Theoretical studies on the interaction of PdO₃ superhalogen with Ca atom

Ambrish Kumar Srivastava and Neeraj Misra[*]

Department of Physics, University of Lucknow, Lucknow, Uttar Pradesh, India

_____

ABSTRACT

Superhalogens may interact with appropriate metal atoms to form complex compounds. In the present study, this idea is demonstrated by considering the interaction of PdO₃ 'superhalogen' with Ca atom which leads to the formation of complex CaPdO₃. DFT and QTAIM approaches are employed to estimate the nature and strength of interaction. We have revealed this interaction as ionic and very similar to that in traditional ionic compound, CaO. The HOMO-LUMO gap and binding energy of CaPdO₃ complex is comparable to that of CaO. Thus, it may be possible to form a new series of compounds using PdO₃ superhalogen as building blocks.

Keywords: PdO₃, superhalogen, interaction, DFT, NBO, QTAIM.

_____

INTRODUCTION

The species having electron affinity exceeding to that of halogens are referred to as 'superhalogen' [1]. Such species typically consist of a central metal or non-metal element with some electro-negative ligands (F, Cl, O etc.). The electron affinity (EA) of such species increases with the increase in the number of ligands. This eventually happens due to extra electron delocalization over ligand atoms. First experimental evidence for the existence of such hypervalent species such as $LiCl_2$, $NaCl_2$ was given by Wang et al. [2]. However, alkali metals (Li, Na etc.) can bind with only a limited number of atoms due to their fixed valency. Later investigations were focused on transition metal elements as they are able with a number of atoms due to their variable oxidation states. Many transition metals are well known to form hexafluoride molecules having EAs higher than that of halogens [3-7].

Superhalogen species lead to the formation of complex compounds [8], by interaction with appropriate metal, possessing exceptionally high oxidizing capabilities. For instance, a complex $KOsF_4$ can be formed by interaction of OsF_4 superhalogen with K atom [7]. More interestingly, a well known oxidizing agent $KMnO_4$ can be realized by $K-MnO_4$ interaction, where MnO_4 behaves as a superhalogen [9]. In the similar way, $KAuO_3$ complex has been predicted on the basis of interaction of AuO_3 superhalogen with K atom [10]. In such complexes, superhalogen moieties closely mimic the behavior of halogen atom. Some other transition metal oxides have also been found to behave as superhalogen with suitable number of O ligands [11, 12].

In a study performed on PdO_n species, we revealed the superhalogen behavior of these species for $n \geq 2$ [13]. In continuation to our previous study, here we investigate the interaction of PdO_3, a superhalogen with an alkaline metal, Ca. Our study aims to answer many queries. To what extent does a PdO_3 superhalogen behave like an oxygen atom? An oxygen atom interacting with an alkaline atom such as calcium Ca forms an ionic compound viz. CaO. How does a PdO_3 superhalogen interact with Ca atom? Does PdO_3 bind more strongly to an alkaline atom than an oxygen atom?

_____

MATERIALS AND METHODS

We have tried to explore answers to all these questions using density functional theory (DFT) and atoms in molecules (AIM) approach. The study is performed within density functional scheme at B3LYP level [14, 15] using SDD basis set via Gaussian 09 program [16]. Gauss View 5.0 [17] is employed to generate all graphics. The present computational method has already been used in our previous study [11-13]. In order to study the interaction, we have performed natural bonding orbital (NBO) analysis at the same level of theory with the help of NBO 3.1 [18] as implemented in Gaussian 09. It is widely accepted that the natural bonding orbital (NBO) and AIM analyses give insights into chemical bonding and interactions. NBO based partial atomic charges are more reliable due to its low basis set dependency [19].

