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CORRELATION OF THE COMPARATIVE REACTIVITY-INERTNESS OF GOLD AND SILVER IN TERMS OF SOME GLOBAL THEORETICAL DESCRIPTORS OF CHEMICAL REACTIVITY AND STABILITY

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ABSTRACT: *In this communication we have correlated the chemical fact demonstrated that gold is more inert than silver in terms of some theoretical reactivity descriptors like absolute radius, ionization energy, global hardness and electrophilicity index. The chemical inertness of Au is attributed to its smaller absolute radius, higher ionization energy, greater hardness value and larger electrophilicity index coupled with relativistic effect compared to that of Ag. Thus our observation is a theoretical rationale of the existing and old view, on the basis of chemical observation, that Au is more inert than Ag.*
Keywords: *Gold, Silver, HSAB, Theoretical reactivity descriptors, Rationale of inertness of gold and silver*

1. INTRODUCTION

Fundamental understanding of intrinsic characteristics and properties nano-particles is important and integral to the fruitful exploitation of nanotechnology. The nano particles of coinage metals form colorful solutions because of the plasmon absorption. Because of their chemico-physical importance, the nano-particles of coinage metals are now integral part of the nano technology. It is widely known that the gold nano particles find wide scientific use and applications(Ghosh & Pal).

2. EFFECTS OF GOLD AND SILVER ON THE ENVIRONMENT

It has been demonstrated that Ag is potentially toxic. Now question is whether the toxicity of silver is related to its more reactivity? We propose to seek a rationale to this question in the following paragraphs.

It is widely known that chemically pure gold is less reactive than silver and gold is insoluble in nitric acid, which dissolves silver. Hence, experimentally it was established that gold is more inert than silver. The inertness of gold atom and its tendency for catenation where one gold atom prefers to bind another gold atom find rationale in the operation of relativistic effect (Pyykko1988, Schwerdtfeger et al 1989) in its electronic structure.

Bulk gold is a noble metal and unlike its lighter congeners of Group 11, copper and silver, was for a long time not considered important in catalysis and surface science in general(Schwerdtfeger 2003). Gold has not been evaluated for its eco-toxicity. However, the biodegradation of gold under aerobic conditions is expected to be very poor and there is no evidence to suggest that it creates ecological problems when released into the environment. Since gold is insoluble in usual solvents, it is believed to have minimal bioaccumulation and bioavailability characteristics.

On the contrary the nano-materials with silver as an ingredient raise new challenges for environmental managers.

Silver itself is classified as an environmental hazard because it is toxic, persistent and bio-accumulative under, at least, some circumstances. Aside from releasing silver, the toxicity, bio-accumulative potential and persistence of nano-silver materials are just beginning to be known(Luoma2008).

It seems that the toxicity of silver-manifest in its physico-chemical reactivity, compared to that of gold, is intrinsic to its electronic constitution.

However, in a recent report, Nath et al(Nath et al 2006) have studied the softness of gold and silver in the light of hard soft acid base (HSAB) principle (Pearson 1963) and have concluded that gold metal is softer compared to silver metal. However, it is unequivocal that this finding contradicts the chemically established fact that Ag is more reactive than gold.

Rationale of inertness of gold atom in terms of the theoretical descriptors. We have already stated that the inertness of gold as compared to silver is chemically established. In the instant report we venture to rationalize this known fact in terms of some present day theoretical descriptors of the chemical reactivity and stability. The descriptors that can be invoked to study the stability and reactivity of atoms and molecules are the atomic radius (r), the ionization energy (I), the global hardness (η), the electrophilicity index (ω) etc.

The legend 'atomic radius' is an important size descriptor of atoms required in correlating, predicting and modeling many physico-chemical properties of atoms, molecules and structural aspects of condensed matter. The right size of ions and atoms are of paramount importance in modeling and understanding bio-chemical processes. The shell structure and screened nuclear charge, the internal constitution of atom control the size of atom. Thus the atomic radii can be used to correlate many chemico-physical behaviour of atoms (Putz 2003, Ghosh & Biswas, 2002 Ghosh et al, 2008). It is established, for a chemical system, that small size indicates more stability or less reactivity and large size indicates less stability or high reactivity.

The first ionization energy of the atom reflects the energy with which the electron is bound to the system and hence it is an important descriptor of the atoms playing important role in the determination of many physical and chemical properties of atoms. For an atom or molecule, high ionization energy indicates more stability or less reactivity and small ionization energy indicates less stability or high reactivity.

The global hardness is a cardinal index of stability and reactivity of a chemical species. The chemical hardness is one of the oldest concepts of chemistry. There is fast time evolution of the concept and fundamental status of hardness from a mere qualitative structure to sound theoretical model ((Mulliken 1952 , Klopman, 1964, Parr & Yang 1989, Parr et al 1978, Parr & Pearson 1983,Pearson 1986, Geerlings et al 2003, Pearson 1987, Ghosh & Islam 2009 , Islam & Ghosh 2010 ,. Ghosh & Islam 2010, Putz et al 2004, Putz 2006, Putz 2007, Putz 2008, Putz 2009).

