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# Fukui Function of Electrophiles and Nucleophiles : A New Method for Study of Metal Ligand Interaction

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Fukui function values at different sites in a number of nucleophiles and at metal in metal halides have been evaluated with the help of computational chemistry using Extended Hackle method. The relative donor ability of nucleophiles and acceptor strength of electrophiles have been explained with the help of these values. The metal-ligand bond strength has been demonstrated with the difference in Fukui function values of acid and base by the equation $\Delta f - f+ = |f^- - f^+|$. The results have been compared with the results of DFT calculations and softness parameters. The results are dependable and are also in conformity with charge transfer ($\Delta N$) and energy lowering ($\Delta E$) calculations.

**Key Words: Metal-ligand interaction, Fukui function, Charge transfer, Lowering of energy.**

## INTRODUCTION

Within the framework of density functional theory[1], a number of variables have been developed to study chemical reactivity problems. Fukui function is one such variable, which is defined[2] as the derivative of the electronic density with respect to number of electrons is given by eqn. (1).

$$f(r) = [\partial\rho(r)/\partial N]_v \quad (1)$$

where $\rho(r)$ is electronic density with space r(x, y, z) and v the external potential.

The knowledge of Fukui function has made it possible to explain the local response in a chemical system; in other words the site of activity in a molecule. Local softness, atomic softness, HOMO density are synonymous terms. This paper presents, a study of Fukui function of a series of metal halides (electrophiles) and organic bases (nucleophiles). The interaction of electrophiles and nucleophiles has been discussed in Fukui function language. The Fukui function has been compared with the study of other variables which are its synonyms.

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## EXPERIMENTAL

All the metal halides and organic bases have been modeled in 3D figure and their geometries have been optimized with the help of Cache software using Extended Huckle method. The Fukui function of an atom in a molecule is calculated by eqns. (2), (3):[3]

$$f^- = q(N) - q(N - 1) \tag{2}$$

$$f^+ = q(N + 1) - q(N) \tag{3}$$

where q is partial charge of the atom in a molecule and N is the total number of electrons of a molecule.

The synonymous terms by which the activity at a particular site in a molecule has been studied are HOMO density[4, 5], local softness[6] and atomic softness of Klopman[7].

The HOMO and LUMO density are the important parameters for study of any chemical reaction. The electron density of the HOMO at an atom is a measure of the relative reactivity at that atom within a single molecule and is associated with donor ability of nucleophiles. The LUMO density is, however, associated with the acceptor property of any atom in a molecule having electrophilic character.

The densities of the compound under study have also been evaluated with the help of density functional theory[8] method DFT-B-88PW-91 for the purpose of comparison.

Another important synonym is atomic softness evaluated through Klopman equation. Softness values have also been obtained for the purpose of comparison[9].

The local softness which has often been referred to as reciprocal of hardness has also been calculated by solving eqn. (4).

The local softness s(r) is obtained by integrating over one of the variables of the softness kernel[10] by $(\partial/\partial\mu)_v = -\int dr\ (\delta/\delta u(r))_\rho$; therefore,

$$(\partial\rho(r)/\partial\mu)_v = \int dr'\ s(r, r') = s(r) \tag{4}$$

where $s(r, r') = -(\delta\rho(r)/\delta u(r'))$ is softness kernel.

The other variables within the framework of DFT which have been found useful for study of chemical reactivity are defined by the following equations[11]

$$\mu = (\partial E/\partial N)_v \tag{5}$$

$$\eta = (1/2)(\partial\mu/\partial N)_v = (I - A)/2 \tag{6}$$

$$\chi = -\mu = (I + A)/2 \tag{7}$$

where N = number of electrons, $\nu$ = potential due to nuclei, I = ionization potential, A = electron affinity, $\eta$ = absolute hardness, $\chi$ = electronegativity, $\mu$ = chemical potential, $\sigma = 1/\eta$ = local softness.

According to Klopman's theorem[11] the ionization potential and electron affinity are the negative of HOMO and LUMO energies respectively as shown below:

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

The above variables have been defined because they have been used for evaluating charge transfer and lowering of energy in metal-ligand interaction. The relevant equations are[12]:

$$\Delta N = (\chi_{A^0} - \chi_{B^0})/[2(\eta_A + \eta_B)] \quad (8)$$

and

$$\Delta E = (\chi_{A^0} - \chi_{B^0})^2/[4(\eta_A + \eta_B)] \quad (9)$$

## RESULTS AND DISCUSSION

### Nucleophiles

The Fukui function values of a series of nucleophiles have been evaluated with the help of eqn. (3) and the results are included in Table-1.

TABLE-1
FUKUI FUNCTION VALUES OF DONOR ATOM IN ORGANIC BASES (NUCLEOPHILES)

| Compound | Atom | q(N + 1) | q(n) | $f^+$ |
|---|---|---|---|---|
| $HCONH_2$ | N | –1.2710 | –0.3906 | –0.8804 |
| | O | –1.1403 | –1.1561 | 0.0158 |
| $CH_3CONH_2$ | N | –1.3235 | –0.4358 | –0.8877 |
| | O | –1.1638 | –1.1819 | 0.0181 |
| $C_2H_5CONH_2$ | N | –1.3258 | –0.4382 | –0.8876 |
| | O | –1.1648 | –1.1812 | 0.0164 |
| $HCONHCH_3$ | N | –1.2416 | –0.3434 | –0.8982 |
| | O | 0 | –1.1598 | 1.1598 |
| $PhCONH_2$ | N | –1.3538 | –0.4731 | –0.8807 |
| $NH_2CONH_2$ | N | –0.4671 | –0.4951 | 0.0280 |
| | N | –1.3747 | –0.4951 | –0.8796 |
| | O | –1.2070 | –1.2265 | 0.0195 |
| $CH_3NHCONH_2$ | N | –0.4721 | –0.4979 | 0.0258 |
| | N | –1.3450 | –0.4539 | –0.8911 |
| | O | –1.2022 | –1.2250 | 0.0228 |
| $CH_3NHCONHCH_3$ | N | –0.4264 | –0.4567 | 0.0303 |
| | N | –1.3496 | –0.4567 | –0.8929 |
| | O | | | |
| $(CH_3)_2NCON(CH_3)_2$ | N | –0.5248 | –0.4229 | –0.1019 |
| | N | –0.5254 | –0.4230 | –0.1024 |
| | O | –1.3334 | –1.2389 | –0.0945 |

