

Organic Compounds

Chapter 1

Three Electron Bond, A New Paradigm in Organic Chemistry- A Review

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Abstract

Although chemical bonds in organic chemistry are mainly comprised of two electrons, spectroscopic and other evidence have confirmed that some bond may have three electron characteristics. These bonds, although not common in nature, may come into play when atoms having specific electronegative difference conjoin to form bonds. The lone pair of electrons on such atoms may be mobile following resonance shift between the epicenters and thus odd electron impart certain covalent character onto the bond already formed between the atoms. Thus the bond could have three electron character which in other words is termed as three electron bond or odd electron bond. Notwithstanding having no direct correlation with applied science field, three electron bond possess enormous significance in describing the basic organic chemistry of the compounds such as paramagnetism, bond length, bond angle, ionic character, $p\pi$ - $d\pi$ back bonding, hybridization, the shape of the molecule and so others. We have aimed to review the development, basic concept, molecular orbital dissection, resonance concept and stability aspect of the three electron bond.

Keywords: bonding orbital; antibonding orbital; resonance; odd electron; paramagnetic system

1. Introduction: Three Electron Bond

Three electron bond concept was introduced by Linus Pauling to provide the sharing of electron pair concept of paramagnetic system like NO, O₂, NO₂, He⁺, CO etc. All the molecules contain an unpaired electron on one atom and paired electron on another atom possessing equivalent energy difference [1].

This is combined action of three electrons with a relative spin that results in the formation of a unique type of bond. These exist as intermediate in various chemical reactions and play a vital role in bond cleavage and bond formation [2].

A Three electron bond theory postulate include

a) Chemical bond formation is observed by the presence of three electrons with oppositely oriented spins, viz



b) An Atom must have an electron that fulfills its octet configuration.

c) The condition for bond formation entails a number of electrons involved is maximum with minimum energy [3].

d) The electron spin is adjusted in such a way that the attraction is minimal for bonding.

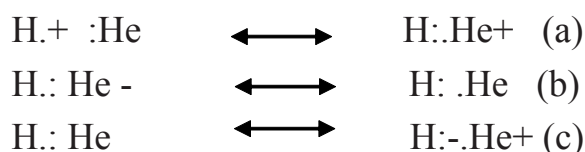
e) The state of the electron is determined by the octet rule.

Stability of various molecule containing odd electrons is explained by the formation of three electron bond [4]. Moreover the concept of Three electron bond is used to calculate delocalization energy, represent the actual structure of various compounds and explain the specificity of an aromatic bond [5].

2. Development of the Idea of Three Electron Bond

Heitler and London proposed that an electron bond pair is formed by the interaction of an unpaired electron in two atoms. Bond Energy depends on resonance or the interchanging energy of the two shared pair of electrons or the electrostatic force. It is observed that a stable molecule is formed when two sharing atoms possess an unpaired electron [6].

A system that consists of a pair of electron belonging to one nucleus and single electron belonging to another nucleus refers to the interchange of 3 electrons. The normal Hydrogen nucleus (H) and Helium nucleus (He) have no affinity to molecule formation. However, if two nuclei have identical energy an additional degenerate orbital of the configuration He: ·H is formed [7]. Such system refers to 2 center- 3 electron bonding. Stability of such bond is attained by resonance between Lewis structures that show charge transfer.



In the above resonance environment, Energy difference must be small to attain stabilization energy [8]. The Energy difference for the neutral species (c) shown above involves least Energy difference of Ionization potential of He and Electron Affinity of H. This

is explained in terms of molecular orbital theory also (**Figure 1**).

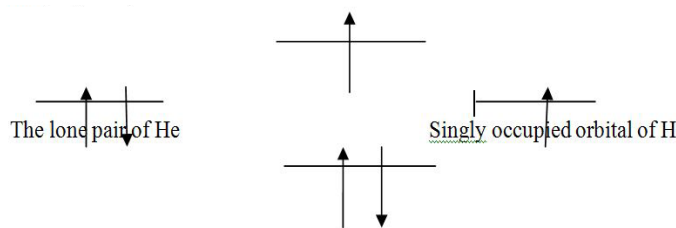


Figure 1: Molecular orbital representation of three electron bond between H and He

Molecular orbital (MO) representation that results in doubly occupied MO and a singly occupied MO of the molecule He: $\cdot\text{H}$ showing bonding and antibonding orbital. It shows the distribution of three electrons between two overlapping atomic orbitals.

Based on the above observation, An American Chemist Linus Pauling in 1931 provided six rules of the shared electron pair.

First, three rules explain the formation of electron bond pair between two atoms. Such pair is formed by the interaction of an unpaired electron of opposite spin on each atom. Once pairing is complete, the two electrons could not participate in additional bond formation.

Last three rules explain about electron exchange when bond formation involves one wave function for the individual atom. The electron available in lowest energy would form the strongest bond. The most overlapping orbital form the strongest bond and orbital orientation predicts molecular structure and bond angle [9].

