1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Organic Chemistry – Some Basic Principles and Techniques: Part 3
Module Id	kech_21203
Pre-requisites	Knowledge about electronegativity, polar groups, reagents and substrate.
Objectives	After going through this lesson, the learners will be able to: • Differentiate between heterolytic and homolytic cleavage • Learn about electron movement in organic reactions • Explain electron displacement effects in covalent bonds • Draw the resonance structure of various organic molecules
keywords	Heterolytic Cleavage, Homolytic Cleavage, Nucleophiles, Electrophile, Electron Displacement Effects, Inductive Effect, Resonance Effect, Electromeric Effect And Hyperconjugation

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1.   Introduction

In this module you will learn about fundamental concepts in organic reaction mechanism of organic molecules. Cleavage of a covalent Bond take place in either heterolytically or homolytically. The heterolytic cleavage can give either carbocation or carbanion, however, the homolytic cleavage can give radical. Carbocation, carbanion, and radical are known as reactive intermediates. Reactive intermediates play very important role in deciding the fate of any organic reaction. In an organic molecule, the electronic displacement may take place under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. These electron displacements can cause permanent or temporary polarlisation of the bond. Inductive effect, resonance effect and electromeric effect are examples of electron displacements.

2. Fundamental Concepts in Organic Reaction Mechanism

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s). The general reaction is depicted as follows:


The reactant which supplies carbon for the new bond is called substrate and the other reactant is called reagent. If carbon for the new bond is supplied by both the reactants then choice is arbitrary, in fact, in that case the molecule on which attention is focused is called substrate. In such a reaction, a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. The sequence of steps that describes details of electron movement, energetics during old bond cleavage and new bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. The information of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis. In the following sections, you will learn some of the principles that explain how these reactions take place.

2.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by: (i) heterolytic cleavage, or by (ii) homolytic cleavage.

2.1.1 Heterolytic Cleavage

In heterolytic cleavage, the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments that means the electrons are not divided equally after bond cleavage. After heterolysis, one species is formed with negative charge indicating that it has both the electrons of the bond (valence octet with at least one lone pair) and the other species is electron deficient (sextet electronic structure) thus positively charged. Thus, heterolytic cleavage of bromomethane will give $^{+}CH_3$ and Br^{-} as shown below:
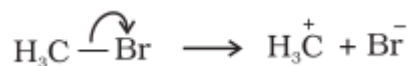
Carbocation is defined as species having a carbon atom possessing a positive charge and sextet of electrons. Carbocation were earlier known as carbonium ion. The $^+CH_3$ ion is known as a methyl carbocation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $CH_3H_2C^+$ (ethyl cation, a primary carbocation), $(CH_3)_2HC^+$ isopropyl cation, a secondary carbocation), and $(CH_3)_3C^+$ (tert-butyl cation, a tertiary carbocation).

Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects. The observed order of carbocation stability is:

$^+CH_3 < CH_3H_2C^+ < (CH_3)_2 HC^+ < (CH_3)_3C^+$.

In carbocations, positively charged carbon is sp^2 hybridised with trigonal planar shape. Thus, shape of $^+CH_3$ may be considered as being derived from the overlap of three equivalent C (sp^2) hybridised orbitals with 1s orbital of each of the three hydrogen atoms. Each bond may be represented as C (sp^2)–H(1s) sigma bond. The remaining carbon p-orbital is perpendicular to the molecular plane with no electrons. [Fig. 1(a)]
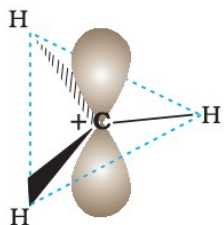

Fig 1 (a). Shape of Methyl Carbocation

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. Such a species is known as carbanion. Thus, carbanion is defined as carbon species carrying a negative charge on carbon atom For example, when group Z attached to the carbon leaves without electron pair, the methyl anion is formed.

In carbanion, negatively charged carbon sp^3 hybridized with distorted tetrahedron structure [Fig. 1 (b)].

Fig 1 (b). Shape of Methyl Carbanion

Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar reactions.