| Compound | Atom | q(N + 1) | q(n) | $f^+$ |
|---|---|---|---|---|
| $PhNHCONH_2$ | N | –0.3134 | –0.3446 | 0.0312 |
| | N | –1.3773 | –0.4934 | –0.8839 |
| | O | –1.1983 | –1.2156 | 0.0173 |
| $Ph_2NCONH_2$ | N | –0.2144 | –0.3128 | 0.0984 |
| | N | –1.3461 | –1.3780 | 0.0319 |
| | O | –1.1995 | –1.1980 | –0.0015 |
| $Ph_2NCONPh_2$ | N | –0.3644 | –0.2388 | –0.1256 |
| | N | –0.2590 | –0.2251 | –0.0339 |
| | O | –1.2673 | –1.3214 | 0.0541 |
| $(C_2H_5)_2NCON(C_2H_5)_2$ | N | –0.5455 | –0.4453 | –0.1002 |
| | N | –0.5455 | –0.4451 | –0.1004 |
| | O | –1.3348 | –1.2369 | –0.0979 |
| $HCSNH_2$ | N | –1.1699 | –0.3787 | –0.7912 |
| | S | –0.3668 | –0.3434 | –0.0234 |
| $HCSNHCH_3$ | N | –1.1259 | –0.3341 | –0.7918 |
| | S | –0.3867 | –0.3685 | –0.0182 |
| $HCSN(CH_3)_2$ | N | –0.4939 | –0.3118 | –0.1821 |
| | S | –0.9431 | –0.3688 | –0.5743 |
| $HCSNHC_2H_5$ | N | –1.2535 | –0.5626 | –0.6909 |
| | S | 0.5453 | 0.6223 | –0.0770 |
| $HCSN(C_2H_5)_2$ | N | | –0.5270 | 0.5270 |
| | S | | 0.5670 | –0.5670 |
| HCSNHPh | N | –1.0559 | –0.3899 | –0.6660 |
| | S | 0.5273 | 0.6301 | –0.1028 |
| $HCSNPh_2$ | N | –0.4445 | –0.2878 | –0.1567 |
| | S | –0.1489 | 0.6547 | –0.8036 |
| $NH_2CSNH_2$ | S | 0.4309 | 0.4752 | –0.0443 |
| | N | –1.3564 | –0.5644 | –0.7920 |
| | N | –1.3564 | –0.5644 | –0.7920 |
| $(CH_3)_2NCSN(CH_3)_2$ | S | –0.4022 | 0.4317 | –0.8339 |
| | N | –0.5768 | –0.5406 | –0.0362 |
| | N | –0.5148 | –0.5023 | –0.0125 |
| $(C_2H_5)_2NCSN(C_2H_5)_2$ | S | –0.4514 | 0.4763 | –0.9277 |
| | N | –0.5425 | –0.5629 | 0.0204 |
| | N | –0.5844 | –0.6100 | 0.0256 |
| $Ph_2NCSNPh_2$ | S | –1.7092 | 0.3198 | –2.0290 |

| Compound | Atom | q(N + 1) | q(n) | $f^+$ |
|---|---|---|---|---|
| | N | –0.6403 | –0.3065 | –0.3338 |
| $CH_3NHCSeHNCH_3$ | N | 1.1935 | –0.3909 | 1.5844 |
| | Se | –0.9807 | –0.3909 | –0.5898 |
| | N | –0.4012 | –0.9798 | 0.5786 |
| $(CH_3)_2NCSeN(CH_3)_2$ | N | –0.4959 | –0.3666 | –0.1293 |
| | Se | –1.0636 | –1.0012 | –0.0624 |
| | N | –0.4948 | –0.3669 | –0.1279 |
| PhNHCSeHNPh | N | –0.2407 | –0.2487 | 0.0080 |
| | Se | –0.9861 | –0.9587 | –0.0274 |
| | N | –1.0176 | –0.2487 | –0.7689 |
| $Ph_2NCSeNPh_2$ | N | –0.1842 | –0.1149 | –0.0693 |
| | Se | –0.8639 | –0.8232 | –0.0407 |
| | N | –0.0910 | –0.1488 | 0.0578 |
| $C_5H_4FN$ | F | –0.6345 | –0.6226 | –0.0119 |
| | N | –0.9670 | –0.8482 | –0.1188 |
| $C_5H_4ClN$ | Cl | –0.1027 | –0.0738 | –0.0289 |
| | N | –1.0126 | –0.9118 | –0.1008 |
| $C_5H_4BrN$ | Br | –0.0991 | –0.0626 | –0.0365 |
| | N | –0.9676 | –0.8568 | –0.1108 |
| $C_5H_4IN$ | I | –0.0591 | –0.0205 | –0.0386 |
| | N | –0.9511 | –0.8412 | –0.1099 |
| $C_5H_4NO_2N$ | N | 1.0073 | 1.3648 | –0.3575 |
| | N | –0.7899 | –0.8073 | 0.0174 |
| | O | –1.1056 | –1.0028 | –0.1028 |
| | O | –1.2842 | –1.2486 | –0.0356 |
| $C_5H_4CH_3N$ | N | –0.9641 | –0.8544 | –0.1097 |
| $PH_3$ | P | –1.2266 | –0.3239 | –0.9027 |
| $(CH_3)_3P$ | P | –0.0404 | 0.2695 | –0.3099 |
| $AsH_3$ | As | –0.9388 | 0.1077 | –1.0465 |
| $(CH_3)_3As$ | As | –0.1696 | 0.2757 | –0.4453 |
| $NH_3$ | N | –1.5509 | –0.7381 | –0.8128 |
| $CH_3NH_2$ | N | –1.5095 | –0.7017 | –0.8078 |
| $(CH_3)_2NH$ | N | –1.4694 | –0.6755 | –0.7939 |
| $(CH_3)_3N$ | N | –0.9544 | –0.6499 | –0.3045 |
| $C_2H_5NH_2$ | N | –1.5217 | –0.7131 | –0.8086 |
| $(C_2H_5)_2NH$ | N | –1.4925 | –0.6975 | –0.7950 |