AIM analysis is based on quantum theory of atoms in molecule [20]. According to this theory, the values of some topological parameters at bond critical point (BCP) decide the nature of chemical interaction. These parameters are Laplacian of charge density,   and ratio of eigen-values of Hessian, $|\lambda_1|/\lambda_3$. According to AIM theory, for covalent bonding, $\nabla^2\rho < 0$ and $|\lambda_1|/\lambda_3$ is greater than unity while ionic bonding is characterized by $\nabla^2\rho > 0$ and $|\lambda_1|/\lambda_3$ less than unity. In order to gain further insights into this interaction, the quantum theory of atoms in molecules (QTAIM) is successfully applied via AIMAll program [21]

RESULTS

First we discuss the structure and property of PdO_3. PdO_3 assumes a trigonal planar geometry with the bond-length Pd−O of 1.77 A°, which increases to 1.85 A° in case of its anion, PdO_3^- [13]. The adiabatic EA of PdO_3 is calculated to be 3.75 eV, which is larger than that of F (3.60 eV) and very large as compared to O which is merely 1.42 eV. This suggests that PdO_3 belongs to the class of superhalogen.

In order to study the interaction of PdO_3 cluster with Ca atom, we put a Ca atom on the top of PdO_3. The structure is, then, fully optimized without any symmetry constraint in the potential energy surface. After optimization, we found a nearly planar structure (C_{2v}) of $CaPdO_3$ complex, in which Ca binds with two O atoms as shown in Fig. 1. The vibrational frequency calculations provide all positive values, implying that the optimized geometry belongs to at least a local minimum in the potential energy surface. The bond-length, Ca−O in this complex is found to be 2.07 A°, whereas Pd−O is increased to 1.93 A°. Note the bond-length of CaO molecule, which is 1.83 A° calculated at the same level of theory.
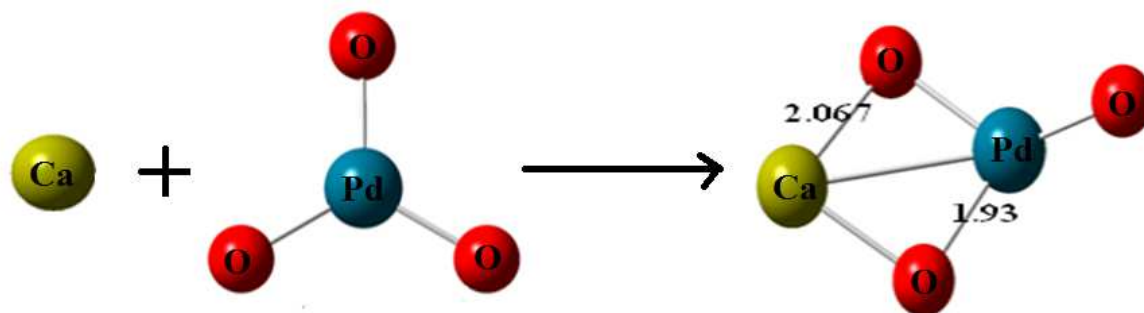

Fig. 1. Equilibrium geometry of CaPdO₃ complex formed by interaction of PdO₃ superhalogen with Ca atom. Bond-lengths (in A°) are also shown

DISCUSSION

First, we discuss the nature of interaction between Ca and PdO_3 in $CaPdO_3$ complex. It is well known that Ca interacting with O forms an ionic compound CaO. We have performed the NBO analysis to compare the role in $CaPdO_3$ complex and CaO molecule. The NBO charge on Ca atom in $CaPdO_3$ complex is found to be 1.504 e while the same in CaO is 1.239 e. Furthermore, the occupancy of Ca–O bond in $CaPdO_3$, 1.8152 is very close to 2 (that in CaO). This may suggest that the interaction of Ca atom with PdO_3 superhalogen is similar to that between Ca and O atom i.e. ionic.

In order to gain further insights into this interaction, AIM analysis is performed for the Ca–O bond that connects Ca and PdO_3 in $CaPdO_3$ complex. For a comparison the same is repeated for CaO molecule. The AIM parameters are

_____

listed in Table 1. In case of CaPdO$_3$, we found at BCP of Ca–O the Laplacian of charge density, $\nabla^2\rho$ positive and ratio $|\lambda_1|/\lambda_3$ less than unity (same as in CaO). This further suggests that the interaction between Ca and PdO$_3$ is essentially ionic.

