Paper II- Organic Chemistry

Chapter-I
Structure and Bonding

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Bond Strengths & Bond Distances

- In general, shorter bonds are stronger bonds.
- Bond strengths increase with increasing s character.
- Bonds become weaker as we move down the Periodic Table. Compare C-O and C-S, or the carbon–halogen bonds C-F, C-Cl, C-Br, C-I.
- Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because p overlap is less than s overlap.

Table-Bond enthalpy, bond length and dipole moments of C-X bonds in CH_3X

Bond	Bond Enthalpy/KJ/mol	Bond Length/^oA	Dipole moment/Debye
CH_3-F	452	1.42	1.847
CH_3-Cl	351	1.77	1.860
CH_3-Br	293	1.91	1.830
CH_3-I	234	2.12	1.636

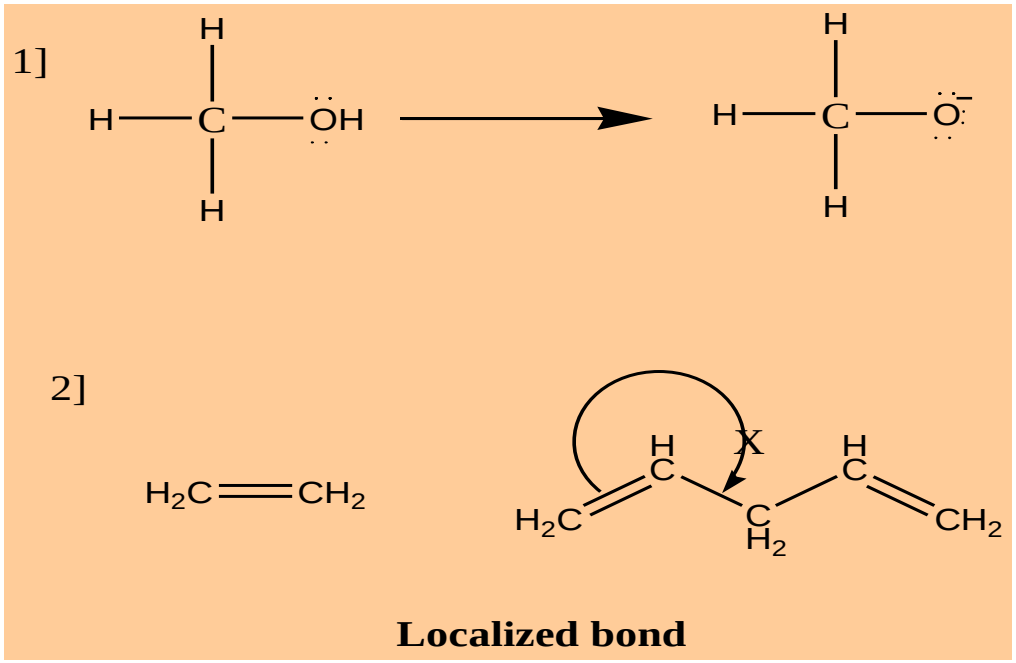
- **The size of halogen atom increases from fluorine to iodine, which increases the C-X bond length .**
  - **Larger the size, greater is the bond length and weaker is the bond formed**

Localized and Delocalized Bond

Localized Bond: (Less stable)

Electronic charge or Pi-bond is not distributed in atoms or molecules called Localized bond.