| Compound | Atom | q(N + 1) | q(n) | $f^+$ |
|---|---|---|---|---|
| $(C_2H_5)_3N$ | N | –0.9333 | –0.6897 | –0.2436 |
| $PhNH_2$ | N | –1.2653 | –0.4518 | –0.8135 |
| $Ph_2NH$ | N | –0.4758 | –0.2617 | –0.2141 |
| $Ph_3N$ | N | –0.4735 | –0.1615 | –0.3120 |

q = charge on the atom, N = number of electrons in the molecule, $f^+$ = Fukui function

Amides have been recognized as donor molecules through their carbonyl oxygen. This has been established previously by several workers[13].

The previous workers have mostly established the donor ability on the basis of negative shifts in carbonyl IR stretching frequency on complex formations. Now we have calculated Fukui function at oxygen and nitrogen atoms of the amides and the results are included in Table-1.

The Fukui function values at carbonyl oxygen are higher in all cases as compared to Fukui function values at nitrogen atom. This supports the experimental results[13]. In order to compare the relative donor ability of amides, the Fukui functions at carbonyl oxygen in number of amides have been evaluated, which suggests the following sequence of base strength of amides:

$$HCONHCH_3 > CH_3CONH_2 > C_2H_5CONH_2 > HCONH_2$$

This sequence of values of Fukui function is in agreement with the experiment results obtained earlier[13].

Ureas have also been extensively used as donor molecules towards a number of metal salts. In all these cases, the coordination site has been reported carbonyl oxygen[14]. The Fukui functions of a number of ureas have been evaluated at carbonyl oxygen as well as at the two nitrogens. The Fukui function values at carbonyl oxygen are always higher as compared to nitrogens. This supports the experimental results reported earlier[14]. It is also interesting to demonstrate the sequence of Fukui function values in different ureas which is as follows

$$Ph_2NCONH_2 > PhNHCONH_2 > NH_2CONH_2 > CH_3NHCONHCH_3 > CH_3NHCONH_2$$
$$> (CH_3)_2NCON(CH_3)_2 > (C_2H_5)_2NCON(C_2H_5)_2 > Ph_2NCONPh_2$$

In case of thioamides and thioureas, sulphur has been reported as coordinating site[15], though some authors have reported nitrogen as coordinating site[16]. The authors have based their results on IR and electronic spectral studies. This controversy could not be finally resolved.

The Fukui function values at both nitrogen and sulphur sites of thioamides and thioureas are calculated. In all the cases, the values of Fukui function are higher at sulphur. It can, therefore, be concluded that sulphur is the site of coordination in thioamides and thioureas. The Fukui function values in certain selenoureas have also been calculated. In such cases, the Fukui function values are higher at nitrogen and not at selenium. Though, reference for the complexes of selenoureas for comparison about the site of bonding have reported, yet on the basis of theoretical calculation of the values of Fukui function, we can predict that the nitrogen will be the site of bonding in selenoureas.

In case of ureas and amides, the highest value of HOMO density is also shown at carbonyl oxygen and in case of thioamides at thioamide sulphur (Table-2). The same result is also indicated by softness values[9]. Thus the sesult of Fukui functions are in conformity with the experimental results as well as with the result obtained by HOMO density and softness values[9].

Pyridine is a recognized nucleophile coordinating through nitrogen. The Fukui function values of various derivatives of pyridine at nitrogen have been evaluated (Table-1). The Fukui function values indicate the following order of the donor ability of the various derivatives:

$$C_5H_4NO_2N > C_5H_4ClN > C_5H_4IN > C_5H_4BrN > C_5H_4FN$$

This order of basicity of pyridine derivatives appears in good agreement with the electron withdrawing character of the substituents.

The values of Fukui function can also be helpful in describing the relative basicity of phosphorus and arsenic bases. Phosphine has Fukui function value of –0.9027 whereas arsine has –1.0465. This clearly shows that $PH_3$ is more basic than $AsH_3$. Their trimethyl derivatives also indicate the same sequence. The Fukui function values of trimethyl derivatives of phosphine and arsine are more basic as compared to phosphine and arsine.

The values of Fukui function (Table-1) indicate highest value for primary amines and lowest for tertiary amines. This sequence of stability is well demonstrated in case of ethyl, methyl and phenyl amines; however, in case of phenyl amines the lowest value is indicated by secondary amines. The order of basicity established on the basis of softness values derived from Klopman equations also indicates the same order[9]. If all the amines are arranged in order of their decreasing Fukui function values, the sequence is as follows:

$$(C_2H_5)_3N > (CH_3)_3N > (CH_3)_2NH > (C_2H_5)_2NH > CH_3NH_2 > C_2H_5NH_2 > NH_3$$

In case of amines and pyridine derivatives, the highest value of HOMO density is observed at nitrogen. In primary amines, this value is higher as compared to secondary and tertiary amines (Table-2). This observation is in consonance with the result obtained by Fukui function values.