3. Basic Criteria of Three Electron Bond

- i) Such bond is formed when an unpaired electron of an atom combine to the lone pair of electron of another atom.
- ii) Electronegative difference between the sharing atom must not exceed 0.5.
- iii) Odd electron-molecule possess larger bond length and less bond energy.
- iv) Odd electron species are stable and paramagnetic in nature.
- v) Mostly observed in radical cations where there is an interaction of an unpaired p-orbital.
- vi) These odd electrons involve orbital hybridization, resonance stabilization, Valence bond theory and Molecular orbital theory.
- vii) The net energy of the system is half the strength of two electron bond system.

4. The Concept of Three Electrons Orbital in Light of Resonance

Unshared pair of an electron can be moved readily because these are not utilized in bonding. While drawing resonance structure we must keep in mind that electrons move to adjacent position viz neighboring atom or group to form a pi bond and that the net charge of all resonating structure must be same. Unless there is a positive charge on the adjacent atom, electrons in another atom are further displaced to preserve the octet rule. Greater the resonance energy greater is the stability.

Strongest Three electron bond occurs in two identical fragment mostly rare gases (like He:..He, Ne:..Ne, Ar:..Ar) and heteroatom from the first and second period (like N:..N, O:..O, F:..F, P:..P, S:..S, Cl:..Cl). Various other molecules like NO, CO₂ show three electron bond of which NO is most stable of the odd electron-molecule [10]. These show 2 centered three electron bonding having two atoms and three electron bond resulting in resonance. Stability of various molecules is explained by the formation of three electron bond. The two resonant structure of NO molecule (I & II) proposed by Pauling is noted herewith (**Figure 2**).



Figure 2: Resonance shift of electron in case of nitric oxide

The Energy difference between the two resonating structure I and II are used to determine the stabilization energy [11]. Resonance between several electronic structures proposed by Lewis are used to determine the bond distance between two atoms [12]. Those radical cations having sulfur are typical models of σ three electron bonding and are extensively studied in solution, solid matrix and in the gas phase by various spectroscopic methods [13]. Stable structure of ClO₂ having 19 electrons (odd electron species) is determined using three electron bond (**Figure 3**).

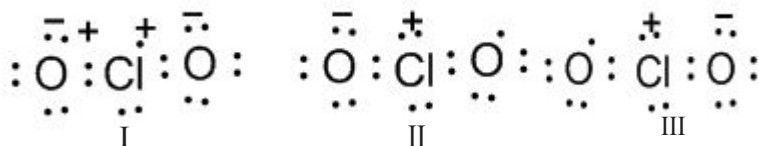


Figure 3: ClO₂ bonding in terms of quantum mechanical rules. The form I, II and III show corresponding resonance shifts.

The above structures I, II, III are possible structures that according to the quantum mechanical rule and finally calculating the energies involved. The formal charge of each atom is indicated which result due to the splitting of an electron pair. From the above structure, the correct one is found by calculating the energy of each [14]. Less energy of the molecule indicates greater stability. Chlorine and Oxygen have an electronegative difference less than 0.5, thus fulfills the criteria of three electron bond. Positive chlorine has greater electronegative value than neutral chlorine that is almost near to electronegative value of Oxygen. Thus in

ClO_2 molecule, transfer of one electron from oxygen to chlorine involves very small energy difference. Thus unshared pair of the electron in Chlorine atom (shown in structure I), and an unshared pair of an electron in Oxygen atom (shown in structure II and III) tend to form three electron bond with the adjacent atom having paired electron. Two types of bond formation are observed in ClO_2 structure which is indicated by two dots for the electron bond and by three dots for three-electron bond (**Figure 4**).



Figure 4: Structures of ClO_2 in terms of three-electron bond. Form IV and V are the structural twists of three electrons between the two oxygen atoms

The structure I and II, as well as Structure I and III, are combined to give three electron bond structures named IV and V that is diagrammatically represented by three dots. In both the structure one electron bond is formed between one atom of oxygen and chlorine and a three electron bond is formed between another atom of oxygen and chlorine. The Structure IV and V have nearly the same energy and are undistinguished, thus correspond to resonating structures. The observed bond distance of the molecule is associated with the strongest type of bond involved in resonating structures. Strongest bonding is determined by most stable resonating structure [15].

Based on the above description of ClO_2 molecule, other paramagnetic species like He, Ar, NO, O_2 , NO_2 etc. are shown diagrammatically with three dots representing the three electron bond (**Figure 5**).



Figure 5: Three electron bond representation in noble gas

The prototype three electron bond with degenerate levels is seen in di-positive ion of Helium [16]. 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 [17]. The same happens for noble gases like Helium and Argon.



