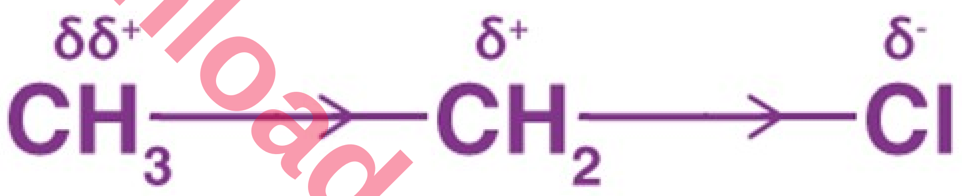
Course: Chemistry-III (6458)
Semester: Autumn, 2021

ASSIGNMENT No. 1

Q. 1 what is meant by inductive effect? Discuss different types of inductive effect?

Inductive Effect refers to the phenomenon wherein a permanent dipole arises in a given molecule due to the unequal sharing of the bonding electrons in the molecule. This effect can arise in sigma bonds, whereas the electromeric effect can only arise in pi bonds.

When an electron-releasing or an electron-withdrawing species is introduced to a chain of atoms (generally a carbon chain), the corresponding negative or positive charge is relayed through the carbon chain by the atoms belonging to it. This causes a permanent dipole to arise in the molecule and is referred to as the inductive effect.

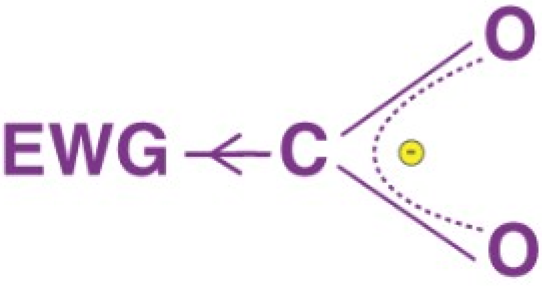


An illustration describing the inductive effect that arises in a chloroethane molecule due to the more electronegative chlorine atom is provided above.

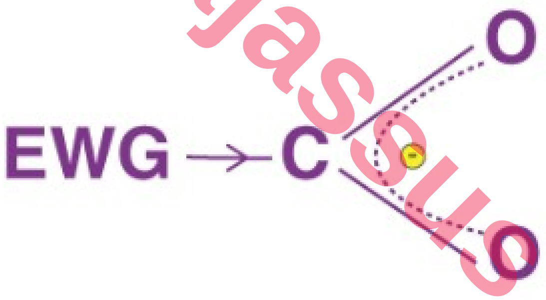
Using the inductive effect, we can predict the acidity and basicity of compounds. As a generalisation, it may be said that the electron-withdrawing groups (EWG) increase the acidity of a compound and electron-donating group decrease the acidity of a compound.

This is because, if we take the conjugate base of the acid, that is, RCOO-, if R is electron-withdrawing, then the conjugate base is stabilised via delocalisation of the formed negative charge.

If R had been electron-donating, then the conjugate base would be destabilised because of inter-electronic repulsions.