TABLE-2
HOMO DENSITY VALUES AND DONOR MOLECULES

| Compound | Atom | $\rho_{HOMO}$ |
|---|---|---|
| $CH_3NH_2$ | N | 0.834 |
| $(CH_3)_2NH_2$ | N | 0.754 |
| $(CH_3)_3N$ | N | 0.695 |
| $C_2H_5NH_2$ | N | 0.818 |
| $(C_2H_5)_2NH$ | N | 0.738 |
| $(C_2H_5)_3NH$ | N | 0.695 |
| $PhNH_2$ | N | 0.354 |
| $Ph_2NH$ | N | 0.325 |

| Compound | Atom | $\rho_{HOMO}$ |
|---|---|---|
| $Ph_3N$ | N | 0.288 |
| $HCONH_2$ | O | 0.793 |
| $CH_3CONH_2$ | O | 0.798 |
| $C_2H_5CONH_2$ | O | 0.778 |
| $HCONHCH_3$ | O | 0.777 |
| $C_6H_5CONH_2$ | O | 0.760 |
| $PhCONH_2$ | O | 0.760 |
| $NH_2CONH_2$ | O | 0.845 |
| $CH_3NHCONH_2$ | O | 0.713 |
| $PhNHCONH_2$ | O | 0.055 |
| $Ph_2NCONH_2$ | O | 0.088 |
| $(CH_3)_2NCON(CH_3)_2$ | O | 0.549 |
| $CH_3NHCONHCH_3$ | O | 0.719 |
| $HCSNHH_2$ | S | 0.009 |
| $HCSNHCH_3$ | S | 0.009 |
| $HCSNHC_2H_5$ | S | 0.257 |
| $HCSN(C_2H_5)_2$ | S | 0.568 |
| $C_5H_4N$ | N | 0.693 |
| $C_5H_4FN$ | N | 0.210 |
| $C_5H_4ClN$ | N | 0.023 |
| $C_5H_4BrN$ | N | 0.026 |
| $C_5H_4IN$ | N | 0.024 |

$\rho_{HOMO}$ is the HOMO density calculated from DFT-PW 91 method, in conjunction with DZVP basis set.

**Electrophiles**

The Fukui function values of a series of transition and non-transition metal halides have been evaluated by solving eqn. (2) and the results are presented in Table-3. It is evident that the Fukui function values are highest in iodide and lowest in fluorides in transition metal halides: $MX_2$ [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II); X = F, Cl, Br, I].

TABLE-3
FUKUI FUNCTION VALUES OF METALS IN METAL HALIDES (ELECTROPHILES)

| Compound | Atom | q(n) | q(n – 1) | $f^-$ |
|---|---|---|---|---|
| $MnF_2$ | Mn | 1.7025 | 2.6659 | –0.9634 |
| $MnCl_2$ | Mn | 0.3682 | 1.2693 | –0.9011 |
| $MnBr_2$ | Mn | –0.0246 | 0.7317 | –0.7563 |
| $MnI_2$ | Mn | –0.3913 | 0.3421 | –0.7334 |
| $Mn(NCS)_2$ | Mn | 0.3099 | 1.1493 | –0.8394 |
| $Mn(NCSe)_2$ | Mn | 1.1541 | 1.9194 | –0.7653 |

| Compound | Atom | q(n) | q(n – 1) | $f^-$ |
|---|---|---|---|---|
| $FeF_2$ | Fe | 1.7471 | 2.7233 | –0.9762 |
| $FeCl_2$ | Fe | 0.3802 | 1.3404 | –0.9602 |
| $FeBr_2$ | Fe | –0.2672 | 0.6382 | –0.9054 |
| $FeI_2$ | Fe | –0.7025 | 0.1741 | –0.8766 |
| $Fe(NCS)_2$ | Fe | –0.8080 | –0.7036 | –0.1044 |
| $CoF_2$ | Co | 1.7572 | 2.7330 | –0.9758 |
| $CoCl_2$ | Co | 0.4325 | 1.1371 | –0.7046 |
| $CoBr_2$ | Co | –0.3250 | 0.1499 | –0.4749 |
| $CoI_2$ | Co | –0.7945 | –0.4602 | –0.3343 |
| $Co(NCS)_2$ | Co | –0.9129 | –1.0426 | 0.1297 |
| $Co(NCSe)_2$ | Co | 0.9369 | 1.6264 | –0.6895 |
| $NiF_2$ | Ni | 1.7797 | 2.7417 | –0.9620 |
| $NiCl_2$ | Ni | 0.5322 | 1.1574 | –0.6252 |
| $NiBr_2$ | Ni | –0.0318 | 0.3737 | –0.4055 |
| $NiI_2$ | Ni | –0.4146 | –0.1286 | –0.2860 |
| $Ni(NCS)_2$ | Ni | –0.0199 | –0.0512 | 0.0313 |
| $Ni(NCSe)_2$ | Ni | 1.3812 | 1.9272 | –0.5460 |
| $CuF_2$ | Cu | 1.7505 | 2.7284 | –0.9779 |
| $CuCl_2$ | Cu | 0.6704 | 1.2244 | –0.5540 |
| $CuBr_2$ | Cu | 0.2266 | 0.4353 | –0.2087 |
| $CuI_2$ | Cu | 0.0663 | 0.1709 | –0.1046 |
| $Cu(NCS)_2$ | Cu | 0.2815 | 0.3145 | –0.0330 |
| $Cu(NCSe)_2$ | Cu | 0.7236 | 1.8939 | –1.1703 |
| $ZnF_2$ | Zn | 1.7725 | 1.7749 | –0.0024 |
| $ZnCl_2$ | Zn | –0.0285 | 0.9313 | –0.9598 |
| $ZnBr_2$ | Zn | 0.7876 | 0.7877 | –0.0001 |
| $ZnI_2$ | Zn | 0.6810 | 0.6810 | 0 |
| $Zn(NCS)_2$ | Zn | 1.1702 | 1.0691 | 0.1011 |
| $Zn(NCSe)_2$ | Zn | 1.2380 | 1.1656 | 0.0724 |
| $CdF_2$ | Cd | 1.8099 | 1.8100 | –0.0001 |
| $CdCl_2$ | Cd | 0.8460 | 0.8459 | 0.0001 |
| $CdBr_2$ | Cd | 0.6648 | 0.6646 | 0.0002 |
| $CdI_2$ | Cd | 0.4758 | 0.4759 | –0.0001 |
| $Cd(NCS)_2$ | Cd | 1.2726 | 1.2654 | 0.0072 |
| $Cd(NCSe)_2$ | Cd | 1.3074 | 1.1797 | 0.1277 |

