13.7 Preliminary Idea of Reaction Mechanism

Learning outcomes

After the lesson, the students will be able to:

Give a preliminary idea of reaction mechanism (homolytic and heterolytic fission, electrophiles, nucleophiles, and free radicals, inductive effect: +I and –I effect, resonance effect: +R and –R effect, steric hindrance).

Introduction

Organic reactions are generally complex and occur in multiple steps. Therefore, a detailed study of each step is required to understand a chemical reaction. The reaction mechanism is a thorough study of each step of a reaction, with special attention to the reactants, products, intermediates, energy changes involved, and rates of each step.

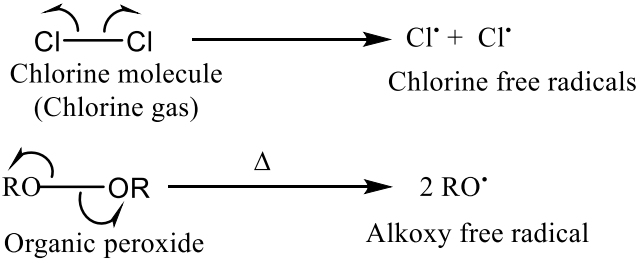
Some fundamental knowledge necessary to study the reaction mechanisms is discussed here.

Concept of Bond Breaking/ Cleavage/ Fission

During a chemical reaction, existing chemical bonds break and new bonds form. Organic compounds have covalent bonds. Hence, organic reactions involve the breaking of existing bonds and the formation of new covalent bonds. A covalent bond undergoes cleavage in either of the following two ways.

1. **Homolysis (**Homolytic bond fission/ Symmetrical or non-polar bond cleavage)

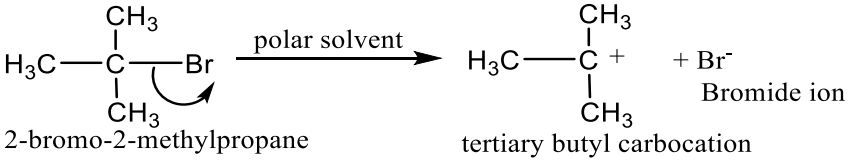
It is the breaking of bonds with an equal distribution of bonding electrons among bonding atoms. It generally takes place when bonding elements **have nearly equal electronegativities**. Typically, it takes place **in the gas phase** in the presence of **heat or sunlight.** e.g.,



This leads to the formation **of free radicals**.

2. **Heterolysis** (Heterolytic bond fission/Unsymmetrical or polar bond fission)

It is the breaking of bonds where one of the bonding atoms takes both the electrons, and the other gets none. It generally takes place when bonding elements have a large **difference in electronegativities**. It generally takes place **in polar solvents**.



Heterolysis leads to the formation **of cations and anions**.

Types of Reagents

Generally, reactants of organic reactions involve two species: the main organic molecule called the substrate and a species that attacks the substrate, called the reagent or attacking species.

Nucleophile (Greek: Nucleo = Nucleus; phile = loving)

Atom or groups of atoms that are **electron-rich species** that attack electron-deficient centres.

Nucleophiles can be negatively charged ions like OH^-, CN^-, I^-, OR^- or neutral molecules with **lone pairs of electrons** like H_2O, NH_3, ROH, ROR, RNH_2 etc.

Electrophile (Greek: Electro = Electron; phile = loving)

Atoms or group of atoms that are **electron-deficient species** that attack electron-rich centres.

Electrophiles may be **positively charged ions** like H^+, Cl^+, Br^+, NO_2^+, R^+ etc. **or neutral electron deficient** species like BF_3, $AlCl_3$, $FeCl_3$, CO_2, SO_3 etc.