EWG stabilises the (COO) and increases the acidity

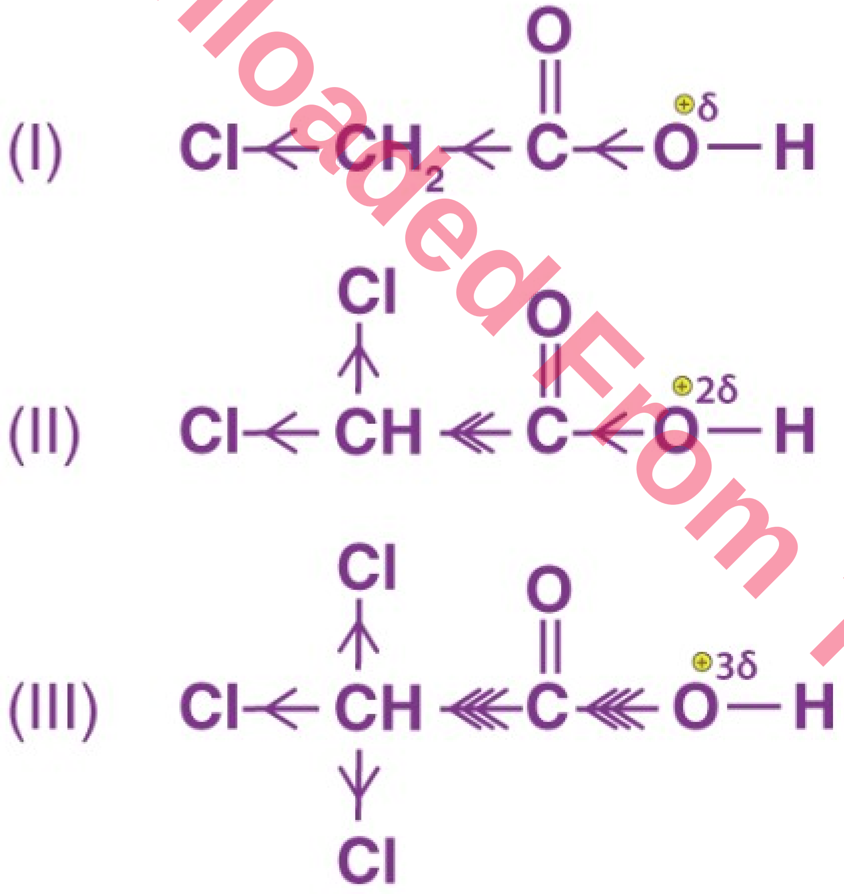


EDG stabilises the (COO) and decreases the acidity

Thus, it can be said that, +I groups decrease acidity (or increase basicity) and –I groups increase acidity (or decrease basicity) of compounds.

For Example, formic acid (HCOOH) is more acidic than acetic acid (CH3COOH) due to the +I inductive effect of the methyl group attached to the carboxylic acid group.

If Ka of acid is high, it is a strong acid, but if PKa of acid is high, it is said to be a weak acid [pka = -log(ka)] Same logic applies to bases. Consider, the acidity of mono-, di- and trichloroacetic acid.



It can be said that the presence of three Cl atoms make oxygen highly electron deficient and thereby, polarising the O-H bond the most. Therefore, the acidity order for the above compounds would be, III > II > I.

Types of Inductive Effect

- Negative inductive effect or -I effect
- Positive inductive effect +I effect

-I Effect (Negative Inductive Effect)

When an electronegative atom, such as a halogen, is introduced to a chain of atoms (generally carbon atoms), the resulting unequal sharing of electrons generates a positive charge which is transmitted through the chain.

This causes a permanent dipole to arise in the molecule wherein the electronegative atom holds a negative charge and the corresponding effect is called the electron-withdrawing inductive effect, or the -I effect.

+I Effect (Positive Inductive Effect)

When a chemical species with the tendency to release or donate electrons, such as an alkyl group, is introduced to a carbon chain, the charge is relayed through the chain and this effect is called the Positive Inductive Effect or the +I Effect

Inductive Effect on Stability of Molecules

The charge on a given atom and the charge on a group bonded to the atom play a strong part when determining the stability of the resulting molecule as per the inductive effect.

An example of this can be observed when a group displaying the -I effect is bonded to a positively charged atom and the positive charge on the resulting molecule is amplified, reducing its stability.

On the other hand, when a negatively charged atom is introduced to a group displaying a -I effect, the charge disparity is somewhat quenched and the resulting molecule would be stable as per the inductive effect.

Also,

When a group displaying the -I effect is bonded to a molecule, the electron density of the resulting molecule effectively reduces, making it more likely to accept electrons and thereby increasing the acidity of the molecule.