2.1.2 Homolytic Cleavage

If a covalent bond breaks in such a fashion that each atom gets one electron of the shared pair, it is called homolytic cleavage. Thus, the movement of a single electron takes place instead of an electron pair in homolytic cleavage. The single electron movement is shown by 'half headed' (fish hook:) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals. Like carbocations and carbanions, free radicals are also very reactive and unstable. Homolytic cleavage can be shown as:
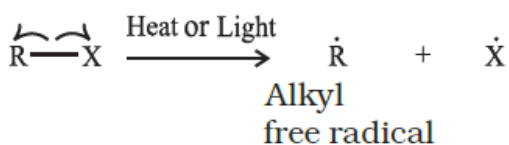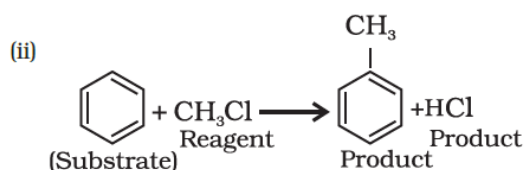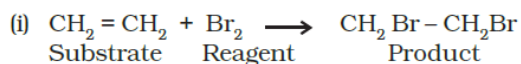

Alkyl radicals are also be classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary:
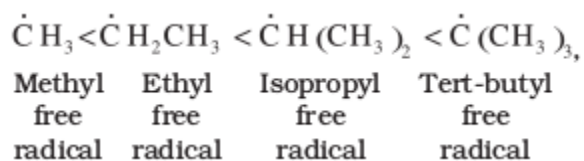
Organic reactions, which proceed by homolytic fission, are called free radical or homopolar or nonpolar reactions.

2.2 Substrate and Reagent

In organic reactions, generally, ions are not formed. In fact, molecules as such participate in the reaction. As we have already discussed, it is convenient to name one reagent as substrate and other as reagent. Substrate is reactant whose carbon is involved in new bond formation and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. For Example:

(i) $\underset{\text{Substrate}}{CH_2 = CH_2} + \underset{\text{Reagent}}{Br_2} \longrightarrow \underset{\text{Product}}{CH_2Br - CH_2Br}$

(ii)

2.3 Nucleophiles and Electrophiles

The reactive site of the substrate is attacked by reagents. The reactive site may be electron deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. A reagent that supplies an electron pair to the reactive site is called a nucleophile (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**.

However, if attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g., π electrons in a double bond. A reagent that takes away an electron pair from reactive site is called electrophile (E^+) i.e., electron seeking and the reaction is called **electrophilic**.

During a polar organic reaction, a nucleophile attacks at electron deficient part of the substrate (electrophilic carbon of the substrate). However, the electrophiles attack electron rich centre of the substrate (nucleophilic carbon of the substrate). Thus, during bonding interaction the electrophiles receive electron pair from the substrate and a curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3C:^-$). Neutral molecules having lone pair of electrons such as $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{N}H$ etc., can also act as nucleophiles. Electrophiles are usually positively charged e.g., carbocations ($^+CH_3$) and neutral molecules having functional groups like carbonyl

group (>C=O) or alkyl halides (R₃C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 1

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.
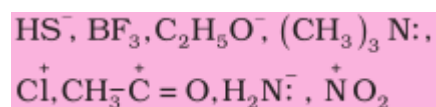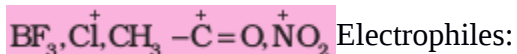(a) CH_3–SCH_3, (b) CH_3–CN, (c) CH_3–Cu

Solution:
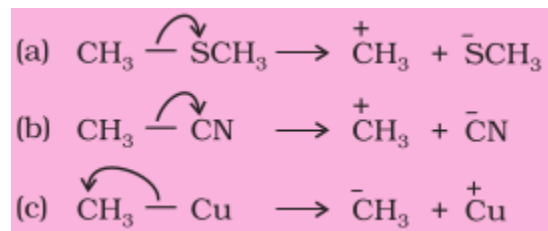
Problem 2

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

Solution

Nucleophiles: **HS⁻, C₂H₅O⁻, (CH₃)₃N:, H₂N⁻**

These species have unshared pair of electrons, which can be donated and shared with an electrophile.

 Electrophiles:

Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 3

Identify electrophilic centre in the following: $CH_3HC=O$, CH_3CN, CH_3I.

