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Trends in Equalized Electronegativity and its Relationship to pK and Hardness of Acids and Stability of Metal Complexes

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Equalized electronegativity (X_{eq}) is an important property of a compound and tends to increase across a given period and tends to decrease down a group in case of hydrides, halides and XH_4^- (where X = B, Al and Ga) salts of alkali metal cations. A positive correlation (r = 0.97) exists between pK and X_{eq} values of binary hydrides of halogens and chalcogenides and also holds good in conjugate acid-base pairs and inorganic oxyacids. The metal complex having greater stability has greater X_{eq} value.

INTRODUCTION

Although the principle of electronegativity equalization has been cited in chemistry literature since 1951 but the usefulness of equalized electronegativity (X_{eq}) has not been fully exploited except the calculation of partial charges on atoms and groups[1–3] and its relation to oxidation-reduction of organic compounds[4].

Equalized electronegativity (X_{eq}) was calculated by Bratsch method[2] according to the equation

$$X_{eq} = \frac{N + q}{\Sigma(V/x)}$$

where N = ΣV = the number of atoms in the species formula and *q* is the charge of the species. The net partial charge on a group was given by

$$\delta_G = N_G\left(\frac{X_{eq} - X_G}{X_G}\right)$$

where N_G is the number of atoms in the group formula, X_G is calculated by

$$X_G = \frac{N_G}{\Sigma(V/x)}$$

RESULTS AND DISCUSSION

Trends in X_{eq}

Equalized electronegativity is an important property of a compound and shows a regular trend in a period or group in case of hydrides and halides of elements. X_{eq} tends to increase across a given period (*e.g.*, LiH to HF or NaH to HCl; LiH 1.3560, BeH_2 1.9404, BH_3 2.1577, CH_4 2.2621, NH_3 2.3632, OH_2 2.5004, HF

2.8336), and tend to decrease down a group (*e.g.*, LiH to CsH or BeH_2 to BaH_2; LiH 1.3560, NaH 1.3073, KH 1.1947, RbH 1.1947, CsH 1.1620; BeH_2 1.9404, MgH_2 1.7938, CaH_2 1.5714, SrH_2 1.5293, BaH_2 1.476). This is also true for XH_4^- (where X = B, Al, Ga) salts of alkali metal cations ($LiBH_4$ 1.8024, $NaBH_4$ 1.7732, KBH_4 1.7007, $RbBH_4$ 1.7007, $CsBH_4$ 1.6787; $LiAlH_4$ 1.7342, $NaAlH_4$ 1.7072, $KAlH_4$ 1.6399, $RbAlH_4$ 1.6399, $CsAlH_4$ 1.6194; $LiGaH_4$ 1.7693, $NaGaH_4$ 1.7412, $KGaH_4$ 1.6712, $RbGaH_4$ 1.6712 and $CsGaH_4$ 1.6500).

TABLE 1

CORRELATION BETWEEN X_{eq}^* AND LATTICE ENERGY† (kcal mol^{-1}, 298 *Q*) OF HYDRIDES, FLUORIDES, CHLORIDES, BROMIDES AND IODIDES OF Li, Na, K, Rb AND Cs

	F	Cl	Br	I	r
Li	1.5727* 245.1†	1.4960 201.1	1.4725 189.9	1.4323 176.2	0.993
Na	1.5145 216.0	1.4370 183.5	1.4153 175.5	1.3782 164.3	0.997
K	1.3598 191.5	1.3021 167.9	1.2843 161.3	1.2536 152.4	0.997
Rb	1.3598 183.6	1.3021 162.0	1.2843 156.1	1.3536 148.0	0.996
Cs	1.3183 171.0	1.2640 153.1	1.2472 149.6	1.2182 142.5	0.995
r	0.976	0.979	0.983	0.984	

In case of halides of elements, X_{eq} also shows regular trend (Table 1). In case of alkali halides, X_{eq} values follow the sequence MF > MCl > MBr > MI (where M = Li, Na, K, Rb, Cs); LiX > NaX > KX > RbX > CsX (where X = F, Cl, Br and I). A positive correlation exists between X_{eq} and lattice energies[5] for alkali metal halides. Similar trend is also observed for halides of Mg, Ca, Sr and Ba (data not shown).