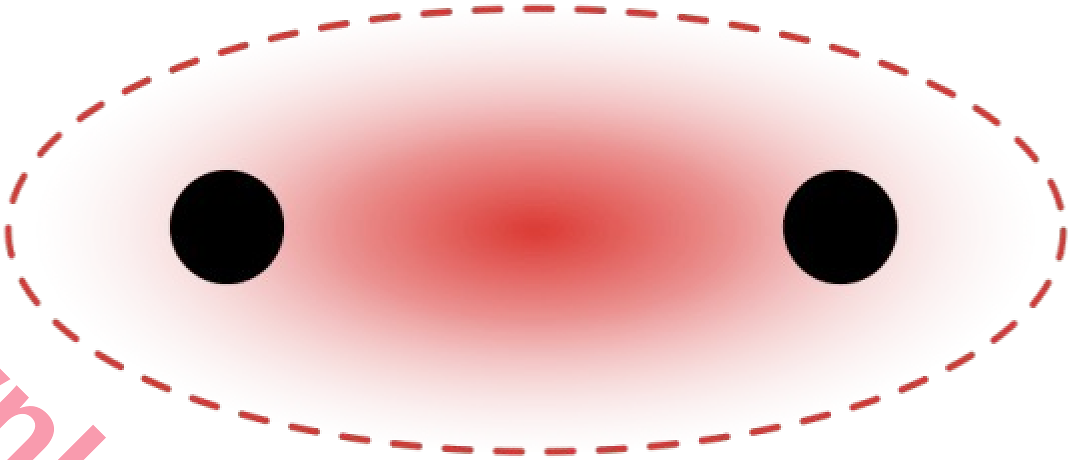
When a +I group attaches itself to a molecule, there is an increase in the electron density of the molecule. This increases the basicity of the molecule since it is now more capable of donating electrons.

Q. 2 Explain Delocalized Chemical bonding with the help of suitable examples.

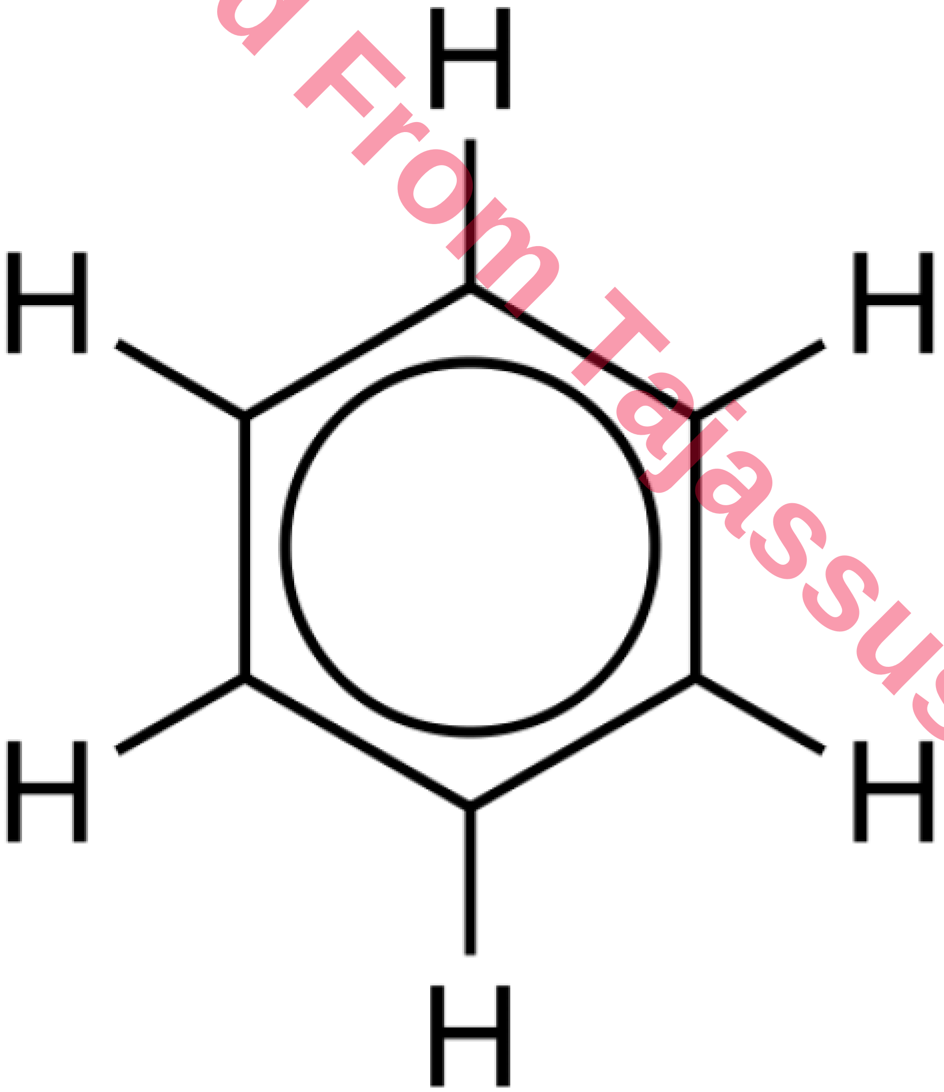
The **key difference** between localised and delocalised chemical bonds is **that localised chemical bond is a specific bond or a lone electron pair on a specific atom whereas delocalised chemical bond is a specific bond that is not associated with a single atom or a covalent bond.**