Table 1. Charge density (ρ), Laplacian of ρ ($\nabla^2\rho$), ratio of eigen-values of Hessian ($|\lambda_1|/\lambda_3$), Kinetic energy density (G) and potential energy density (V) for Ca–O bonds in CaPdO$_3$ and CaO by AIM analysis (all parameters are measured in a.u.).

AIM parameters	CaPdO$_3$	CaO
Charge density, ρ(Ca–O)	0.0703	0.1417
$\nabla^2\rho$(Ca–O)	0.4375	0.6050
$|\lambda_1|/\lambda_3$	0.1750	0.2095
Kinetic energy, G(Ca–O)	0.1112	0.1962
Potential energy, V(Ca–O)	-0.1131	-0.2413

In Fig. 2, we plot the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of CaPdO$_3$. For a visual comparison, the same for CaO are also plotted. It is evident that in CaPdO$_3$, the main contributions are from PdO$_3$. Ca contributes neither to HOMO nor to LUMO. This is in contrast to CaO molecule where the Ca sites contribute to HOMO as well as LUMO. The HOMO-LUMO gap of CaPdO$_3$ complex, 2.18 eV is slightly smaller than that of CaO, which is found to be 2.43 eV at the same level. Thus, CaPdO$_3$ is slightly more reactive as compared to CaO, which can be expected due to higher EA of PdO$_3$ moiety in CaPdO$_3$ as compared to that of O in CaO.
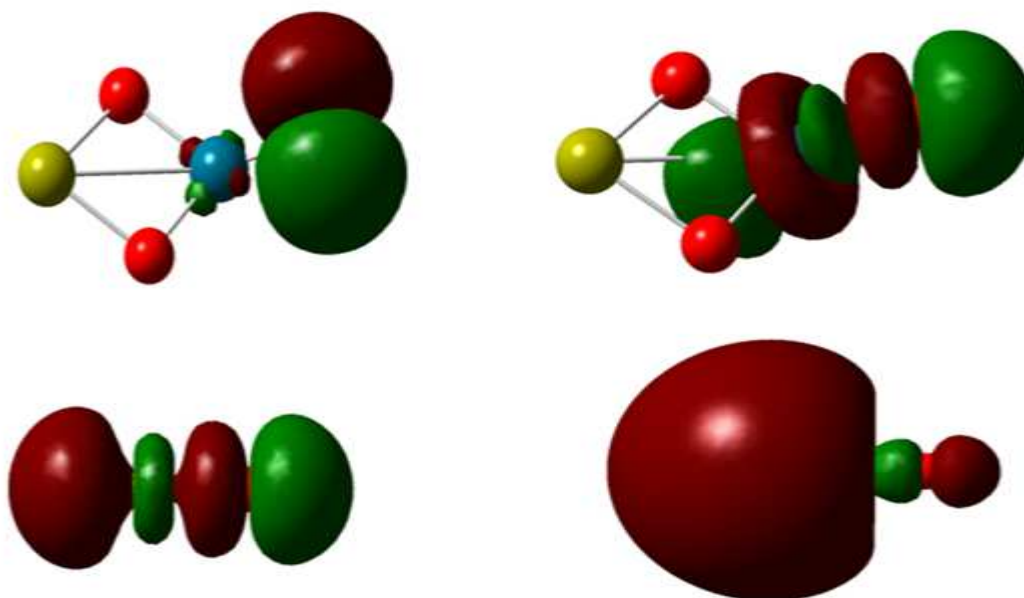

Fig. 2. HOMO (left) and LUMO (right) surfaces of CaPdO$_3$ (upper set) and CaO (lower set). The red represents electronegative regions and green represents electropositive region with an isovalue of 0.2

In order to estimate the interaction energy of Ca and PdO$_3$ in CaPdO$_3$, we have calculated the binding energy (BE) of CaPdO$_3$. The BE of CaPdO$_3$ dissociating to Ca and PdO$_3$, is calculated as 5.92 eV, which is slightly smaller than the BE of CaO molecule is thus calculated to be 6.78 eV.

