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SEM-II

Physical Chemistry

Unit - IV

1. Electron density
2. π -Bond order
3. Free Valence

* Electron density *

The probability that an electron will be found in small volume element $d\tau$ is ψ^2 where ψ is normalised wave function

$$\text{Consider } \psi = \sum a_r P_r$$

$$\int \psi^2 d\tau = \int \sum a_r^2 P_r^2 d\tau$$

As the P_r atomic orbital are normalised

$$\text{so, } \int P_r^2 d\tau = 1$$

$$\int \psi^2 d\tau = \sum a_r^2 \quad \text{--- (1)}$$

thus, a_r^2 represent the probability of electron density due to one electron at the atom r but there may be several electrons distributed in a number of HMOⁿ.

The total electron density

$$a_r^2 = \sum n_j a_{jr}^2 \quad \text{--- (2)}$$

Where, a_{jr} is the coefficient of the atom r in the j^{th} HMO and n_j is the number of electrons in that HMO.

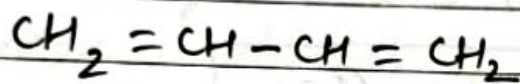
eg- Butadiene system

$$\Psi_1 = 0.372 P_1 + 0.602 P_2 + 0.602 P_3 + 0.372 P_4$$

$$\Psi_2 = 0.602 P_1 + 0.372 P_2 - 0.372 P_3 - 0.602 P_4$$

$$\Psi_3 = 0.602 P_1 - 0.372 P_2 - 0.372 P_3 + 0.602 P_4$$

$$\Psi_4 = 0.372 P_1 - 0.602 P_2 + 0.602 P_3 - 0.372 P_4$$



$$C_1 = 2 \times (0.372)^2 + 2 \times (0.602)^2 = 1.0$$

$$C_2 = 2 \times (0.602)^2 + 2 \times (0.372)^2 = 1.0$$

$$C_3 = 2 \times (0.602)^2 + 2 \times (-0.372)^2 = 1$$

$$C_4 = 2 \times (0.372)^2 + 2 \times (-0.602)^2 = 1$$

Total electron density = 4

* π -Bond order *

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The HMO coefficient can be used to calculate the π -electron distribution in the bonds. A very important quantity called π -bond order P_{rs} representing the degree of π -bonding between adjacent carbon atom r and s was first introduced by Coulson in 1939.

It is defined as -

$$P_{rs} = \sum n_j a_{jr} a_{js}$$

in which n_j is the number of electrons in the j^{th} HMO.

Q.uesr: Calculate the π -bond order in ground state in butadiene system.

Ans: In ground state of butadiene, only first two HMO ψ_1 and ψ_2 will be used.

$$P_{12} = 2 \times 0.372 \times 0.602 + 2 \times 0.602 \times 0.372 \\ = 0.896$$

$$P_{23} = 2 \times 0.602 \times 0.602 + 2 \times 0.372 \times (-0.372) \\ = 0.448$$

$$P_{34} = 2 \times 0.602 \times 0.372 + 2 \times (-0.372) \times (-0.602) \\ = 0.896$$

The above calculation show that

- (i) $0 < P_{rs} < 1.0$ meaning that each of the three bond is neither a full double bond nor a single bond, all have partial double bond character.
- (ii) $P_{12} = P_{34} > P_{23}$ meaning that the terminal bonds C_1-C_2 and C_3-C_4 have more double bond character.
- (iii) The terminal bonds C_1-C_2 and C_3-C_4 should be shorter than the central C_2-C_3 but longer than the olefinic ($C=C$) bond.
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* Free Valence *

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The concept of free valence at a Carbon atom is used as index to indicate to that carbon.

It gives a measure of the reactivity that position will be most reactive which has the largest free valence.

The free valence f_r at an atom 'r' is defined as

$$f_r = N_{max} - N_r \quad \text{--- (1)}$$

Where N_{max} is the max^m possible π -bonding that a carbon atom is capable of and N_r is the actual amount of π -bonding that it exhibits in the molecule.

The amount of π -bonding is taken as the sum of all the π -bond order involving that atoms.

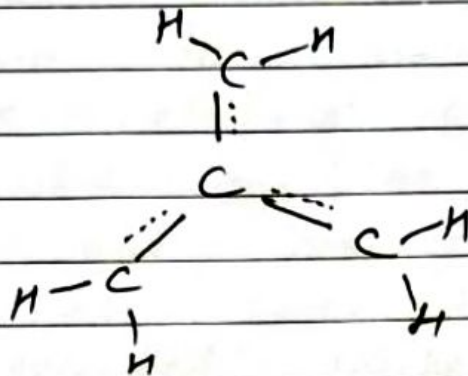
To determine the value of N_{max} , central atom in trimethylenemethane is considered.

This atom is involved in π -bonding

to the maximum extent.

f_1 is equal to $\sqrt{3}$

$$f_2 = \sqrt{3} - 2f_1$$



m Butadiene

$$F_1 = \sqrt{3} - 0.896 = 0.836$$

$$F_4 = \sqrt{3} - 0.896 = 0.836$$

for Carbon 2,

extent of π -bonding is -

$$P_{12} + P_{23} = 0.896 + 0.448 = 1.344$$

for Carbon 3,

extent of π -bonding is

$$P_{23} + P_{34} = 0.448 + 0.896 = 1.344$$

$$\text{Hence, } F_2 = F_3 = \sqrt{3} - 1.344 = 0.338$$

SO, C_2 and C_3 are much deeply involved in bonding that C_1 and C_4 have smaller free valence. This explains that terminal Carbon atoms are more reactive in butadiene.