X_{eq} versus pK

The simplest class of Bronsted acids are the hydrides of chalcogenides and halides within a group. For homolytic fission, the acid strength increase in the series[6] $H_2O < H_2S < H_2Se < H_2Te$ and HF < HCl < HBr < HI and this sequence is parallel to their X_{eq} values which are H_2O 2.5004, H_2S 2.3136, H_2Se 2.3055, H_2Te 2.1328; HF 2.8336, HCl 2.5940, HBr 2.524, HI 2.4082. A positive correlation ($r = 0.97$) was observed between pK and X_{eq} values of binary hydrides of halogens and chalcogenides. The pK values[6] are H_2O 16, H_2S 7, H_2Se 4, H_2Te 3; HF 3, HCl 7, HBr −9, HI −10.

The relationship (greater X_{eq}, greater pK) also holds good in Bronsted acid-base pairs. Conjugate base of any Bronsted acid has greater X_{eq} value or vice versa. This is evident from their comparison of X_{eq} values of conjugate acid-base pairs

($H_3PO_4/H_2PO_4^-$ 2.6818/2.7684, $H_2PO_4^-/HPO_4^{2-}$ 2.7684/2.8930, CH_3COOH/CH_3COO^- 2.505/2.198, NH_4^+/NH_3 2.794/2.363, H_2S/SH^- 2.313/1.687, H_3O^+/H_2O 0.022/2.500, H_2CO_3/HCO_3^- 2.740/2.327 and HCO_3^-/CO_3^{2-} 2.327/1.582).

X_{eq} versus hard and soft acids

Species having relatively greater X_{eq} values are hard acids while those having relatively less X_{eq} are soft acids. BF_3 and CF_3 having X_{eq} values 3.215 and 3.191 respectively are hard acids while BH_3 and CH_3 having X_{eq} values 2.157 and 2.780 are soft acids. Further the preference for hard-hard interaction between hard acid Li^+ and hard base F^- forming strong bond results in large X_{eq} values for LiF while soft-soft interaction between soft acid Cs^+ and soft base I^- forming less stable bond has lower X_{eq} values (eqn. 1).

$$\text{LiI} + \text{CsF} \rightarrow \text{LiF} + \text{CsI} \qquad (1)$$

The support for strong bond (hard-hard interaction) in LiF and CsF while soft-soft interaction in LiI and CsI finds support by heats of atomization data of these compounds[7]. The favour for hard-hard over hard-soft or soft-soft interactions in terms of X_{eq} values is also evident from equations 2–5.

$$\begin{array}{lccccccc} & \text{Hard–soft} & & \text{Soft–hard} & & \text{Hard–hard} & & \text{Soft–soft} \\ & BF_3H^- & + & BH_3F^- & \rightarrow & BF_4^- & + & BH_4^- \\ X_{eq} = & 1.9001 & & 2.2350 & & 2.6752 & & 1.7328 \end{array} \qquad (2)$$

$$\begin{array}{lccccccc} & \text{Hard–soft} & & \text{Soft–hard} & & \text{Hard–hard} & & \text{Soft–soft} \\ & CF_3H & + & CH_3F & \rightarrow & CF_4 & + & CH_4 \\ X_{eq} = & 3.1240 & & 2.4912 & & 3.5786 & & 2.2621 \end{array} \qquad (3)$$

$$\begin{array}{lccccccc} & \text{Soft–hard} & & \text{Hard–soft} & & \text{Soft–Soft} & & \text{Hard–hard} \\ & CH_3HgF & + & HSO_3^- & \rightarrow & CH_3HgSO_3^- & + & HF \\ X_{eq} = & 2.3932 & & 2.3334 & & 2.2756 & & 2.8336 \end{array} \qquad (4)$$

$$\begin{array}{lccccccc} & \text{Soft–hard} & & \text{Hard–soft} & & \text{Soft–Soft} & & \text{Hard–hard} \\ & CH_3HgOH & + & HSO_3^- & \rightarrow & CH_3HgSO_3^- & + & HOH \\ X_{eq} = & 2.3325 & & 2.2334 & & 2.2756 & & 2.5004 \end{array} \qquad (5)$$