A chemical bond is a connection between two atoms. This connection occurs due to the overlapping of molecular orbitals. There are two major forms of bonds as localised and delocalised chemical bonds. Localised chemical bonds are the normal molecular orbital overlappings such as sigma bonds and pi bonds. However, delocalised chemical bonds are different.

Localised chemical bonds are normal sigma and pi bonds or lone electron pairs that exist on a single atom. These bonds are concentrated on a limited region of a molecule. These regions have a concentrated electron distribution. In other words, the electron density of this region is very high.



Delocalised chemical bonds are the chemical bonds that do not associate with only a single atom but with several atoms or other chemical bonds. We call the electrons in these bonds as ‘delocalised electrons’. Delocalization occurs in the conjugated pi system. A conjugated pi system has double bonds and single bonds in an alternating pattern.



For example, the benzene ring has three single bonds and three double bonds in an alternating pattern. Each carbon atom in this ring has a p orbital that does not undergo frontal overlapping. Therefore these p orbitals can have side overlapping. This kind of overlapping is the delocalization. We can indicate this as two circles on the top of the benzene ring and the bottom of the ring. These electrons are free to move throughout the molecule because they do not have a permanent binding to a single atom or a covalent bond.

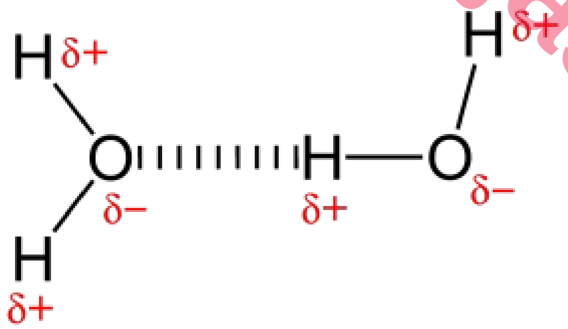
Localised chemical bonds are normal sigma and pi bonds or lone electron pairs that exists on a single atom. These bonds form due to frontal overlapping between s orbitals, p orbitals or s and p orbitals. Moreover, these electrons are limited to a particular region between two separate atoms. Delocalised chemical bonds are the chemical bonds that do not associate with only a single atom but with several atoms or other chemical bonds. These bonds have electrons spread throughout the molecule that are free to move. These bonds form due to side overlapping of p orbitals. This is the main difference between localised and delocalised chemical bonds.

A chemical bond is a connection between two atoms. There are two forms of chemical bonds as localised and delocalised chemical bonds. The difference between localised and delocalised chemical bonds is that a localised chemical bond is a specific bond or a lone electron pair on a specific atom whereas a delocalised chemical bond is a specific bond that is not associated with a single atom or a covalent bond.

Q. 3 Define Hydrogen bonding. Explain the significance and properties of Hydrogen Bonds.

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.



Hydrogen Bonding

Hydrogen bonding is important in many chemical processes. Hydrogen bonding is responsible for water's unique solvent capabilities. Hydrogen bonds hold complementary strands of DNA together, and they are responsible for determining the three-dimensional structure of folded proteins including enzymes and antibodies.

An Example: Water

A simple way to explain hydrogen bonds is with water. The water molecule consists of two hydrogens covalently bound to an oxygen. Since oxygen is more electronegative than hydrogen, oxygen pulls the shared electrons more closely to itself. This gives the oxygen atom a slightly more negative charge than either of the hydrogen atoms. This imbalance is called a dipole, causing the water molecule to have a positive and negative side, almost like a tiny magnet. Water molecules align so the hydrogen on one molecule will face the oxygen on another molecule. This gives water a greater viscosity and also allows water to dissolve other molecules that have either a slightly positive or negative charge.

