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The Use of Electronegativity and Hardness Towards Understanding Pearson's Hard-Soft Acid-Base Principle

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The advent of Density Functional Theory [DFT] realises the two new concepts namely electronegativity χ and hardness η. These two parameters have been very useful in understanding the insight of atoms, molecules, ions in isolated system, which are further extended to study the chemical reactions, namely double displacement reactions. These reactions were categorised on the basis of Pearson's HSAB principle which indicates that hard-hard and soft-soft interactions are preferable to hard-soft interaction. The present work is devoted to some reactions and their feasibility on the basis of change in hardness ($\Delta\eta$) and change in electronegativity ($\Delta\chi$).

INTRODUCTION

The intrinsic properties of isolated chemical species (atoms, ions, molecules) are significant input for the eletermination of the properties of combined systems. Though, they are in a no simple sense, completely sufficient.

One atomic parameter has been of great use in chemistry, namely, the electronegativity (χ_s) obtained approximately from experimental ionization potential (l) and electron affinity (A)

$$\chi_s = 1/2\,(l_s + A_s) \tag{1}$$

This has been, theoretically, reached to the exactness through Density Functional theory (DFT),[1] in the form

$$\chi = (\partial E/\partial N)_v = -\mu \tag{2}$$

Where E is the electronic energy, N is the number of electron transferred and 'v' is the nuclear potential. In fact the advent of DFT realises the two new concepts[2, 3] namely electronegativity (χ) and hardness (η). The parameter absolute hardness (η) which takes the form,

$$\eta = 1/2\,(\partial^2 E/\partial N)^2_v = 1/2\,(\partial\chi/\partial N)_v \tag{3}$$

has been very useful in chemistry. The reasons for its usefulness lies in a way that earlier Pearson[4] adopted the qeneralized acid-base view of chemistry indroduced by Lewis

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$$A + :B \rightleftharpoons A:B$$

Where A is electron acceptor and B is electron donor, which could not be quantified.

Pearson[4, 5] used the actual experimental data to exchange reaction such as,

$$A:B'_{(g)} + A':B'_{(g)} \rightarrow A':B'_{(g)} + A:B_{(g)}$$

If other bond-determining factors are constant, the reaction will be exothermic. If A′ is softer than A and B′ is softer than B. This may be re-stated as,

$$hs + sh \rightleftharpoons hh + ss \quad \Delta H < O$$

So, the density functional theory confirms and amplifies the reasons for HSAB[5, 6] prniciple. Soft acid and bases form covalent bonds stabilized by mutual polarization including hyper-conjugation. Hard acids and bases form ionic bonds.

Recently, Datta and Singh[7] used the concepts of chemical hardness and dissociative (heterolytic) Pauling's bond-energy equation to study the exothermicity and endothermicity of the exchange reactions (neutral molecules and molecular species) on the basis of γ-parameter, given as

$$D(A^+B^-) - 1/2[D(A^+A^-) + D(B^+B^-)] = 2|\Delta\gamma|^2$$

for hard-hard and soft-soft interaction. These workers have succesfully made the universal scale of γ-parameters for most of atomic and molecular ionic species. Most of the reactions (*ca.* 2 5 5) of double-displacement nature have been explained and are given in Tables 1 and 2.

TABLE-1

EXPERIMENTAL IONIZATION POTENTIAL AND ELECTRON AFFINITIES OF THE VARIOUS ATOMS AND RADICALS USED IN THE PRESENT STUDY[a]

Atom/radicals	i.p.	e.a.	n
H	13.60	0.75	6.43
Li	5.39	0.62	2.39
F	17.42	3.40	7.01
Na	5.14	0.55	2.30
Cl	13.01	3.62	4.70
K	4.34	0.50	1.92
Cu	7.73	1.23	3.25
Br	11.84	3.36	4.24
Rb	4.18	0.49	1.85
I	10.45	3.06	3.70
Cs	3.85	0.47	1.71
SiH_3	8.14	1.41	3.37
NO_2	9.78	2.38	3.70

a. Taken from reference 10.

TABLE-2
EXCHANGE REACTIONS OF THE TYPE AB + CD → AD + BC (Ref. No. 7)

	Reaction	ΔH^0 (k cal mol^{-1})^a	$\Delta\Delta\gamma$/LHS	$\Delta\Delta\gamma$/RHS
1.	$LiI + CsF \rightarrow LiF + CsI$ 4.0 7.0 6.0 5.0	–14.0	3.0	1.0
2.	$CuCl + IF \rightarrow CuF + ICl$ 5.5 5.0 6.5 4.5	15.7	0.5	2.0
3.	$SiH_3 + CH_3F \rightarrow SiH_3 + CH_3Cl$ 3.5 6.5 4.5 3.0	–20.0	3.0	1.5
4.	$CH_3F + HNO_2 \rightarrow CH_3NO_2 + HF$ 6.5 5.5 10.0 2.0	19.3	1.0	8.0
5.	$CsF + HI \rightarrow CsI + HF$ 7.0 0.0 5.0 2.0	–24.6	7.0	3.0

a. Taken From Reference 7.