X_{eq} versus stability of metal complexes

A positive relationship exists between stability constant (log K) and Xeq value of metal complex. Greater is the X_{eq} value, greater is the log K of the metal complex. This is evident from log K and X_{eq} values of pyrophosphate $P_2O_7^{4-}$ complexes[8] of Mg^{2+} (9.2, 2.1555), Ca^{2+} (6.8, 2.0263), Sr^{2+} (5.4, 1.9996) and Ba^{2+} (4.6, 1.9648). Irving-Williams order[9] of stability for first row transition metal ion complexes is well known and follows the trend $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Zn^{2+}$. A similar trend (Fig. 1) is observed for X_{eq} values of metal complexes for several bidentate ligands.

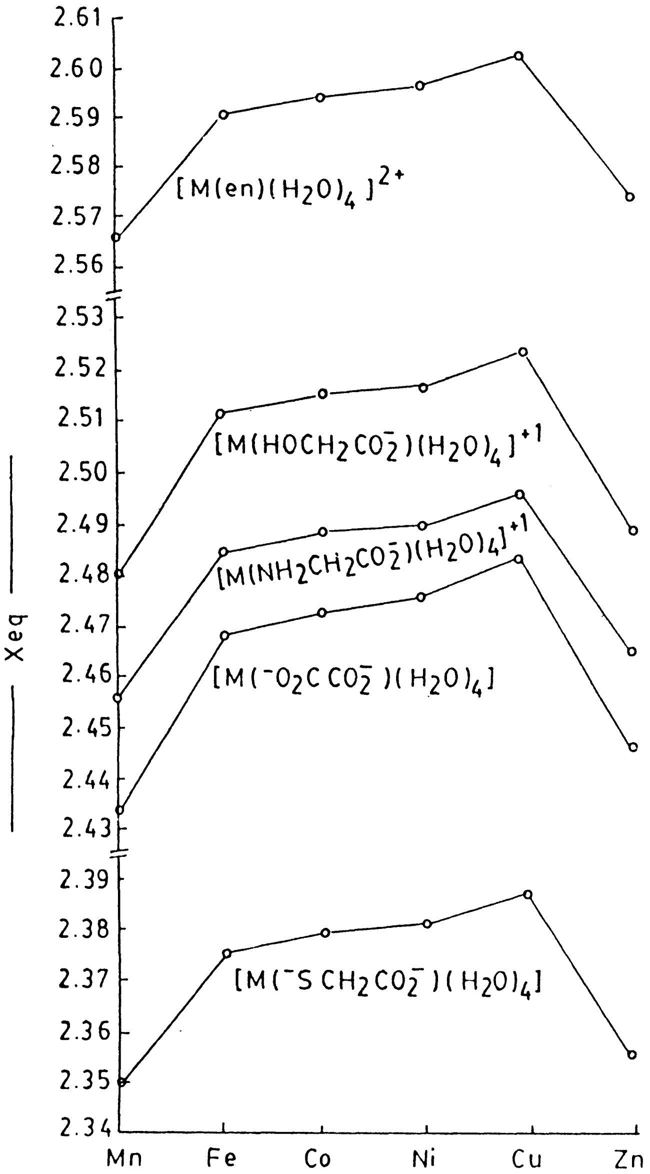

Fig. 1 Variation in X_{eq} for complexes of first row transition metal ions (M^{2+} with several bidentate ligands.

REFERENCES

1. R.T. Sanderson, *Science*, **114**, 670 (1951).
2. S.G. Bratsch, *J. Chem. Educ.*, **62**, 101 (1985).

3. B.S. Sekhon, *Natl. Acad. Sci. Letters*, **13**, 235 (1990).
4. B.S. Sekhon, *Proc. Indian Natn. Sci. Acad.*, **57A**, 423 (1991).
5. J.C. Bailor, H.J. Emeleus, R.S. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon (1973).
6. R.P. Bell, The Proton in Chemistry, Methuen, London, p. 87 (1959).
7. J.E. Huheey, Inorganic Chemistry, Harper and Row Publishers, New York, p. 320 (1983).
8. L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, Special Publication Nos. 17 and 25, The Chemical Society, London (1964 and 1971).
9. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953); *Nature*, **162**, 746 (1948).

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