Figure 6: Three electron bond of EN atom of Period 2)

Lewis had concluded that of all the odd molecule, NO shows the least amount of unsaturation at ordinary conditions and temperature. It does not associate to form a dimer. The odd electron is held firmly in the NO molecule. The different electronegative atom Nitrogen and Oxygen have same effective nuclear charge and slight EN difference. The two states occur as shown which have nearly same energy. Resonance between the structures shown leads to a double and a three electron bond [18].

Both EN atoms contain overlapping atomic orbital that occupies three electrons. Oxygen molecule has one pair bond and two three electron bond. The Oxygen molecule is not highly unsaturated as they are stabilized by three electron bond system.

Specificity of an aromatic bond of Benzene molecule is explained by the concept of three-electron bond. It explains Huckel's rule of aromaticity. The Benzene molecule is represented in the following form as well carbon benzene atoms have octet equal to 8. It should be pointed out that due to the maximum distance from atom nuclei the central electron of the 3-electron bond is assumed to be the most mobile electron compared to other electrons of the 3-electron bond.

Three electrons between two carbon atoms of benzene ring with oppositely oriented spin ($\uparrow\downarrow\uparrow$) form a chemical bond.

The spin of the central electron specie is opposite to that of the side electron. The benzene nucleus has six central electrons. Taking for example the carbon 1 gets attracted to carbon 2 and carbon 6 as carbon 1 possess a spin opposite to that of carbon 2 and 6. The distance between two atoms is 1.2\AA as the distance between the central electron 1 and side electron 2 and between 1 and 6 is equal to the acetylene molecule which has a bond distance of 1.2\AA (**Figure 7**).

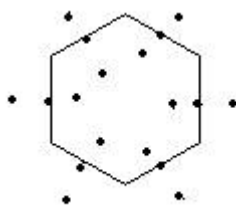


Figure 7: Three electron structure of benzene ring

Interaction of the electrons is as shown below where central electron leads to bond formation and others form π bond. The bond angle is 120° where the resultant vector of interaction is towards the center [19].

Structural analysis is the most useful and direct method for the study of odd-electron bonds. Though many three-electron sigma-bonding systems $X\cdot :X$ and $X:\cdot Y$ (He, N, S, P, halogen) has been researched in solid matrix, in the gas phase and characterized by various spectroscopic methods in addition to the theoretical calculations, few of them are stable in room temperature as they are either much reactive or tend to dimerize in solid state [20-25]. Three species have been isolated and structurally featured by single X-ray crystal diffraction.

5. Stability of Three-Electron Bond

Stability of species showing 3-electron bonding depends on resonance showed by two Lewis structure which is mutually related to transfer of charge. It has been observed that a

significant resonance energy is required for like stability of two resonating Lewis Structure [26]. According to Clark, three electron bond energy of ions shows an exponential decrease with the difference in Electron affinity and the Ionization potential of the Lewis structures. Most three electron bond molecule are homo nucleated species or have same ionization potential and Electron affinity.

3-electron bond molecules are observed to be held together by 3-electron configuration symbolized as $\cdot\cdot$ in which one antibonding molecular orbital is singly occupied and corresponding bonding molecular orbital is doubly occupied that leads to a net bond order of $\frac{1}{2}$ [27].

Radom and Clark carried out systematic calculations on several radical cations involving 3e-bonds between various atoms of first and second rows of a periodic table, substituting hydrogen atom [28].

Electron correlation is much essential to calculate of 3e-bonding energy. After examining the nature of three electron bond, molecular orbital theory and weighing the corresponding valence bond wave function easy explanation of the essence of the dynamic correlation can be done.

If we start from Hartree-Fock wave function of a homonuclear molecule like $Ax \cdot\cdot Ay$, which is shown to display 3-electron bond between respective atomic orbital leads to the resonating Valence bond structural description like $Ax \cdot\cdot :Ay \leftrightarrow Ax : \cdot Ay$. This representation is explained in corresponding wave functions 3e-bond in equations as under:

$$\sigma = \chi_X + \chi_Y \quad (\text{Bonding Orbital})$$

$$\sigma^* = \chi_X - \chi_Y \quad (\text{Antibonding Orbital})$$

Hence, both Valence Bond Theory and Molecular Orbital theory converge to the same conclusion of 3 electron bond where the two Lewis structures represent 100% of the wave function and are mutually related by charge-shift.

Of course, at this computational level, both wave functions possess a common set of orbitals which are optimized for an average neutral situation in which the charge (or atomic occupancy) is equally shared by Ax and Ay .

Intra-molecular sulfur-nitrogen [$S \square N$] and sulfur-sulfur [$S \square S$] 3-electron bonded radical cationic species and radicals like sulfur-oxygen [$S \square O$] have been generated in aqueous solutions of various peptides under pulse radiolytic condition. Cationic sulfur species shows protolytic equilibrium. Resonance structures, in reality, 2 does not exist thus by assuming the existence of 3 electron bond, the real formula of various organic compounds, benzene, ozone, oxygen etc. can be explained. The multiplicity of various bonds is explained by molecular method calculation.

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