| Compound | Atom | q(n) | q(n – 1) | $f^-$ |
|---|---|---|---|---|
| $HgF_2$ | Hg | 1.6898 | 2.5118 | –0.8220 |
| $HgCl_2$ | Hg | 0.6815 | 0.7106 | –0.0291 |
| $HgBr_2$ | Hg | 0.4942 | 0.5028 | –0.0086 |
| $HgI_2$ | Hg | 0.4012 | 0.4058 | –0.0046 |
| $Hg(NCS)_2$ | Hg | 0.7482 | 0.7010 | 0.0472 |
| $Hg(NCSe)_2$ | Hg | 0.4695 | 0.9258 | –0.4563 |
| $SnCl_4$ | Sn | 2.0795 | 2.0919 | –0.0124 |
| $SnBr_4$ | Sn | 1.7365 | 1.7386 | –0.0021 |
| $SnI_4$ | Sn | 1.4691 | 1.4707 | –0.0016 |
| $PhSnCl_3$ | Sn | 1.9725 | 2.0851 | –0.1126 |
| $Ph_2SnCl_2$ | Sn | 1.8574 | 1.9789 | –0.1215 |
| $Ph_3SnCl$ | Sn | 1.7358 | 1.8619 | –0.1261 |
| $(CH_3)SnCl_3$ | Sn | 1.9840 | 2.0981 | –0.1141 |
| $(CH_3)_2SnCl_2$ | Sn | 1.8862 | 2.0233 | –0.1371 |
| $(CH_3)_3SnCl$ | Sn | 1.7842 | 1.9412 | –0.1570 |
| $(CH_3)_2SnCl_2$ | Sn | 1.8862 | 2.0233 | –0.1371 |
| $(CH_3)_3SnCl$ | Sn | 1.7842 | 1.9412 | –0.1570 |
| $(CH_3)_3SnCl$ | Sn | 1.7842 | 1.9412 | –0.1570 |

q = charge on the atom, N = number of the electrons in the molecule, $f^-$ = Fukui function of electrophiles

If the Fukui function values of the iodides of these metals are compared, the sequence is as below:

$$Cu > Ni > Co > Mn > Fe$$

This sequence is almost similar to the established trend[17].

In $MX_2$ [X = SCN, SeCN] the Fukui function value is higher in thiocyanates than in their selenocyanate counterpart, except in case of manganese. In case of $MX_2$ [M = Zn(II), Cd(II), Hg(II); X = Cl, Br, I] the Fukui function values of iodide are highest in case of zinc and mercury, and bromide in cadmium; the lowest values are of fluoride in cadmium and mercury and of chloride in zinc.

If the highest values of these halides are compared, the sequence of Fukui function values is as Zn > Cd > Hg.

In case of Sn(IV) halides, the highest Fukui function value is shown by iodide and lowest by chloride. The order is as follows:

$$SnI_4 > SnBr_4 > SnCl_4$$

On phenyl and methyl substitution, the Fukui function value of $SnCl_4$ is reduced. The methyl substitution causes more reduction in value as compared to phenyl substitution. The sequence of Fukui function values on phenyl and methyl substitution becomes as below:

$$SnCl_4 > Ph_3SnCl_3 > Ph_2SnCl_2 > Ph_3SnCl$$

and $SnCl_4 > CH_3SnCl_3 > (CH_3)_2SnCl_2 > (CH_3)_3SnCl$

The LUMO and HOMO densityies of manganese halides are not calculated by the density functional method. The LUMO densities of other transition metal halides at metal atom have been calculated and are shown in Table-4. The established trend[17] in acceptor strength of the transition metal is as:

Fe > Co > Ni > Cu

This trend is shown by Fukui function valus is as Cu > Ni > Co > Mn > Fe. The trend is the same but in a reverse direction.

TABLE-4
HOMO AND LUMO DENSITIES ON METAL ATOMS OF TRANSITION METAL HALIDES

| Metal | Atom | $\rho_{LUMO}$ | $\rho_{HOMO}$ |
|---|---|---|---|
| $FeF_2$ | Fe | 0.999 | 0.060 |
| $FeCl_2$ | Fe | 0.725 | 0.039 |
| $FeBr_2$ | Fe | 0.255 | 0.040 |
| $FeI_2$ | Fe | 0.129 | 0.047 |
| $Fe(CNS)_2$ | Fe | 0.052 | 0.006 |
| $Fe(CNSe)_2$ | Fe | 0.001 | 0.017 |
| $CoF_2$ | Co | 0.999 | 0.815 |
| $CoCl_2$ | Co | 0.568 | 0.816 |
| $CoBr_2$ | Co | 0.983 | 0.055 |
| $CoI_2$ | Co | 0.928 | 0.072 |
| $Co(CNS)_2$ | Co | 0.367 | 0.155 |
| $Co(CNSe)_2$ | Co | 0.081 | 0.427 |
| $NiF_2$ | Ni | 0.878 | 0.966 |
| $NICl_2$ | Ni | 0.604 | 0.686 |
| $NiBr_2$ | Ni | 0.552 | 0.993 |
| $NiI_2$ | Ni | 0.509 | 0.999 |
| $Ni(CNS)_2$ | Ni | 0.011 | 0.030 |
| $Ni(CNSe)_2$ | Ni | 0.272 | 0.648 |
| $CuF_2$ | Cu | 0.525 | 0.474 |
| $CuCl_2$ | Cu | 0.368 | 0.314 |
| $CuBr_2$ | Cu | 0.307 | 0.255 |
| $CuI_2$ | Cu | 0.236 | 0.186 |
| $Cu(CNS)_2$ | Cu | 0 | 0.158 |
| $Cu(CNSe)_2$ | Cu | 0.122 | 0.114 |

$\rho_{LUMO}$ is LUMO density, $\rho_{HOMO}$ is HOMO density calculated from DFT-PW 91 method, in conjunction with DZVP basis on Cache Pro software.

