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To study the stability of complexes by various parameters specially with softness parameters

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Abstract

Pearson (1) in 1963 was introduced H.S.A.B. Principle. He suggested that hard acids prefer to bind with hard bases and soft acids to soft bases. Though Pearson was the first author of H.S.A.B. principle yet a number of earlier papers have been a source of ideas and inspiration. The first paper in this regard was published by Edward (2) in which he introduced a four parameters equation to describe the stability of the compounds. In 1956 Schwarzenbach (4) and Ahrland Chatt and Davis (5) classified the metal ions into two classes 'a' and 'b' type. They explained that class 'a' type of metals prefer to bind with class 'a' type of donors and similarly class 'b' type of metals prefer to interact with class 'b' type of donors. Since it was described that class 'a' type of metals prefer to interact with class 'a' type of ligands. It was conceived that such an interaction shall lead to the formation of a more stable compound. Schwarzenbach in 1961 presented a detailed account on the factors influencing the stabilities of metal complexes (6). In his description he pointed out that class 'b' type of metals form more stable complexes with class 'b' type of ligands.

Keywords: stability, complexes, various parameters specially, softness parameters

Introduction

It has been the efforts of several workers to find out the suitable parameters by which the stability of compound formed by an acid and a base or in other words between metal ion and ligand. This was later called the oxybase scale.

$$\text{Log}(K/K_0) = \alpha_{En} + \beta_H \text{-----} \quad (1)$$

Where K/K_0 is a relative (to water) rate or Equilibrium constant (3), E_n is a redox factor defined by -----

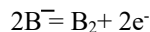
$$E_n = E^0 + 2.60$$

E^0 is the standard oxidation potential for the process. H is a basicity factory defined by

$$H = 1.74 + pK_a$$

α and β are substrate constants.

Both definitions are arranged so that $H = 0$ and $E_n = 0$ for water at 25°C. K_0 is, therefore, a constant when the base B is water.



Edwards mostly confined himself to explain the organic reactions.

To explain the stability, a general term 'A' and 'B' have been used to represent an acid and a base respectively. A-B has been used to represent a compound formed by them. The first equation to explain the stability of A-B compound was given by them.

$$\text{Log } K = S_A \cdot S_B \text{-----} \quad (2)$$

Where S_A and S_B are the strength factors of A and B respectively.

Usually the above equation was not adequate and it was replaced with a more complex equation involving two parameters. This equation was represented by -----

$$\text{Log } K = S_A \cdot S_B + \sigma_A \cdot \sigma_B \text{-----} \quad (3)$$

Where σ_A and σ_B are the parameters for each A and B which measures some different characteristics from that of strength. These parameters were later termed as softness parameters by Pearson.

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The way in which α and β in eqn. (I) depend upon the Lewis acid substrate is quite revealing. Table-I shows a compilation of α and β for the formation of a number of metal complexes with various bases. It can be seen that β is large for Lewis acid with a high positive charge and small size of ion and small for Lewis acid of low charge and low size. In other words β varies just exactly as S_A is expected to vary in eqn. (II). The term that it is multiplied by 'H' is simply another way of expressing S_B . We can accordingly identify the product β_H with S_A . S_B . Then αE_n must be identified with σ_A and σ_B which means that σ_B is large for bases that are easily oxidized Such as Γ and small or negative for bases that are hard to oxidize such as F^- . We can also see that α and σ_A is large for Lewis acids of large size, low positive charge and containing unshared electrons in p or d orbitals in the valency shell, such as Ag^+ . Also σ_A is small for Lewis acids of the opposite characteristic, such as Mg^{++}

While the Edwards Equation is of the form of equation (II), it is not the only equation that might be used even in aqueous solution. In fact if the equation (II) or (III) were valid an equation of the form.

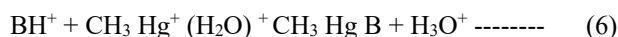
$$\log (K/K_0) = \gamma \log (K'/K'_0) + \delta \log (K''/K''_0) \text{ ----- (4)}$$

Should generally exist, where K, K' and K'' are any series of related equilibrium constants. The constants K' might be taken as the H values of Edward equation and K'' might be values for a typical Lewis acid with the opposite properties to the proton in Table-I, such as Hg^{+2} .

An even better standard is the methyl mercury (I) cation, CH_3Hg^+ for which a large amount of equilibrium data in aqueous solution has been accumulated by Schwarzenbach.



Like the proton, $CH_3 Hg^+$ has the advantage of having a coordination number of one, which simplifies the equilibria involved. With two reference acids of different properties, we can test various bases to see if they prefer to bind to H^+ or $CH_3 Hg^+$. Table-2 shows some data (8) for the equilibrium constant for the exchange reaction.



The important features which we note is that bases in which the donor atom is NO or F prefer to coordinate to the proton and bases in which the donor atom is P,S,I, Br, Cl Or C prefer to coordinate to mercury. The donor atoms in the first group are those which are of high electronegativity of low polarizability and hard to oxidize. Pearson called the bases containing these donor atoms (N,O,F) as hard bases on the basis of the fact that they hold on to their electrons more tightly. The donor atoms of the other bases (P, S, I, Br, Cl) are of low electronegativity, of high polarizability and easy to oxidize. These were called by him as soft bases, a term which describes the looseness with which they hold their valence electrons.

