed with any alkylating agent. Isocyano compounds are only formed with highly reactive electrophiles that react without an activation barrier because the diffusion limit is approached. It is claimed that the knowledge of absolute rate constants and not of the hardness of the reaction partners is needed to predict the outcome of alkylations of the cyanide ion.[16]

5 Criticism

In 2011, Herbert Mayr et al. from Ludwig Maximilian University of Munich (LMU) published a critical review in Angewandte Chemie.[17] Consecutive analysis of various types of ambident organic system reveals that an older approach based on thermodynamic/kinetic control describes reactivity of organic compounds perfectly, while the HSAB principle actually fails and should be abandoned in the rationalization of ambident reactivity of organic compounds.

6 See also

- Acid-base reaction
- Oxophilicity

7 References

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