LUMO densities at M in M(II) thiocyanates [M = Zn, Cd, Hg] have also been evaluated by DFT method (Table-5). The LUMO density is highest in case of fluorides and lowest in iodide. The LUMO density again rises in their thiocyanates and selenocyanate derivatives indicating that the thiocyanates and selenocyanates are better acceptors than their halide counterparts. In case of Fukui function the values of iodides are highest and those of fluorides are lowest. This clearly shows a reverse order for the acceptor strengths; in other words, the lower value in case of Fukui function indicates better acceptor strength whereas a higher value of LUMO density shows better acceptor strength.

TABLE-5
LUMO AND HOMO DENSITIES ON METAL ATOMS OF NON-TRANSITION METAL HALIDES

| Chemical Sample | Atom | $\rho_{LUMO}$ | $\rho_{HOMO}$ |
|---|---|---|---|
| $ZnF_2$ | Zn | 0.818 | 0.088 |
| $ZnCl_2$ | Zn | 0.702 | 0.671 |
| $ZnBr_2$ | Zn | 0.736 | 0.034 |
| $ZnI_2$ | Zn | 0.644 | 0.025 |
| $Zn(NCS)_2$ | Zn | 0.834 | 0.014 |
| $Zn(NCSe)_2$ | Zn | 0.821 | 0.011 |
| $CdF_2$ | Cd | 0.806 | 0.045 |
| $CdBr_2$ | Cd | 0.729 | 0.026 |
| $Cd(NCS)_2$ | Cd | 0.710 | 0.010 |
| $Cd(NCSe)_2$ | Cd | 0.794 | 0.008 |
| $HgF_2$ | Hg | 0.649 | 0.053 |
| $HgI_2$ | Hg | 0.414 | 0.012 |
| $Hg(NCS)_2$ | Hg | 0.621 | 0.010 |
| $Hg(NCSe)_2$ | Hg | 0.649 | 0.078 |
| $SnCl_4$ | Sn | 0.487 | 0 |
| $SnBr_4$ | Sn | 0.411 | 0 |
| $SnI_4$ | Sn | 0.293 | 0 |
| $PhSnCl_3$ | Sn | 0.518 | 0 |
| $Ph_2SnCl_2$ | Sn | 0.257 | 0 |
| $Ph_3SnCl$ | Sn | 0.082 | 0 |
| $(CH_3)SnCl_3$ | Sn | 0.520 | 0 |
| $(CH_3)_2SnCl_2$ | Sn | 0.572 | 0.092 |
| $(CH_3)_3SnCl$ | Sn | 0.688 | 0.090 |

$\rho_{LUMO}$ is LUMO density, $\rho_{HOMO}$ is HOMO density calculated from DFT-PW 91 method, in conjunction with DZVP basis on CachePro software.

In case of Sn(IV) halides the highest LUMO density is exhibited by Sn(IV) chloride and lowest by Sn(IV) iodide. The Fukui function values however show a reverse trend. Amongst the methyl and phenyl substituted Sn(IV) halides the LUMO density at tin increases as the number of methyl substitution increases and in case of phenyl substitution the density decreases as the number of phenyl substitution increases. The Fukui function values of methyl and phenyl substituted derivatives of Sn(IV) chlorides show the following trend:

$PhSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl$ and $SnCl_4 > CH_3SnCl_3 > (CH_3)_2SnCl_2 > (CH_3)_3SnCl$

## Metal Ligand Interaction

The difference in softness values of donor and acceptor molecules has been used as a measure of metal-ligand bond strength[9]. Similarly the difference in values of HOMO-LUMO energies of nucleophiles and electrophiles has been found to have direct relationship with the stability of the complexes formed between them[18]. The metal-ligand interaction has been examined in terms of Fukui function values of the electrophiles and nucleophiles. The Fukui function values of certain electrophiles and nucleophiles are presented in Table-6. For drawing the relative stability of the metal-ligand bond, the difference in Fukui function values has been evaluated which is represented by $\Delta f^- f^+$

$$\Delta f^- f^+ = |f^- - f^+| \quad (10)$$

A reference to the table indicates that most stable complexes are formed by zinc chloride when reaction takes place with pyridine, nicotinamide, triphenyl phosphine and pyridine oxide.

TABLE-6

DIFFERENCE IN FUKUI FUNCTION VALUE ($\Delta f^- f^+$) OF NON-TRANSITION METAL HALIDES AND ORGANIC BASES

| Complexes | $f^-$ | $f^+$ | $\Delta f^- f^+$ | ΔLH |
|---|---|---|---|---|
| $SnCl_4$·2EU | –0.0124 | –0.1040 | 0.0916 | 0.291 |
| $SnBr_4$·2EU | –0.0021 | –0.1040 | 0.1019 | 0.367 |
| $SnI_4$·2EU | –0.0016 | –0.1040 | 0.1024 | 0.485 |
| $SnCl_4$·2ETU | –0.0124 | –0.6782 | 0.6658 | 0.422 |
| $SnBr_4$·2ETU | –0.0021 | –0.6782 | 0.6761 | 0.498 |
| $SnI_4$·2ETU | –0.0016 | –0.6782 | 0.6766 | 0.616 |
| $SnCl_4$·2ATU | –0.0124 | –0.6805 | 0.6681 | 0.403 |
| $SnBr_4$·2ATU | –0.0021 | –0.6805 | 0.6784 | 0.479 |
| $SnI_4$·2ATU | –0.0016 | –0.6805 | 0.6789 | 0.597 |
| $Zn(NCS)_2$·2PY | 0.1011 | 0.1056 | –0.0045 | 0.141 |
| $Cd(NCS)_2$·2PY | 0.0072 | 0.1056 | –0.0984 | 0.017 |
| $Hg(NCS)_2$·2PY | 0.0472 | 0.1056 | –0.0584 | 0.072 |
| $ZnCl_2$·2NIA | –0.9598 | –0.2155 | –0.7443 | 0.132 |
| $CdCl_2$·2NIA | 0.0001 | –0.2155 | 0.2156 | 0.182 |
| $HgCl_2$·2NIA | –0.0291 | –0.2155 | 0.1864 | 0.031 |