Protein Folding

Protein structure is partially determined by hydrogen bonding. Hydrogen bonds can occur between a hydrogen on an amine and an electronegative element, such as oxygen on another residue. As a protein folds into place, a series of hydrogen bond "zips" the molecule together, holding it in a specific three-dimensional form that gives the protein its particular function.

DNA

Hydrogen bonds hold complementary strands of DNA together. Nucleotides pair precisely based on the position of available hydrogen bond donors (available, slightly positive hydrogens) and hydrogen bond acceptors (electronegative oxygens). The nucleotide thymine has one donor and one acceptor site that pairs perfectly with the nucleotide adenine's complementary acceptor and donor site. Cytosine pairs perfectly with guanine through three hydrogen bonds.

Antibodies

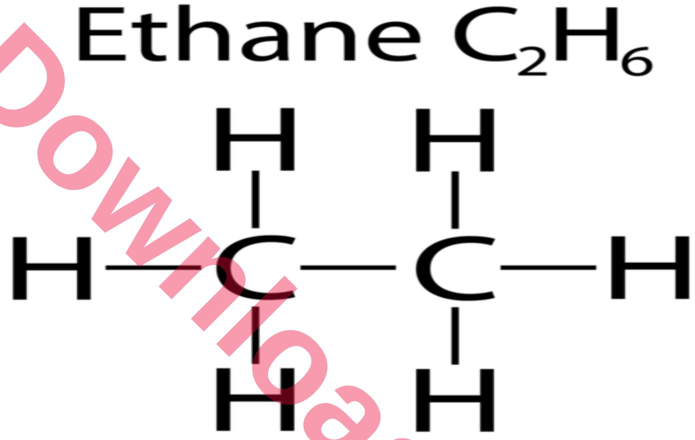
Antibodies are folded protein structures that precisely target and fit a specific antigen. Once the antibody is produced and attains its three-dimensional shape (aided by hydrogen bonding), the antibody will conform like a key in a lock to its specific antigen. The antibody will lock onto the antigen through a series of interactions including hydrogen bonds. The human body has the capacity to produce over ten billion different types of antibodies in an immunity reaction.

Chelation

While individual hydrogen bonds are not very strong, a series of hydrogen bonds is very secure. When one molecule hydrogen bonds through two or more sites with another molecule, a ring structure known as a chelate is formed. Chelating compounds are useful for removing or mobilizing molecules and atoms such as metals.

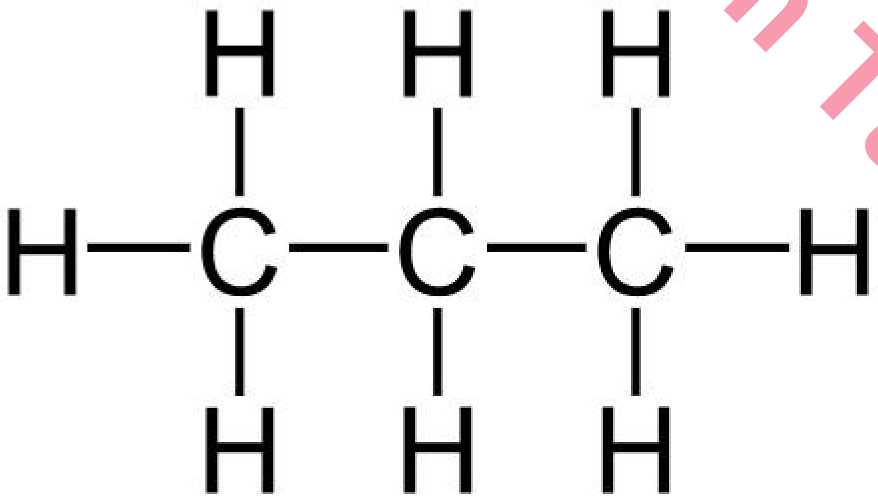
Q. 4 enlist the chemical properties of alkanes and discuss the reactions of alkanes.

