Three Electron Bond

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Abstract

Chemical bonds are mainly composed of two electrons that help in the formation of chemical bond. Spectroscopic evidence has confirmed that some bond may show three electron characteristics. These bonds, however not common in nature, may come into occurrence when atoms having specific electronegative difference adjoin to form bonds. Such atoms have mobile lone pair of electrons as they follow resonance shift between the epicenters and hence odd electron imparts various covalent character into the bond so formed between the atoms. Thus the bond is seen to have three electron character which in other words is termed as odd electron bond or three electron bond. Despite having no direct parallel connection with the field of applied science, three electron bond possess huge significance in vivid description of the basic organic chemistry of the compounds such as bond length, ionic character, bond angle, the shape of the molecule hybridization etc. In addition three electron bond concept is used to calculate delocalization energy, explain the specificity of an aromatic bond and represent the actual structure of various compounds. We have aimed to review the basic concept, resonance hypothesis and stability aspect of the three electron bond.

Keywords: odd electron; ionic character; resonance; hybridization

INTRODUCTION

The concept of Three electron bond was introduced by Pauling (1931) who described that odd electron are used to form them. Presence of odd electron in paramagnetic species like O_2, He+, CO, NO, NO_2, etc show relevance of three electron bond. The mentioned molecules contain a paired electron on one atom and an unpaired electron on another and possess equivalent energy difference [1].

It is combined effect of three electrons with relative spin resulting in the formation of unique type of bond.These play a vital role in bond formation and bond cleavage as well as exists as intermediate in various chemical reactions [2].

The Idea of Three Electron Bond was developed by Heitler and London. They proposed that an electron bond pair is formed by the interaction of unpaired electrons in two atoms. It is observed that a stable molecule is formed when two sharing atoms possess an unpaired electron [3].

The system consists of a single electron belonging to one nucleus and a pair of electron belonging to another nucleus refers to the interchange of three electrons. Here we consider the example of Hydrogen atom having single electron and a paired electron containing specie Helium atom.The normal Helium nucleus (He) and Hydrogen nucleus (H) have no affinity to molecule formation. However, if two nuclei have identical energy an additional degenerate orbital of the configuration He: **.**H is formed [4].

H.+ :He ⟷ H:.He+ (i)

H.: He - ⟷ H: .He (ii)

H.: He ⟷ H:-.He+ (iii)

Such system refers to two center- three (2c-3e) electron bonding. Such Lewis structures are resonance stabilized and show charge transfer.

Energy difference must be small to acquire stabilization energy [5, 6].

The Energy difference for the neutral species (iii) shown above involves least Energy difference between Ionization potential of He and Electron Affinity of H. There is a distribution of three electrons between two overlapping atomic orbital [7].

Thus Postulates of three electron bond theory include presence of three electrons with oppositely oriented spins, consists of atom that has completed its octet configuration, electron spin adjustment is done in such a way that the attraction is minimum for bonding [8]. It is mostly observed in radical cation with an interaction of an unpaired p-orbital. The net energy of the system is calculated as half the strength of two electron bond system. The Electronegative difference between the sharing atom must not exceed 0.5.Such bond is formed when an unpaired electron of an atom combine to the lone pair of electron of another atom.

Resonance Stabilization

Bond Energy depends on interchanging energy of the two shared pair of electrons or resonance or the electrostatic force [9]. While drawing resonance structure we take care that electrons move to adjacent position neighboring atom or group to form a pi bond and that the net charge of all resonating structure must be same.

Strongest Three electron bond occur in two identical fragment mostly and heteroatom from first and second period (like N:.N, O:.O, F:.F, P:.P, S:.S, Cl:.Cl) rare gases (like He:. He, Ne:.Ne, Ar:. Ar).Various other molecule like NO, CO_2 show three electron bond of which NO is most stable of the odd electron molecule [10]. Stability of various molecules is explained by the formation of three electron bond.

The Energy difference between the two resonating structure are used to determine the stabilization energy [11]. Resonance between several electronic structures proposed by Lewis is used to determine the bond distance between two atoms [12]. The two resonant structure of NO molecule (I & II) proposed by Pauling is noted herewith (Fig. 1).

Fig. 1. Resonant structure of NO molecule

Other paramagnetic species like He, Ar, O_2, NO_2, NO etc. are shown diagrammatically with three dots representing the three electron bond. The three electron bond prototype having degenerate levels is seen in di-positive Helium ion [12]. Various evidence show that a neutral helium molecule is formed by one excited helium atom containing an unpaired 1s electron and one normal helium atom that forms Helium band [13]. The same happens for noble gases like Helium and Argon(Fig. 2) and gasses like nitric oxide and oxygen (Fig. 3).

Fig. 2. Three dot representation of Three Electron Bond

Fig. 3. Three dot representation of electronegative atom Nitrogen & Oxygen

Various electronegative atoms like Nitrogen and Oxygen have slight EN difference and same effective nuclear charge. Resonance between the structures shown lead to a double and a three electron bond [14].

Stabilization of Three Electron Bond

Stability of nucleus showing three electron bonding depends on resonance exhibited by two Lewis structures which is related to transfer of charge. It is observed that significant resonance energy is required for stability of two resonating Lewis Structure [15]. According to Clark, three electron bond energy of ion show an exponential decrease with the difference in Ionization potential and the Electron affinity of the Lewis structures. He carried out systematic calculation on several radical cations involving three electron bond between various atoms of first and second rows of a periodic table, substituting hydrogen atom [16].

Three electron bond is however a new concept that involves three electrons and are distributed among two overlapping atomic orbital. The hypothesis of three electron bond can be explained by Valence bond theory and Molecular Orbital Theory. Valence bond theory explains overlapping of two half filled orbital and when the atomic orbital contains more than a single unpaired electron, there can be formation of more than one bond. Molecular orbital Theory represents doubly occupied Molecular Orbital (MO) and a singly occupied MO of the molecule He: **.**H depicting bonding and antibonding orbital. The distribution of three electron between two overlapping atomic orbitals is validated by the least energy difference of Ionization potential and Electron affinity. Thus both Valence Bond Theory and Molecular Orbital theory divulge into the same conclusion and the two Lewis structure are mutually related by charge-shift.

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