The above discussions reveal the ionic character of the interaction between Ca atom and PdO$_3$ superhalogen, forming a stable CaPdO$_3$ complex, just similar to that between Ca and O forming CaO molecule. Thus, PdO$_3$ superhalogen behaves like a single O atom when it interacts with an alkaline metal. Furthermore, the BE of CaPdO$_3$ is found to be comparable to that of CaO molecule. Thus the present study suggests synthesis of a new class of salts by interaction of PdO$_3$ superhalogen with appropriate main group metal elements. These complex salts are expected to possess high oxidizing capabilities.

_____

CONCLUSION

We have performed theoretical studies on the interaction of PdO_3 superhalogen with Ca atom which forms a stable $CaPdO_3$ complex. On combining NBO and AIM analyses, this interaction is characterized as ionic and the similar to that in CaO molecule. However, unlike CaO, in $CaPdO_3$, Ca site neither contributes to HOMO nor to LUMO. The binding energy of $CaPdO_3$, 5.92 eV is comparable to that of CaO molecule. Thus, our findings motivate the formation of complex ionic compounds by metal-superhalogen interaction.

REFERENCES

[1] GL Gutsev, AI Boldyrev, *Chem. Phys.,* **1981,** 56, 277-283.
[2] XB Wang, CF Ding, LS Wang, AI Boldyrev, J Simons, *J. Chem. Phys.,* **1999,** 110, 4763-4771.
[3] GL Gutsev, AI Boldyrev, *Chem. Phys. Lett.,* **1984,** 108, 250.
[4] Q Wang, Q Sun, P. Jena, *J. Chem. Phys.,* **2009,** 131, 124301.
[5] J Yang, XB Wang, XP Xing, LS Wang, *J. Chem. Phys.,* **2008**, 128, 201102.
[6] P Koirala, M Willis, B Kiran, AK Kandalam, P Jena, *J. Phys. Chem. C,* **2010**, 114, 16018-16024.
[7] AK Srivastava, N Misra, *J. Fluorine Chem.,* **2014**, 158, 65-68.
[8] AK Srivastava, N Misra, *New J. Chem.,* **2014,** 38, 2890-2893.
[9] AK Srivastava, N Misra, *Int. J. Quantum Chem.,* **2014**, 114, 521-524.
[10] GL Gutsev, BK Rao, P Jena, XB Wang, LS Wang, *Chem. Phys. Lett.,* **1999,** 312, 598-605.
[11] AK Srivastava, N Misra, *Mol. Phys.,* **2014,** 112, 1639-1644.
[12] AK Srivastava, N Misra, *Mol. Phys.,* **2014,** 112, 1963-1968.
[13] AK Srivastava, N Misra, *Int. J. Quantum Chem.,* **2014,** 114, 328-332.
[14] AD Becke, *J. Chem. Phys.,* **1993,** 98, 5648-5652.
[15] C Lee, W Yang, RG Parr, *Phys. Rev. B,* **1988,** 37, 785-789.
[16] MJ Frisch et al., Gaussian 09 Rev. B.01, Gaussian Inc., Wallingford, CT, **2010**.
[17] R Dennington, T Keith, J Millam, GaussView, Version 5.0, Semichem Inc*.,* KS, **2005**.
[18] ED Glendening, JK Badenhoop, AE Reed, JE Carpenter, F Weinhold, NBO. 3.1
Program, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1996**.
[19] AE Reed, RB Weinstock, F Weinhold, *J. Chem. Phys.,* **1985,** 83, 735-746.
[20] RFW Bader, *Atoms in Molecules: A quantum theory*, 2nd edition, Oxford University Press, Oxford, **1994**.
[21] TA Keith, T K Gristmill Software, AIMAll (Version 12.09.23), Overland Park KS, USA, **2012**.