Saturated hydrocarbons are hydrocarbons that contain only single bonds between carbon atoms. They are the simplest class of hydrocarbons. They are called saturated because each carbon atom is bonded to as many hydrogen atoms as possible. In other words, the carbon atoms are saturated with hydrogen. You can see an example of a saturated hydrocarbon in the **Figure** below. In this compound, named ethane, each carbon atom is bonded to three hydrogen atoms. In the structural formula, each dash (-) represents a single covalent bond, in which two atoms share one pair of valence electrons.



A Saturated hydrocarbon is a hydrocarbon in which all the carbon-carbon bonds are single bonds. A hydrocarbon is an organic compound whose only constituents are carbon and hydrogen. As the name suggests, saturated hydrocarbons are hydrocarbons in which all the carbon atoms are bonded to four other atoms and are 'saturated', implying that no carbon-carbon multiple bonds exist in these organic compounds.

Generally, the term 'saturated hydrocarbon' is used to refer to alkanes – acyclic hydrocarbons containing only sp^3 hybridized carbon atoms. The general formula of an alkane is C_nH_{2n+2}. An illustration describing the structure of a propane molecule (C_3H_8) is provided below.



It can be observed that a propane molecule is 'saturated' with hydrogen atoms and cannot accommodate any more in the parent chain. A few other examples of saturated hydrocarbons are listed below.

- Butane (C_4H_{10})
- Octane (C_8H_{18})
- Cyclohexane (C_6H_{12})
- Cyclopropane (C_3H_6)

Cycloalkanes are the alkanes that have a monocyclic ring structure. Since all the carbon-carbon bonds in cycloalkanes are single bonds, they are considered to be saturated hydrocarbons. Therefore, the general formula of a saturated hydrocarbon can be written as $C_nH_{(2n+2-2r)}$, where 'r' is the total number of rings in the molecule.

The names of all alkanes end with -ane. Whether or not the carbons are linked together end-to-end in a ring (called cyclic alkanes or cycloalkanes) or whether they contain side chains and branches, the name of every carbon-hydrogen chain that lacks any double bonds or functional groups will end with the suffix -ane.

Alkanes with unbranched carbon chains are simply named by the number of carbons in the chain. The first four members of the series (in terms of number of carbon atoms) are named as follows:

1. CH_4 = **methane** = one hydrogen-saturated carbon
2. C_2H_6 = **ethane** = two hydrogen-saturated carbons
3. C_3H_8 = **propane** = three hydrogen-saturated carbons
4. C_4H_{10} = **butane** = four hydrogen-saturated carbons

Alkanes with five or more carbon atoms are named by adding the suffix -ane to the appropriate numerical multiplier, except the terminal -a is removed from the basic numerical term. Hence, C_5H_{12} is called pentane, C_6H_{14} is called hexane, C_7H_{16} is called heptane and so forth.

Straight-chain alkanes are sometimes indicated by the prefix n- (for normal) to distinguish them from branched-chain alkanes having the same number of carbon atoms. Although this is not strictly necessary, the usage is still common in cases where there is an important difference in properties between the straight-chain and branched-chain isomers: e.g. n-hexane is a neurotoxin while its branched-chain isomers are not.

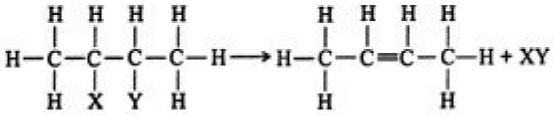
The same concept can be applied to any of the straight chain alkane names provided in the table above.

Name	**Molecular Formula**	**Condensed Structural Formula**
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$

Name	Molecular Formula	Condensed Structural Formula
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

Q. 5 discuss the use of alkenes in preparation of polymers and industry product.

Alkenes are generally prepared through β elimination reactions, in which two atoms on adjacent carbon atoms are removed, resulting in the formation of a double bond.



Preparations include the dehydration of alcohols, the dehydrohalogenation of alkyl halides, and the dehalogenation of alkanes.