Examples:

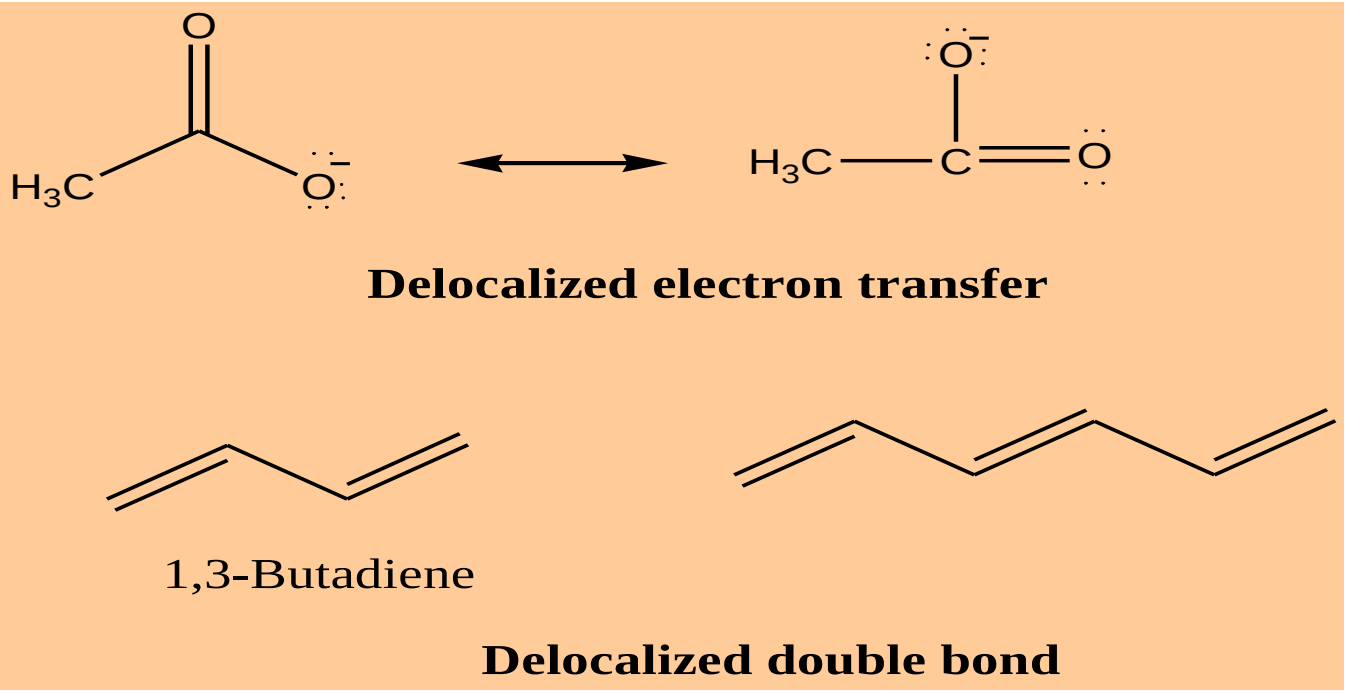


Localized bond

Delocalized Bond: (More stable)

Electronic Charge or pi-bond distributed due to resonance in atoms or molecules called delocalized bonding.

Examples:

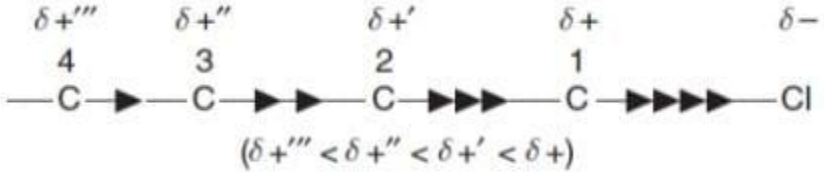


Inductive effect

Ideally, a covalent bond between two atoms must share the pair of electrons equally. If the electronegativities of the two atoms are different, this sharing of electrons is not equal and the more electronegative atom gets a fractional negative charge due to the greater attraction of the shared pair of electrons towards itself and the other atom gets a fractional positive charge. Fractional or partial negative charge is represented by δ- (pronounced as delta minus) and Fractional or partial positive charge is represented by δ+ (pronounced as delta plus), δ signifying the very less magnitude of charge. For example, C - X (X = halogen) bond is polar with C having a δ+ charge and the halogen having a δ- charge. The magnitude or value of these fractional charges increases with an increase in the electro negativity of the halogen i.e. for halogens, it is in the order F > Cl > Br > I.