In the present work, the author has taken same reactions as given by Datta and Singh[7], and studied them and characterize the hard-hard, soft-soft interactions on the basis of absolute hardness.

RESULT AND DISCUSSION

The preliminary reaction studied studied earlier, is as follows

	Li^+I^-	+	Cs^+F^-	$\longrightarrow$	Li^+F^-	+	Cs^+I^-	$\Delta H^0 = -14.0$ Kcal/mol
	hs		sh		hh		ss	
$\Delta\gamma$	4.0		7.0		6.0		5.0	
$\Delta\Delta\gamma$		3.0				1.0		

so $\Delta\Delta\gamma$/L.H.S. > $\Delta\Delta\gamma$/R.H.S.

hence the reaction will go in forward direction. Another reaction

	Cu^+Cl^-	+	I^+F^-	$\longrightarrow$	Cu^+F^-	+	I^+Cl^-	$\Delta H^0 = 15.7$ Kcal/mol
$\Delta\gamma$	5.5		5.0		6.5		4.5	
$\Delta\Delta\gamma$		0.5				2.0		

since $\Delta\Delta\gamma$/L.H.S < $\Delta\Delta\gamma$/R.H.S., hence the reaction will go in the backward direction.

There are certain exceptions where $\Delta\gamma$-scale does not match the experimental findings. The reasons are obvious, being, polarization, steric requlsions are not taken into account.

If the hardness parameter is taken as the fundamental tool for the molecular reactions, most of the ambiguities are removed. The results of the present study are given in Table 3. It can be seen from the table, that all the reactions explain their feasibility on the basis of change in hardness on reactant side and the product side.

Recently Sekhon[8] used the electronegativity equalisation concept to study HSAB principle through protonated and double-displacement reactions. Some of his results are listed in Table 4. He used Bratch method to calculate. Values for molecules, as

$$\chi_{eq} = \frac{N + q}{\Sigma(v/\chi)} \tag{4}$$

Where $N = \Sigma v =$ the number of atoms in the species formula q is the charge of the species and χ is the Pauling electronegativity as determined by Allred and Rochow.[9] We have applied our concept of change in hardness to these reactions and it is intersting to note that it testifies the HSAB principle successfully[10].

TABLE-3

EXCHANGE REACTIONS OF THE TYPE AB + CD → AD + BC[b]

Reactions	ΔH^{0a}(k cal mol)[a]	L.H.S ($\Delta\eta$)	R.H.S. ($\Delta\eta$)
CsCl + KI → CsI + KCl	0.99	0.865	0.869
CuF + ICl → CuCl + IF	–15.70	0.381	0.411
CsBr + KCl → CsCl + KBr	6.00	0.902	0.812
C_2H_5F + CsI → C_2H_5I + CsF	14.30	0.705	0.635
CsF + RbH → CsH + RbF	0.00	0.723	0.723
LiF + HBr → LiBr + HF	–14.40	0.413	0.449
*CH_3F + HNO_2 → CH_3NO_2 + HF	–7.60	0.270	0.198
*SIH_3H + HI → SiH_3I + HH	–14.50	0.143	0.119

(a) Taken from reference 7. (b) The present work.
*Reactions are not occuring according to the theory.

TABLE-4

X_{eq} AND ΔX_{eq}. VALUES FOR EXCHANGE REACTIONS OF THE TYPE AB + CD → AD +BC

Reaction	ΔH^0 (K Cal/mol)[a]	$\Delta\chi_{eq}$(RHS) ($\Delta\eta_{eq}$(RHS)[b])	$\Delta\chi$(LHS) ($\Delta\eta_{eq}$(LHS))
LiF + HI → LiI + HF	–10.6	1.4070	0.8355
1.5727 2.4082 1.4323 2.8390		(7.3500)	(0.7300)
LiCl + NaF → LiF + NaCl	–9.5	0.1357	0.0185
1.4960 1.5145 1.5727 1.4370		(2.4000)	(2.2200)
CsF + HCl → CsCl + HF	–16.7	1.5750	1.2757
1.3183 2.5940 1.2640 2.8390		(7.0300)	(2.4100)
HI + NaF → HF + NaI	–23.4	1.4610	0.8937
2.4082 1.5145 2.8390 1.3782		(7.4400)	(0.8200)
LiI + CsF → LiF + CsI	–14.0	0.3045	0.1140
1.4323 1.3183 1.5287 1.2182		(3.9900)	(2.6300)

(a) Taken from reference 7. (b) Values in parantheses are from the present work.

Conclusion

The usefulness of the absolute electronegativity and absolute hardness are the essential parameters to understand HSAB prinicple specifically the insight of electronic structure of atom, molecules and their ionic species. Since these form the basis for any reaction and assigning the feasibility of the reactions. It has got vast application in organic reactions and synthesis. Further, the clear picture will emerge when in each atomic species, the charges are calculated and then collectively used for the χ and η values.

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