Dehydration of alcohols. In dehydration reactions, a molecule of water is eliminated from an alcohol molecule by heating the alcohol in the presence of a strong mineral acid. A double bond forms between the adjacent carbon atoms that lost the hydrogen ion and hydroxide group.

$$\mathrm{CH_3CH_2CH_2\ddot{O}H + H_2SO_4 \xrightarrow{heat} CH_3CH{=}CH_2 + H_2O}$$

The mechanism of this dehydration reaction consists of the following steps.

1. Protonation of the alcohol.

$$\mathrm{CH_3CH_2CH_2\overset{H}{\ddot{O}}H \longrightarrow CH_3CH_2\overset{+}{C}H_2 + H_2O}$$

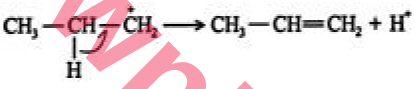
This step is a simple acid-base reaction, which results in the formation of an **oxonium ion**, a positively charged oxygen atom.

2. Dissociation of the oxonium ion.

$CH_3CH_2CH_2\overset{H}{\ddot{O}}H \longrightarrow CH_3CH_2\overset{+}{C}H_2 + H_2O$

Dissociation of the oxonium ion produces a **carbocation**, which is a positively charged carbon atom and an unstable intermediate.

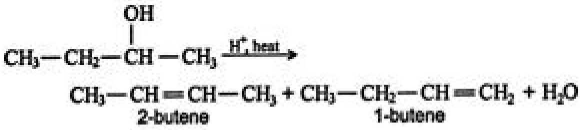
3. Deprotonation of the carbocation.



$CH_3-\underset{H}{CH}-\overset{+}{C}H_2 \longrightarrow CH_3-CH{=}CH_2 + H^+$

The positively charged end carbon of the carbocation attracts the electrons in the overlap region that bond it to the adjacent a carbon. This electron movement makes the α carbon slightly positive, which in turn attracts the electrons in the overlap regions of all other atoms bonded to it. This results in the hydrogen on the α carbon becoming very slightly acidic and capable of being removed as a proton in an acid-base reaction.

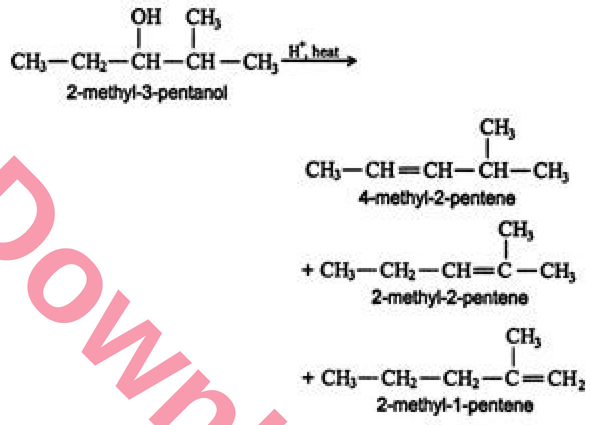
Zaitsev rule. It may be possible in some instances to create a double bond through an alcohol dehydration reaction in which hydrogen atoms are lost from two different carbons on the carbocation. The major product is always the more highly substituted alkene, that is, the alkene with the greater number of substituents on the carbon atoms of the double bond, an observation called the Zaitsev rule. Thus, in the dehydration reaction of 2-butanol, the following products are formed.



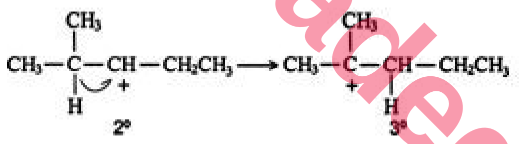
$CH_3-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow{H^+,\ heat} \underset{\text{2-butene}}{CH_3-CH{=}CH-CH_3} + \underset{\text{1-butene}}{CH_3-CH_2-CH{=}CH_2} + H_2O$

The Zaitsev rule predicts that the major product is 2-butene. Notice that each carbon atom involved in the double bond of 2-butene has one methyl group attached to it. In the case of 1-butene, one carbon atom of the double bond has one substituent (the ethyl group), while the other carbon atom has no substituents.