1. **Define electrophile and nucleophile with one example each. 2**
2. **How is an electrophile different from a nucleophile? Give a suitable example of both. 2**
3. **Distinguish between electrophile and nucleophile with an example of each.**
4. **How is an electrophile different from a nucleophile? Give an example of each.**
5. **What is meant by electrophile? Write suitable examples of it. 2**
6. **Define nucleophiles, giving examples. 2**

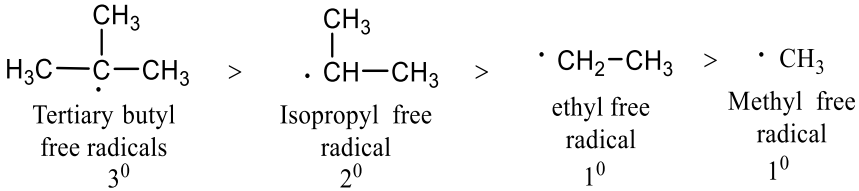
Reaction Intermediates

Free radicals

A free radical is an atom or group of atoms with an odd or **unpaired electron**. These are short-lived and very reactive reaction intermediates with no net charge. The extreme reactivity of the free radicals is due to the tendency of the unpaired electron to get paired. These are a result of homolysis. e.g.

$\dot{C}H_3$ methyl free radical $\dot{Cl}$ chloride free radicals $CH_3C\dot{O}O$ Alkanoate free radical

The relative stabilities of different degrees of alkyl free radicals are:



Electronic Transitions in the covalent bonds (Organic Effects)

Inductive effect (I effect)

When two atoms having different electronegativities are linked together by a covalent bond, the electron pair shifts towards the more electronegative atom resulting in a certain degree of polarity in the bond. When a carbon atom is bonded to a hydrogen atom or another carbon atom by a covalent bond as in alkane, the sharing of electron pairs is symmetrical between them, and the bond is non-polar.

Thus, the polarity produced in a molecule due to the higher electronegativity of one atom compared to another is called an inductive effect. This type of polarity migrates in the carbon chain. It is indicated as arrows in the direction of electron displacement. This type of polarity migrates in the carbon chain. It is relayed up to the third or fourth carbon atom and fades afterwards.

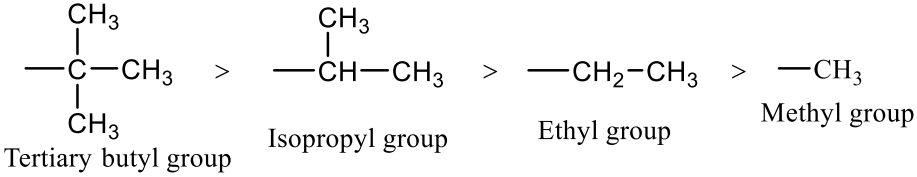
$$C \text{——} C \text{——} C \rightarrow Cl^{\delta-}$$

Depending on the nature of groups attached to a C chain, the following two inductive effects are observed.

[A] Positive Inductive effect (+I effect):

If the group attached to C- atom pulls the bonded electrons to a lesser extent than an H atom, the C atom gets a partial negative charge; the group gets a partial positive charge. Such an inductive effect is called a positive inductive effect. Such groups are called electron-releasing groups. E.g., $-CH_3$, $-COO^-$, $-CH_2R$, $-CHR_2$, $-CR_3$ etc.

The + I effect of the different alkyl groups is in the following order.



Tertiary butyl group | Isopropyl group | Ethyl group | Methyl group

[B] Negative Inductive effect (-I effect)

If a group attached to the carbon atom pulls the electrons to a more extent than an H – atom, the bond pair of electrons are displaced towards the group. Such groups get a partial negative charge; the carbon atom gets a partial positive charge. Such an inductive effect is called a negative inductive effect. Such groups are called electron-withdrawing groups. e.g., $-NO_2$, -CN, -COOH etc.

These groups are arranged in the increasing order of their –I effect as:

$-NO_2$ > -CN > -COOH > -F > -Cl > -Br > -I etc.

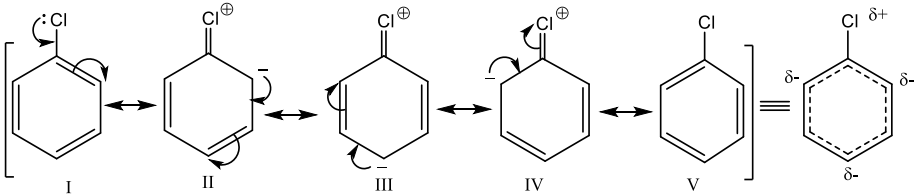
Resonance effect (R-effect)

The phenomenon where a molecule or ion couldn't be represented by a single structure but rather should be represented by more than one structure to justify its properties is called resonance.