Solution

Among $CH_3HC*=O$, $H_3CC*\equiv N$, and $H_3C*–I$, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

2.4 Electron Movement in Organic Reactions

In organic reactions, the movement of electrons can be shown by curved-arrow notation. Curved-arrow shows the changes in bonding during the reaction due to electronic redistribution. curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron is shifted. Presentation of shifting of electron pair is given below:
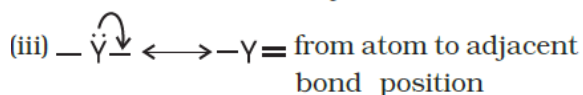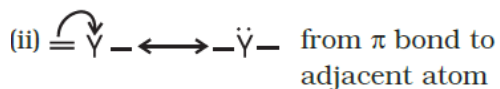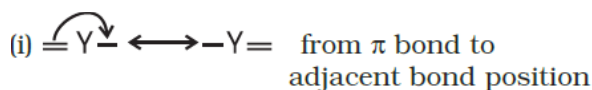
Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:
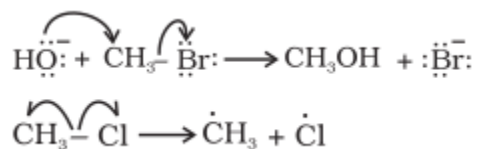
3. Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements.

Temporary electron displacement effects can also be seen in organic molecules when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections you will learn about these types of electronic displacements.

3.1 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.
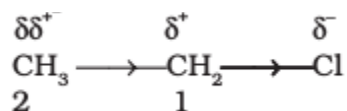
In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent s-bond is referred to as the inductive effect.

This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substituents can be classified as electron-withdrawing or electron donating groups relative to hydrogen. Halogens and many other groups such as nitro ($-NO_2$), cyano (-CN), carboxy (-COOH), ester (-COOR), aryloxy (-OAr, e.g.

–OC$_6$H$_5$), etc. are electronwithdrawing groups. On the other hand, the alkyl groups like methyl (–CH$_3$) and ethyl (–CH$_2$–CH$_3$) are usually considered as electron donating groups.

Problem 4

Which bond is more polar in the following pairs of molecules: (a) H$_3$C-H, H$_3$C-Br (b) H$_3$C-NH$_2$, H$_3$C-OH (c) H$_3$C-OH, H$_3$C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, since O is more electronegative than N, (c) C–O, since O is more electronegative than S.

Problem 5

In which C–C bond of CH$_3$CH$_2$CH$_2$Br, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

3.2 Resonance Structure

Behavior of many organic molecules cannot be explained by a single Lewis structure. For example, characteristic properties of benzene cannot be explained by its cyclic structure containing alternating C–C single and C=C double bonds.
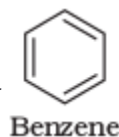
Benzene

As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, it is found experimentally that benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single (154pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.
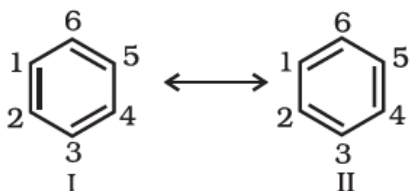
Therefore, according to the resonance theory the actual structure of benzene cannot be adequately represented by either of two structures, rather it is a hybrid of the two structures (I and II) called resonance structures. The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule. They contribute to the actual structure in proportion to their stability. Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.

However, it is known that the two N–O bonds of nitromethane are of the same length (intermediate between a N–O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the **resonance stabilisation energy** or simply the resonance energy. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

Problem 6

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.
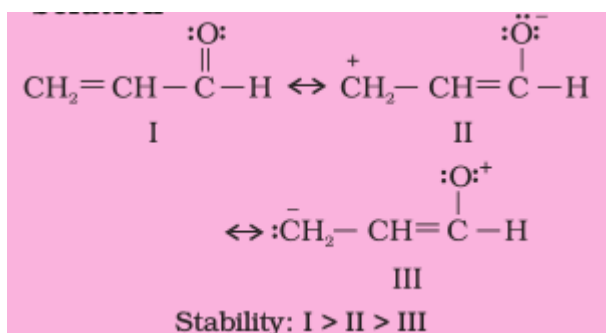
Solution

First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.
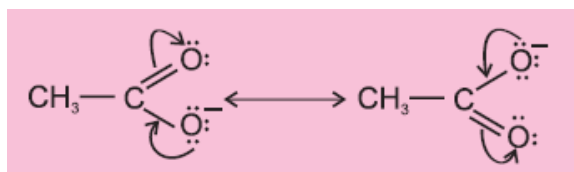
Problem 7

Write resonance structures of $CH_2=CH–CHO$. Indicate relative stability of the contributing structures.

Solution:

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].