Carbocation rearrangement. The carbocation in an alcohol dehydration may undergo **rearrangement** to form more stable arrangements. Dehydration of 2-methyl-3-pentanol, for example, leads to the production of three alkenes. The mechanism for the reaction shows that the extra compound formation is due to rearrangement of the carbocation intermediate.



The 2-methyl-1-pentene molecule is formed via rearrangement of the intermediate carbocation.

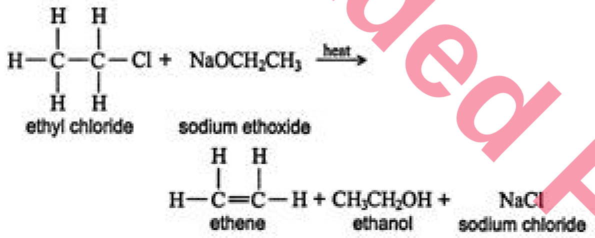


The movement of a hydride ion (H: $^{-}$) leads to the formation of a more stable carbocation. Carbocations are classified as primary, secondary, and tertiary, as are the carbon atoms. **A primary carbocation** has one alkyl group attached to it; a **secondary carbocation** is bonded to two alkyl groups; and a **tertiary carbocation** has three alkyl groups around it.

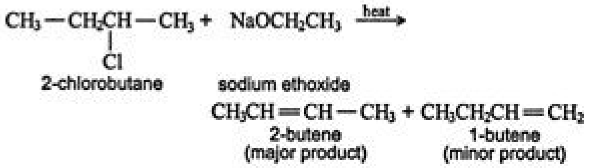
Alkyl groups theoretically have the ability to “push” electrons away from themselves. This phenomenon is called the **inductive effect.** The greater the number of alkyl groups “pushing” electrons toward a positively charged carbon atom, the more stable the intermediate carbocation will be. This increase in stability is due to the delocalization of charge density. A charge on an atom creates a stress on that atom. The more the stress is spread over the molecule, the smaller the charge density becomes on any one atom, reducing the stress. This lessening of stress makes the ion more stable. Thus, tertiary carbocations, with three alkyl groups on which to delocalize the positive charge, are more stable than secondary carbocations, which have only two alkyl groups on which to delocalize the positive charge. For the same reason, secondary carbocations are more stable than primary carbocations.

In reality, alkyl groups do not “push” electrons away from themselves, but rather they have electrons removed from them. When an atom picks up a positive charge and becomes an ion, its electronegativity changes. In the original σ bond between two carbon atoms, the location of the overlap region relative to each carbon atom is fixed in part by the electronegativity of the two atoms. With an increase in the electronegativity of one of the carbon atoms due to ion formation, the overlap region shifts closer to the more electronegative, positively charged carbon atom. This rearrangement of electron density produces a partial positive charge on the neighboring carbon. The amount of charge gained by the second carbon corresponds to the amount lost by the fully charged carbon atom. In this manner, the charge becomes delocalized over the two carbons.

Dehydrohalogenation of alkyl halides. The **dehydrohalogenation of alkyl halides**, another β elimination reaction, involves the loss of a hydrogen and a halide from an alkyl halide (RX). Dehydrohalogenation is normally accomplished by reacting the alkyl halide with a strong base, such as sodium ethoxide.

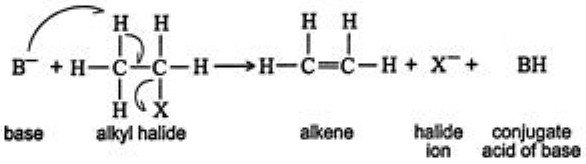


This reaction also follows the Zaitsev rule, so in the reaction of 2-chlorobutane with sodium ethoxide, the major product is 2-butene.



Dehydrohalogenation reactions proceed via the following mechanism.

1. A strong base removes a slightly acidic hydrogen proton from the alkyl halide via an acid-base reaction.
2. The electrons from the broken hydrogen-carbon bond are attracted toward the slightly positive carbon atom attached to the chlorine atom. As these electrons approach the second carbon, the halogen atom breaks free, leading to the formation of the double bond. The diagram below summarizes this mechanism.



Dehalogenation. Vicinal dihalides, which are alkane molecules that contain two halogen atoms on adjacent carbon atoms, can form alkenes upon reaction with zinc.