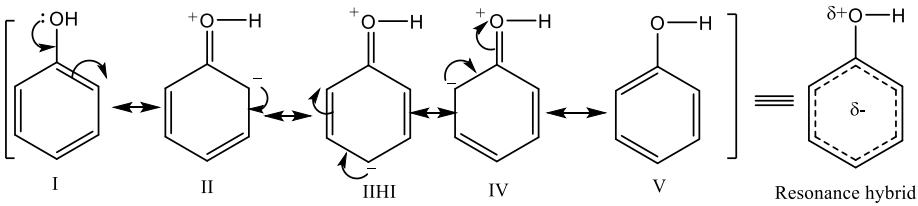
Such structures are called resonance structures and the actual structure is considered a resonance hybrid.

The increase or decrease in electron density in some parts of a molecule due to the existence of resonance is called the resonance effect. The resonance effect can also be positive or negative.

-R effect of aryl group (phenyl group) in Chlorobenzene:

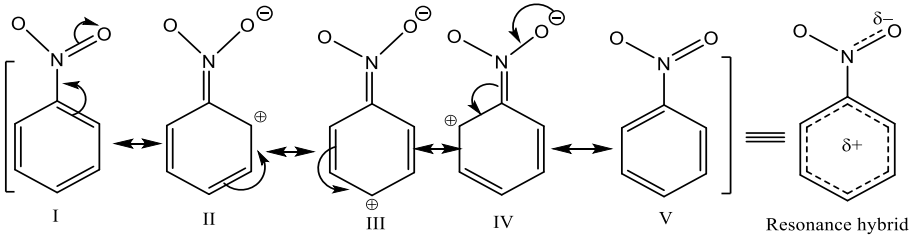


-R effect of aryl group (phenyl group) in Phenol:



Resonating structures of phenol

+ R effect of aryl (phenyl) group in nitrobenzene



Resonating structures of Nitrobenzene

7. What is meant by inductive effect? Give its one application. 2

8. Write a short note on the inductive effect. 5

1. Homolytic bond fission results in the formation of
   a. Carbocations c. Carbanion
   b. Free radicals d. Nitrenes
2. Homolytic fission of carbon to carbon covalent bond gives
   a. Carbocations c. Carbanions
   b. Ion radicals d. Free radicals
3. Heterolytic fission of carbon to carbon bond gives
   a. Free radicals c. Charged species
   b. Neutral species c. None of these
4. Which of the following statements is true regarding nucleophiles?
   a. They have an unpaired electron.
   b. They have a lone pair of electrons.
   c. They have empty orbitals.
   d. They have an overall positive charge.
5. Which of the following is a nucleophile?
   a. $AlCl_3$ b. NH_3 c. Br^+ d. NO_2^+
6. Which of the following is not a nucleophile?
   a. OH^- b. NH_2^- c. BF_3 d. NH_3

7. Which of the following can act as a nucleophile?
   a. BF_3 b. $FeCl_3$ c. $ZnCl_2$ d. C_2H_5MgBr
8. Which of the following is not a nucleophile?
   a. H_2O b. CH_3OH c. H_2 d. NH_3
9. Which of the following is an electrophile?
   a. NH_3 b. H_2O c. CN^- d. SO_3
10. Which of the following is an electrophile?
   a. Cl^- b. H_2O c. BF_3 d. ROH
11. Which of the following is not an electrophile?
   a. H_3O^+ b. CN^- c. $AlCl_3$ d. Br^-
12. Which of the following statements is not true?
   a. Free radicals are electron-deficient.
   b. Free radicals are the result of homolytic fission.
   c. Free radicals carry a positive charge.
   d. Free radicals have sp^2 hybridization.
13. The presence of chlorine in an organic compound causes
   a. -I effect b. + I effect c. Resonance d. None of them
14. Which of the following groups exert the +I effect?
   a. $-CH_3$ b. –Cl c. –COOH d. $-NO_2$
15. Transfer of electrons in multiple bonds in the presence of an attacking reagent is
   a. Electromeric effect c. Hyperconjugation
   b. Inductive effect d. Resonance

*** This note is insufficient. It is to guide you. Study the prescribed textbooks too. ***