| Complexes | $f^-$ | $f^+$ | $\Delta f^- f^+$ | ΔLH |
|---|---|---|---|---|
| $ZnCl_2 \cdot 2PPh_3$ | –0.9598 | –0.0009 | –0.9589 | 0.177 |
| $CdCl_2 \cdot 2PPh_3$ | 0.0001 | –0.0009 | 0.0010 | 0.227 |
| $HgCl_2 \cdot 2PPh_3$ | –0.0291 | –0.0009 | –0.0282 | 0.014 |
| $ZnCl_2 \cdot 2PYO$ | –0.9598 | –0.0346 | –0.9252 | 0.165 |
| $CdCl_2 \cdot 2PYO$ | –0.0001 | –0.0346 | 0.0347 | 0.215 |
| $HgCl_2 \cdot 2PYO$ | –0.0291 | –0.0346 | 0.0055 | 0.002 |

EU-Ethylene urea PY = Pyridine ETU = Ethylene thiourea NIA = Nicotinamide
ATU = Allyl thiourea $PPh_3$ = Triphenylphosphine PYO = Pyridine oxide
$f^-$ = Fukui function values of electrophiles $f^+$ = Fukui function values of nucleophiles
$\Delta f^- f^+$ = Difference in Fukui function values of electrophiles and nucleophiles
ΔLH = Difference in LUMO density of transition metal halides and HOMO density of IQ and PY

The next is mercury chloride and the last is cadmium chloride. In case of thiocyanates, the stability sequence is changed and the sequence is

$$Hg(SCN)_2 > Cd(NCS)_2 > Zn(NCS)_2.$$

In case of complexes of Sn(IV) halides with ethylene urea, ethylene thiourea and allylthiourea, the most stable complexes are formed by $SnCl_4$ and the sequence of acceptor strength is as follows:

$$SnCl_4 > SnBr_4 > SnI_4$$

The acceptor strengths of Sn(IV) halides as evaluated by HOMO and LUMO densities of the donors and acceptors show the same sequence for acceptor strength of Sn(IV) halides. The values derived from softness values of Klopman[9] in respect of the acceptor strengthof the Sn(IV) halides also show a similar trend of acceptor strength of these halides. The Fukui function values of certain transition metal halides (electrophiles) and Fukui function values of isoquinoline and pyridine(nucleophiles) are presented in Table-7. The $\Delta f^- f^+$ values indicate that in all the complexes the chlorides have the highest and the iodides have the lowest acceptor strength. This observation is in conformity with the established trends.

The LUMO densities of the M(II) halides [M = Fe, Co, Ni, Cu] and HOMO densities of pyridine and isoquinoline at their nitrogen ends have also been evaluated and are presented in the same Table-7. The difference in HOMO and LUMO densities ΔLH do not provide a similar trend as indicated by $\Delta f^- f^+$. The difference in softness values derived by Klopman[9] equation of these transition metal halides and the pyridine and isoquinoline also does not furnish a trend similar to the trend obtained by Fukui function values. It can, therefore, be inferred that Fukui function values provide a better means for deriving the relative strength of metal, ligand bond. If $\Delta f^- f^+$ values of chlorides of Fe, Co, Ni, Cu are compared the sequence of stability among metal halides is as Cu > Ni > Co > Fe. This trend is similar to the trend obtained by thermodynamic stability (log k) of transition metal complexes[19]. Such a trend could not be clearly observed by

HOMO, LUMO density or the softness values of Klopman. In the above two cases, the trend of stability could however be achieved on addition of one more parameter IP of electrophile to ΔLH values and CFSE value to the difference in softness values of electrophiles and nucleophiles obtained by Klopman method[9].

TABLE-7

DIFFERENCE IN FUKUI FUNCTION VALUES ($\Delta f^- f^+$) OF TRANSITION METAL HALIDES AND OF ISOQUINOLINE AND PYRIDINE

| Compound | $f^-$ | $f^+$ | $\Delta f^- f^+$ | ΔLH |
|---|---|---|---|---|
| $FeCl_2$·IQ | –0.9602 | 0.4573 | –1.4175 | 0.69 |
| $FeBr_2$·IQ | –0.9054 | 0.4573 | –1.3627 | 0.22 |
| $FeI_2$·IQ | –0.8766 | 0.4573 | –1.3339 | 0.12 |
| $CoCl_2$·IQ | –0.7046 | 0.4573 | –1.1619 | 0.53 |
| $CoBr_2$·IQ | –0.4749 | 0.4573 | –0.9322 | 0.95 |
| $CoI_2$·IQ | –0.3343 | 0.4573 | –0.7916 | 0.89 |
| $NiCl_2$·IQ | –0.6252 | 0.4573 | –1.0825 | 0.57 |
| $NiBr_2$·IQ | –0.4055 | 0.4573 | –0.8628 | 0.52 |
| $NiI_2$·IQ | –0.2860 | 0.4573 | –0.7433 | 0.47 |
| $CuCl_2$·IQ | –0.5540 | 0.4573 | –1.0113 | 0.33 |
| $CuBr_2$·IQ | –0.2087 | 0.4573 | –0.6660 | 0.27 |
| $CuI_2$·IQ | –0.1046 | 0.4573 | –0.5619 | 0.20 |
| $FeCl_2$·PY | –0.9602 | 0.4573 | –1.0658 | 0.03 |
| $FeBr_2$·PY | –0.9054 | 0.1056 | –1.0110 | 0.43 |
| $FeI_2$·PY | –0.8766 | 0.1056 | –0.9822 | |
| $CoCl_2$·PY | –0.7046 | 0.1056 | –0.8102 | 0.12 |
| $CoBr_2$·PY | –0.4749 | 0.1056 | –0.5805 | 0.29 |
| $CoI_2$·PY | –0.3343 | 0.1056 | –0.4399 | |
| $NiCl_2$·PY | –0.6252 | 0.1056 | –0.7308 | 0.80 |
| $NiBr_2$·PY | –0.4055 | 0.1056 | –0.5111 | |
| $NiI_2$·PY | –0.2860 | 0.1056 | –0.3916 | |