Problem 8

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.
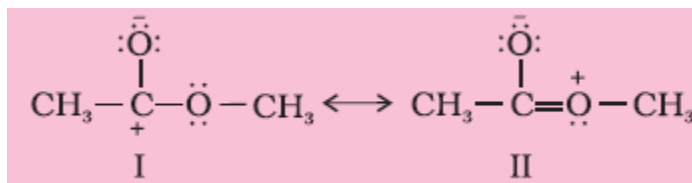

Solution

The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

3.3 Resonance Effect

The polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom is known as resonance effect. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect.

(i) Positive Resonance Effect (+R effect)

In this effect, the electrons are transferred away from an atom or substituent group attached to the conjugated system, it is known as This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as:
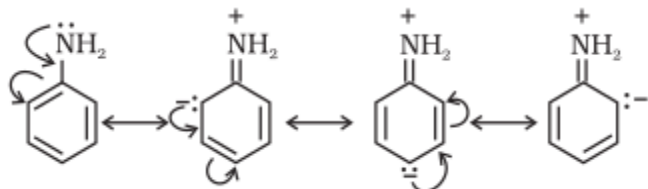
(ii) Negative Resonance Effect (- R effect)

This effect is observed when the electrons are transferred towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as:
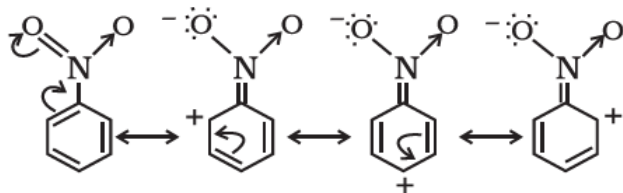
The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, –NH$_2$, –NHR, –NR$_2$, –NHCOR,

**– R effect**: – COOH, –CHO, >C=O, – CN, –NO$_2$

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a **conjugated system**. These systems often show abnormal behaviour. The examples are 1,3-butadiene, aniline and nitrobenzene etc. In such systems, the p-electrons are delocalised and the system develops polarity.

3.4 Electromeric Effect (E effect)

It is a temporary effect. This effect is seen in the organic compounds having a multiple bond (a double or triple bond) in the presence of an attacking reagent only. Electromeric Effect is the complete transfer of a shared pair of p-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is cancelled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (⤷). There are two distinct types of electromeric effect.

(i) Positive Eelctromeric Effect (+E effect)

In this effect the π electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example:

$$\underset{\text{(attacking reagent)}}{>C = C< + H^+} \longrightarrow >\overset{+}{C} - \underset{\underset{H}{|}}{C}<$$
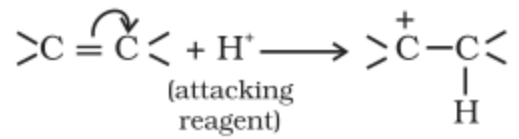
(ii) Negative Electromeric Effect (–E effect)

In this effect the π-electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:

$$\underset{\text{(attacking reagent)}}{>C = C< + \ \overline{C}N} \longrightarrow >C - \underset{\underset{CN}{|}}{\overline{C}}<$$
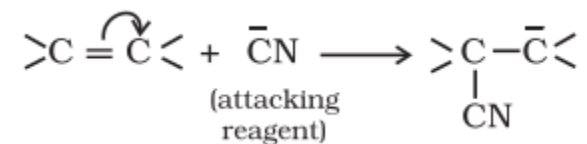
When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates.
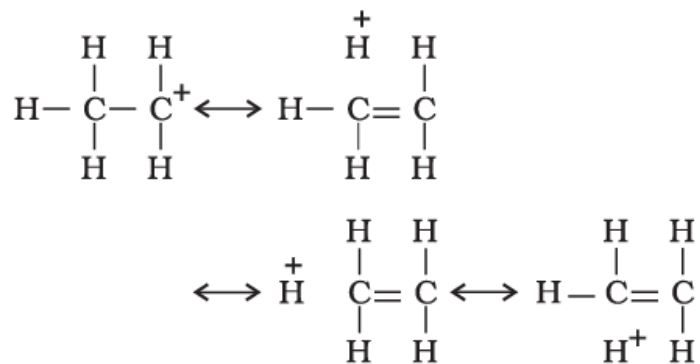
3.5 Hyperconjugation