On the basis of H.S.A.B. principle, a base may be categorized in three types namely, hard, soft, and borderline (Table – 3). A member of a group of periodic table may be hard, soft or borderline irrespective of its outer orbital electronic arrangement eg. In halogen group F^- is hard, Br^- is borderline and I^- is soft. The borderline category takes the account of loosening the valence electrons, especially in nitrogen donor's

eg. C_5H_5N, N_3^-, N_2 etc. The donor properties of an atom is based on two factors ----

- It is easily oxidisable in nature, easy polarisability and
- The equilibrium constant which is obtained by treating it with acceptors.

The results are always similar except a few exception eg. Cl^- being a hard base has high affinity for Hg^{++} ion (soft) and equilibrium constant data also support this phenomenon (Table-2). In the light of above observation Cl^- may be treated as a borderline base as in case of Br^-

The symbol R stands for an alkyl or aryl group. A similar type of classification is also made for Lewis acids i.e. hard, soft and borderline (Table-4).

In this research paper various parameters with an important parameter i.e. softness parameters utilised to explain the stability of complexes.

Methodology

The hard-hard and soft-soft interaction did explain a wide range of chemical phenomena (9 – 15) but on account of it's purely qualitative nature the principle was criticized and several workers either made attempts to give quantitative explanation of the principle or suggested new approaches to explain the stability of the compound, some of these efforts are enumerated below

Misono *et al.* (16) proposed the following equation for determining the values of hardness and softness.

$$Y = 10 (I_n/I_{n+1}) (r_i/\sqrt{n})$$

And

$$(10X)^{1/2} = X_i = X_{M^+} (\sum I_n)^{1/2} \text{ ----- (7)}$$

Where r_i = ionic radius of the metal ion and is the formal charge. X_i and X_m are the electro negativities of the metal ion and neutral metal atom.

The dual parameter scale based on X and Y is as follows --- 'X' is closely related to hardness or electronegativity and 'Y' to softness. With these parameter the log of stability constants of metal ion complexes (log K) is expressed well for hard-hard complexes and to a lesser extent for soft-soft complexes by the equation.

$$\log K = \alpha x + \beta y + Y$$

Where α and β are the basicity parameters of a ligand corresponding to x and y respectively and y is a constant determined for each ligand.

Drago (17) also developed an equation for enthalpy of adduct formation for neutral molecules.

$$H = E_A \cdot E_B + C_A \cdot C_B \text{ ----- (8)}$$

E_A and E_B are the parameters which relate to tendencies to undergo electrostatic bonding for acids and bases, C_A and C_B are the parameters which relate to the tendencies to undergo covalent bonding for acids and bases.

The above equation did not hold good for ionic interaction and ultimately Drago *et al.* developed another equation for ionic interaction (18)

$$H = (D_A - D_B)^2 + (O_A - O_B)^{1/2} \text{ ----- (9)}$$

Where O and D are off-diagonal terms in Hamiltonian matrix formed by M.O. treatment.

Result and Discussion

The overall attempt of these workers was to solve the problem concerning stability, type of reaction and nature of reaction between two class of compounds. Basically various authors (1917) have claimed that the idea of intrinsically strong acids and bases is missing from the H.S.A.B. principle. Klopman (20) made a significant attempt and calculated the softness values of a number of acids and base ions. His calculation were based upon the perturbation theory of charge and frontier controlled reactions. He divided the reaction into two types (a) charged controlled and (b) frontier controlled. The charge controlled reaction were used to explain the ionic interaction and frontier controlled reaction to explain the covalent interaction. The softness values of acid and base ions of both the type of interactions and that of intermediate reaction were calculated by solving the following equations.

$$E_m^{\ddagger} = IP_m - a^2 (IP_m - E_{Am}) - Xr (C_r^m)^2 \text{-----} (1-1/\epsilon) \\ [q_r + 2b^2 Xr (C_r^m)^2] Rr \\ E_n^{\ddagger} = IP_n - b^2 (IP_n - E_{An}) - Xs (C_s^n)^2 \text{-----} (1-1/\epsilon) \\ [q_s + 2b^2 Xs (C_s^n)^2] Rs$$

A hard base is characterised by a low value for the energy of the occupied frontier orbital and a soft base by a higher value. The softness values of base were represented by E_m^{\ddagger} accordingly the hardness of a base increase with the decrease of E_m^{\ddagger} . A hard acid on the contrary is characterized by a higher value for the energy of the empty frontier orbital and is represented by E_n^{\ddagger} the hardness will decrease with the decrease of E_n^{\ddagger} . b^2 and a^2 depend upon whether the reaction is charge controlled or frontier controlled. Thus $a^2 = 1/2$ and $b^2 = 1/2$ frontier controlled $a^2 = 1$ and $b^2 = 0$ charge controlled $a^2 = 3/4$ and $b^2 = 1/4$ for intermediate situations.