IQ = Isoquinoline, PY = Pyridine

$f^-$ = Fukui function values of electrophilies, $f^+$ = Fukui function values of nucleophiles

$\Delta f^- f^+$ = Difference in Fukui function values of electrophiles and nucleophiles

ΔLH = Difference in LUMO density of transition metal halides and HOMO density of IQ and PY.

## Charge Transfer (ΔN) and Energy Lowering (ΔE)

There has been a number of molecular orbital treatments of Lewis acid-base reactions. The Mulliken's[12] treatment has been recognized as best for donor-acceptor interaction in charge transfer complexes. This theory uses only electron affinity $A_A$ for acceptor and only ionization potential $I_B$ for the electron donor. The quantity ($I_B - A_A$) is an energy cost of transfer of per electron for donor to acceptor

to decide which of the two molecules is donor and which is acceptor; we have the following equation[6]:.

$$(I_A - A_B) - (I_B - A_A) = 2(\chi_{A^0} - \chi_{B^0}) \quad (11)$$

A positive value indicates that it costs less energy to transfer an electron from B to A. Thus the direction of electron transfer is determined by the absolute electronegativity. The absolute electronegativity of acceptors A and donors B are included in Table-8. A lower value of electronegativity is indicative of a better donor character whereas a higher value of electronegativity is indicative of a better acceptor character. A reference to the table indicates that electronegativity values of donor molecules are less than of acceptor molecules; hence eqn. (11) has a positive value. The $\chi$ values indicate that the acceptor strength of Sn(IV) halides will be $SnCl_4 > SnBr_4 > SnI_4$ and in case of Zn, Cd and Hg halides, the Hg halides will be the best acceptor when react with donor molecules. On the basis of $\chi$ values the base strength of donor molecules can be arranged as below:

$$EU > ETU > ATU > PPh_3 > PYO > PY > NIA$$

The electronegativity ($\chi$) difference derives the electron transfer and the sum of hardness parameters ($\eta$) inhibits it. The net result of shift in charge $\Delta N$ and lowering in energy $\Delta E$ due to electron transfer is given by eqns. (8) and (9). The values of $\Delta N$ and $\Delta E$ have been evaluated and are reported in Table-8. The $\Delta N$ values clearly indicate that maximum charge transfer is in $SnCl_4$ complexes of EU, ETU and ATU and minimum in case of $SnI_4$ complexes. Similarly the maximum energy lowering $\Delta E$ is exhibited by $SnCl_4$ complexes. In case of Zn, Cd and Hg complexes the maximum values of $\Delta N$ and $\Delta E$ are observed in case of Hg complexes. All the results are in conformity with the result obtained by $\Delta LH$ values and $\Delta E$ um values[7,9].

TABLE-8
THE ABSOLUTE HARDNESS AND ELECTRONEGATIVITY OF METAL HALIDES (A) AND ORGANIC BASE (B) AND $\Delta N$ AND $\Delta E$ DERIVED FROM THEM BY EQNS. (8), (9)

| Acid | Base | $\eta_{acid}$ | $\chi_{acid}$ | $\eta_{base}$ | $\chi_{base}$ | $\Delta N$ | $\Delta E$ | $\Delta f^- f^+$ |
|---|---|---|---|---|---|---|---|---|
| $SnCl_4$ | EU | 1.793 | –6.293 | 2.9665 | –2.6265 | –0.38518 | 15.9958 | 0.0916 |
| $SnBr_4$ | EU | 1.464 | –5.806 | 2.9665 | –2.6265 | –0.35882 | 11.1972 | 0.1019 |
| $SnI_4$ | EU | 1.069 | –5.428 | 2.9665 | –2.6265 | –0.34711 | 7.91806 | 0.1024 |
| $SnCl_4$ | ETU | 1.793 | –6.293 | 1.8720 | –2.628 | –0.50000 | 12.3073 | 0.6658 |
| $SnBr_4$ | ETU | 1.464 | –5.806 | 1.8720 | –2.628 | –0.47632 | 8.42314 | 0.6761 |
| $SnI_4$ | ETU | 1.069 | –5.428 | 1.8720 | –2.628 | –0.47603 | 5.76436 | 0.6766 |
| $SnCl_4$ | ATU | 1.793 | –6.293 | 1.6905 | –2.8625 | –0.49239 | 10.2487 | 0.6681 |
| $SnBr_4$ | ATU | 1.464 | –5.806 | 1.6905 | –2.8625 | –0.46656 | 6.83279 | 0.6784 |

$\eta$ = Absolute Hardness, $\chi$ = Electronegativity
$\Delta f^- f^+$ = Difference in Fukui function values of electrophiles and nucleophiles
EU = Elthylene urea ETU = Ethylene thiourea
ATU = Allyl thiourea $\Delta N$ = Charge transfer calculated from eqn. (8) and
$\Delta E$ = Lowering of energy calculated from eqn. (9) by using DFT-PW 91 method, in conjunction with DZVP basis on CachePro software

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