Hyperconjugation is a general stabilizing interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of $CH_3CH_2^+$ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in **Fig. 2(a).**
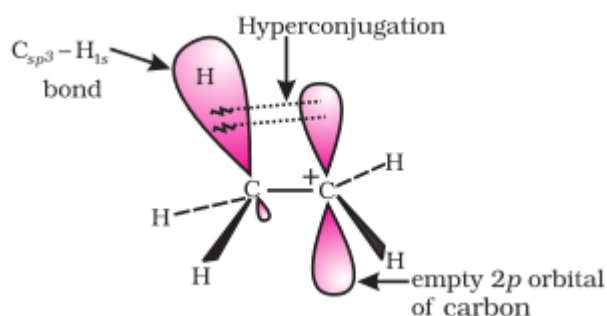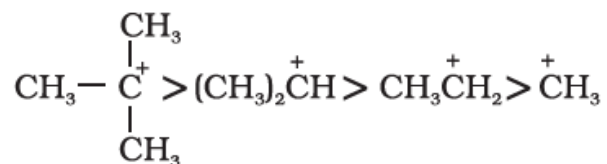

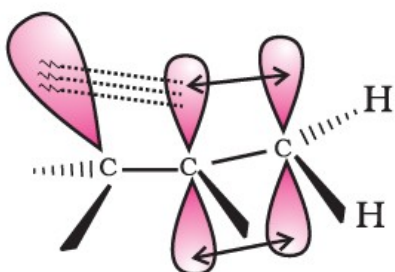**Fig 2(a)** Orbital diagram showing hyperconjugation in ethyl carbocation

This type of overlap stabilises the carbocation because electron density from the adjacent s bond helps in dispersing the positive charge.

In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{C}}} > (CH_3)_2\overset{+}{CH} > CH_3\overset{+}{CH}_2 > \overset{+}{CH}_3$$

Hyperconjugation is also possible in alkenes and alkylarenes. Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 2(b).

Fig 2(b) Orbital diagram showing hyperconjugation in propene carbocation

There are various ways of looking at the hyperconjugative effect. One of the ways is to regard C —H bond as possessing partial ionic character due to resonance.
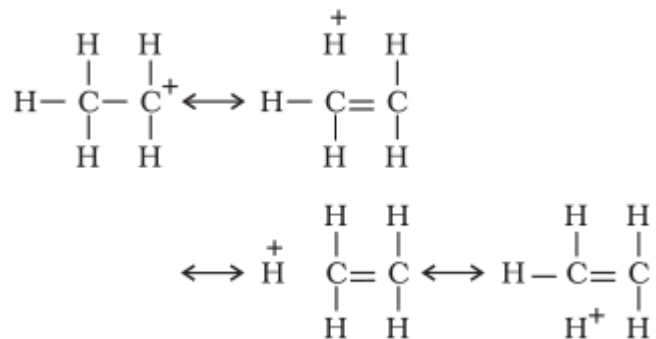
The hyperconjugation may also be regarded as no bond resonance.

Problem 9

Explain why $(CH_3)_3C^+$ is more stable than $CH_3H_2C^+$ and $^+CH_3$ is the least stable cation.

Solution

Hyperconjugation interaction in $(CH_3)_3C^+$ is greater than in $CH_3H_2C^+$ as the $(CH_3)_3C^+$ has nine C-H bonds. In $^+CH_3$, vacant p orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus, $^+CH_3$ lacks hyperconjugative stability.

4. Types of Organic Reactions

Organic reactions can be classified into the following categories:

(i) Substitution reactions

(ii) Addition reactions

(iii) Elimination reactions

(iv) Rearrangement reactions

5. Summary

- Mechanism of any organic reaction is based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents, the electron displacement effects and the conditions of the reaction.

- Organic reactions involve breaking and making of covalent bonds. A covalent bond can be cleaved in heterolytically or homolytically. Heterolytic fission of a covalent bond in organic molecule generates either carbocation or carbanion and the homolytic fission generates radical.

- Carbocations, carbanions, and radicals are known as reactive intermediates. Reactive intermediates are formed during the course of any organic reactions. They are very unstable.

- The electronic displacement in organic molecules may take place under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. Inductive effect, resonance effect and electromeric effect are examples of electron displacements.

- The inductive, resonance, electromeric and hyperconjugation effects may help in the polarisation of a bond making certain carbon atom or other atom positions as places of low or high electron densities.

- Organic reactions can be broadly classified into following types; substitution, addition, elimination and rearrangement reactions.