Let us consider a carbon chain, with the end carbon joined to a more electronegative atom say Cl, then Cl will attract electrons (σ electrons between C and Cl) more towards itself. Hence, the carbon atom will become slightly electron deficient and get a fractional positive charge (δ+) due to a difference of electronegativity.

This polarization is not restricted till here, but it induces polarity further and hence the name as inductive effect.

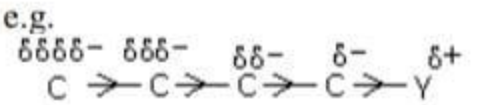


Here, C1 acquires slight positive charge (δ+) due to the electronegativity of Cl which in turn acquires slight negative charge (δ-). C1 thus becomes electron deficient and it exerts a pull on the electrons forming covalent bond between C1 and C2 but less strongly. As a result, C2 acquires a lesser positive charge (δδ+) as that on C1. C3 similarly acquires even lesser positive charge (δδδ+) and so on. Thus a polarity is slowly induced throughout the carbon chain. However, the effect is very very less beyond carbon 3 or 4. In pother words, the effect diminishes as one moves further in the carbon chain relative to the position of the group. The phenomenon of transmission of charge arising due to electronegativity difference in a covalent bond (i.e. dipole) through a chain of carbon atoms linked by sigma bonds is called inductive effect.

Such an effect is therefore propagated in the entire chain of carbon atoms, which were otherwise non-polar (in the absence of group Cl). So the atom/group responsible for the induction in polarity is Cl. Remember that group Cl attracting electrons towards itself is normal due to the difference of electronegativity but induction of polarity in an otherwise non-polar bond due to the attachment of a more electronegative atom in the chain is known as inductive effect. The atoms/groups like Cl which are more electronegative than carbon gain a slight negative charge on them and withdraw the electrons of the carbon chain towards themselves are known to exert -I Effect (pronounced as “minus I effect”)

Similarly, if a more electropositive group (say Y) is attached to an otherwise non-polar carbon chain, the group Y gets a fractional positive charge and the carbon linked to it gets a fractional negative charge. This slightly electron rich carbon then acquires induced electropositive character and shares its excess electron density with the next carbon, which also acquires a fractional negative charge and so on.

e.g.



Induced electropositive character

The atoms/groups which are more electropositive than carbon gain a slight positive charge on them and push the electrons of the carbon chain away from themselves are known to exert +I Effect (pronounced as "plus I effect")

There are very few atoms or groups forming compounds with carbon which are more electropositive than carbon e.g. H and Mg. However, the most important group exhibiting +I effect is the alkyl group, which due to a difference in electronegativities of hydrogen and carbon, makes the carbon slightly electron rich.

Inductive effect has the following characteristics:

1. It is a permanent effect.
2. It operates through sigma bonds. (Note that all the single, double and triple bonds have a sigma bond in them.)
3. Its magnitude goes on decreasing with increase in distance from the atom/group responsible for the same. Inductive effect is almost negligible after the third or fourth atom.
4. -I effect of some groups is in the order -H < -C6H5 < -OCH3 < -OH < -I < -Br < -Cl < -F < -COOH < -CN < -NO2 < -N+ (CH3)3

   +I effect of some of the groups is in the following order:

   H- < D- < -CH3 < -CH2R < CHR2 < -CR3 < -COO-

Inductive effect is not a hypothetical phenomenon but is actually operative in the molecules. This has been demonstrated by the fact that it is commonly used to explain the properties like origin of dipole moment, increase or decrease in bond lengths, strength of acids or bases, etc. In order to classify most of the neutral groups into +I or –I just look at the following parameters required (given in following table) for the nature of first atom. If it is a charged group, then every positively charged group shall exert –I effect because it shall be electron attracting/withdrawing and similarly every negatively charged group shall exert +I effect because it shall be electron repelling.

Thank You…