Since these descriptors are fundamentally conundrums and are not the objects of the real world, the possibility of their quantum mechanical evaluation is ruled out. In order to assign some number to each of these abstract concepts, it is required that these descriptors be reified goaded by their physico-chemical behavior and consistent with the quantum mechanical picture of the atoms. After the modeling, some semi-empirical algorithm is developed and some mathematical formulae be suggested for their evaluation.

There is a paradigm shift in the realm of conceptual and qualitative chemistry due to the density functional underpinning of Parr et al and others (Parr & Yang 1989 , Parr et al 1978, Parr & Pearson 1983, Pearson 1986, Geerlings et al 2003, Pearson 1987). Some old but very useful but qualitative entities like hardness, electronegativity which were abstract semiotic representations are now considered as theoretical quantities of cognitive representations.

It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. Thus, the hardness as conceived in chemistry signifies the resistance towards the deformation of charge cloud of chemical systems under small perturbation encountered during chemical processes. Thus the general operational significance of the hard-soft chemical species may be understood in the following statement. If the electron cloud is strongly held by the nucleus, the chemical species is 'hard' but if the electron cloud is loosely held by the nucleus the system is 'soft'.

The electrophilicity index of atoms seems to be an absolute and fundamental property of atoms because it simply signifies the energy lowering process on soaking electrons from donors. This tendency must develop from the screened nuclear charge of the atoms. So, it is unequivocal that the electrophilicity indices of atoms are intimately connected to the shell structure of the atoms. Thus, it is expected that, for atoms, the electrophilicity is a measure of the electron attracting power of the screened charge nucleus, like the electronegativity and hardness.

Recently, we have published good number of papers, where we have discovered the fundamental origin and operational significance of the quantum

mechanical as well as density functional theoretical descriptors like atomic radius(Ghosh & Biswas, 2002 Ghosh et al,2008, Islam & Ghosh 2011), electronegativity (Ghosh 2005, Ghosh & Islam 2011), hardness (Islam & Ghosh 2010 , Ghosh & Islam 2010), polarizability (Ghosh & Biswas 2002) etc.

We have presented some sets of atomic radii data, hardness data, ionization energies and electrophilicity indices of Ag and Au in Tables 1, 2, 3 and 4 respectively.

Table 1
Different Sets of Atomic Radii (a.u) of the Elements Ag and Au

Element	*Spectroscopic atomic radii of Ghosh et al.*	*Absolute raddi of Ghosh et al.*	*Desclaus's radii*	*Waber Cromer's radii*
Ag	1.774511	3.809	2.729	4.762
Au	1.319757	0.991	2.456	1.416

Table 2
Different Sets of Global Hardness Data(eV) of the Elements Ag and Au

Atom	$\eta_{Ghosh\ Islam}$	$\eta_{Pearson}$	$\eta_{Robles\ Bartolotti}$
Ag	3.40	3.14	3.5
Au	6.37	3.46	3.44

Table 3
Ionization Energy Data of the Elements Ag and Au

Atom	$I_{(Expt)}$ *in au*
Ag	0.27843
Au	0.33903

Table 4
Electrophilicit Indices of the Elements Ag and Au

Atom	$\omega_{\text{Ghosh Islam}}$ *in eV*	$\omega_{\text{Parr et al in}}$ *in eV*
Ag	2.235086	1.57
Au	5.67477	2.41

3. RESULTS AND DISCUSSION

A look at the Table 1 reveals that in every set of calculation, viz, Waber Cromer(Waber &Cromer 1965), Ghosh et al(Ghosh et al 2008), Desclaux (Desclaux 1973), and the spectroscopic atomic radii(Islam &Ghosh2011) recently computed in our laboratory, the size data of Ag is greater than that of Au. The chemical inertness of Au and its state of aggregation is attributed to its small size and least deformability under small perturbation(Pyykko1988, Schwerdtfeger et al 1989).

Thus the size data clearly demonstrates that Ag is most likely more reactive than Au.

A look at the Table 2 reveals that in all calculations viz, our work (Ghosh & Islam 2009), Pearson's work (Pearson 1987) and the work of Robles and Bartolotti (Robles&Bartolotti 1984), the hardness data of Ag is less than that of Au.

From Table 3 that furnishes a comparative study of the ionization energies of Au and Ag, unequivocally demonstrates that the Ag atom is more reactive than Au atom.

A look at the Table 4 reveals that the electrophilicity index of Au atom is quite higher than that of Ag in both sets- the data published by Islam & Ghosh (Islam & Ghosh 2010) and Parr et al (Parr et al 1999). Thus, the comparative study of the electrophilicity indices of Au and Ag unequivocally demonstrates that the Ag atom is more reactive than Au atom.

4. CONCLUSION

Nath et al tried to posit in the light of hard soft acid base (HSAB) principle that gold metal is softer compared to silver metal. This finding is in contradiction with a long standing belief that Au atom is more inert chemically than Ag. We have made a detailed comparative and critical study of reactivity of these atoms in terms of as many as three fundamental chemico-physical descriptors well-known to determine the intrinsic chemical reactivity of elements. The chemical inertness of Au is attributed to its smaller absolute radius, higher ionization energy, greater hardness value and greater electrophilicity index data coupled with relativistic effect compared to that of Ag. Thus, our observation is a theoretical rationale of the existing old view that Au is more inert than Ag.

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