Conclusion

Klopman divided various acids and base ions, according to their numerical values into hard, soft and borderline. The sequence of softness of acids and bases suggested by Pearson

on qualitative basis and the sequence obtained by Klopman were mostly found to be same.

Table 1: A Comparison of α and β values for the Eq....(i) Lewis Acid

Lewis Acid	α	β
Hg ²⁺	5.786	-0.031
Cu ⁺	4.060	0.143
Ag ⁺	2.812	0.171
Pb ⁺²	1.771	0.110
Cd ⁺²	2.132	0.171
Cu ⁺²	2.259	0.233
Mn ⁺²	1.438	0.166
Au ⁺³	2.442	0.353
Mg ⁺²	1.402	0.243
Zn ⁺²	1.367	0.252
Fe ⁺³	1.939	0.523
Ba ⁺²	1.786	0.411
Al ⁺³	-0.749	1.339
H ⁺	0.000	1.000
I ₂	3.04	0.000

Table 2: Equilibrium constant in H₂O at 25°C for reaction.

Base B	Log Keq
F ⁻	-1.35
Cl ⁻	12.25
Br ⁻	15.62
I ⁻	18.1
OH ⁻	-6.3
S ⁻²	7.0
SCN ⁻	6.7
SO ₃ ⁻²	1.3
S ₂ O ₃ ⁻²	9.0
N ₃ ⁻	1.3
NH ₃	-1.8
NH ₂ C ₆ H ₄ SO ₃ ⁻ (p)	-0.5
NH ₂ CH ₂ CH ₂ NH ₂	-1.8
P(C ₂ H ₅) ₃	6.2
CN ⁻	5.0
CH ₃ ⁻	30

Table 3: Classification of Bases as Hard, Soft and Borderline

Hard	Soft	Borderline
H ₂ O, OH ⁻ , F ⁻ , CH ₃ COO ⁻ & PO ₄ ⁻³ , SO ₄ ⁻² , Cl ⁻ , CO ₃ ⁻² , ClO ₄ ⁻ , NO ₃ ⁻ , ROH, RO ⁻ , R ₂ O, NH ₃ , RNH ₂ , N ₂ , H ₄	R ₂ S, RSH, RS ⁻ , SCN ⁻ , I ⁻ , S ₂ O ₃ ⁻² , R ₃ P, R ₃ As, (RO) ₃ P, CN ⁻ , RNC, C ₂ H ₄ , C ₆ H ₆ , H ⁻ , R ⁻	C ₆ H ₅ NH ₂ , C ₅ H ₅ N, N ₃ ⁻ , B ₆ , NO ₂ ⁻ , SO ₃ ⁻² , N ₂

Table 4: Classification of Lewis Acids

Hard	Soft
H ⁺ , Li ⁺ , Na ⁺ , K ⁺ , Be ⁺² , Mg ⁺² , Ca ⁺² , Sr ⁺² , Mn ⁺² , At ⁺³ , Sc ⁺³ , Ga ⁺³ , In ⁺³ , La ⁺³ , N ⁺³ , Cl ⁺³ , Gd ⁺³ , Lu ⁺³ , Cr ⁺³ , Co ⁺³ , Fe ⁺³ , As ⁺³ , CH ₃ Sn ⁺³ , Si ⁺⁴ , Ti ⁺⁴ , Zr ⁺⁴ , Th ⁺⁴ , Cl ⁺⁴ , PCI ⁺⁴ , Ce ⁺³ , Hf ⁺⁴ , W ⁺⁴ , Sn ⁺⁴ , ClO ₂ ⁺² (CH ₃) ₂ , Sn ⁺² , V ⁺² , Mo ⁺³ , BeMe ₂ , F ₃ B(OR) ₃ , Al(CH ₃) ₃ , RPO ₂ ⁺ , ROPO ₂ ⁺	Cu ⁺ , Ag ⁺ , Au ⁺ , TI ⁺ , Hg ⁺ , Pb ⁺² , Cd ⁺² , Pt ⁺² , Hg ⁺² , CH ₃ Hg ⁺ , Co(CN) ₅ ⁻² , Pt ⁺⁴ , Te ⁺⁴ , TI ⁺³ , TI(CH ₃) ₃ , BH ₃ , Ga(Me) ₃ , GaCl ₃ , GaI ₃ , InCl ₃ , RS ⁺³ , RSe ⁺³ , RTe ⁺ , I ⁺ , Br ⁺ , HO ⁺ , RO ⁺ , I ₂ , Br ₂ , ICN etc. Trinitrobenzene etc. Chloranil, quinones etc. Tetracyano ethylene etc.

Borderline

Fe⁺², Co⁺², Ni⁺², Cu⁺², Zn⁺², Ph⁺², Sn⁺², Sb⁺³, Bi⁺³, Rh⁺³, Ir⁺³, B(CH₃)₃, SO₂, NO⁺, Ru⁺², OS⁺², R₃C⁺, C₆H₅⁺, GaH₃.

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