Chapter 2

Reaction Mechanism

Day – 1

Reaction Mechanism

A **mechanism** for a reaction is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reaction proceeds.

A mechanism is a proposal from which you can work out a rate law that agrees with the observed rate laws. The fact that a mechanism explains the experimental results is not a proof that the mechanism is correct. A mechanism is our rationalization of a chemical reaction, and devising mechanism is an excellent academic exercise in itself.

Basic Definitions:-

1° Carbon → Carbon	attached to	only	one	Carbon
2° Carbon → Carbon	attached to	only	two	Carbon
3° Carbon → Carbon	attached to	only	three	Carbon
4° Carbon → Carbon	attached to	only	four	Carbon
1° Hydrogen → Hydrogen	attached to	only	1°	Carbon
2° Hydrogen → Hydrogen	attached to	only	2°	Carbon
3° Hydrogen → Hydrogen	attached to	only	3°	Carbon

In CH_4 the C is called super 1°

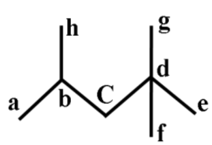
Some other common terms

Conjugated double bond **Isolated double bond** **Cummulated double bond**

($CH_2 = CH$ –) Vinylic

($CH_2 = CH – CH_2$ –) Allylic

Example 1:-



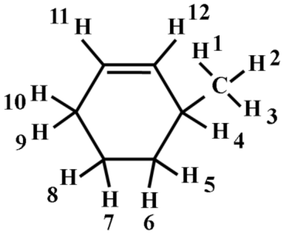
1°C → a, e, f, g, h

2°C → c

3°C → b

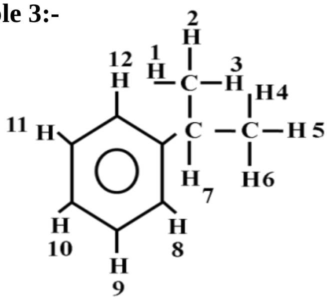
4°C → d

Example 2:-



$1°$Hyd → 1, 2, 3
$2°$Hyd → 5, 6, 7, 8
$3°$Allylic → 4
$2°$Allylic → 9, 10
$2°$Vinylic → 11, 12

Example 3:-



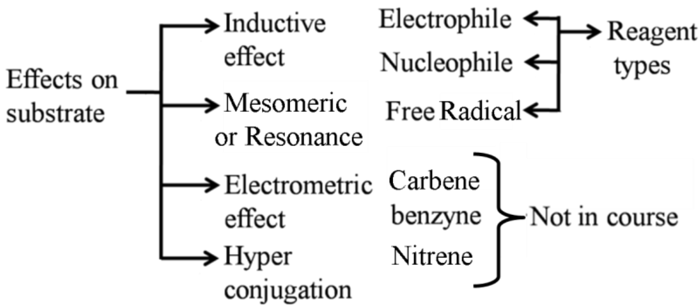
1^o HYd → 1,2,3,4,5,6
3^o Benzylic → 7
Phenylic → 8, 9, 10, 11, 12

Introduction

A chemical equation is a symbolic representation of a chemical. Reaction it indicates the initial reactants and final products involved in a change. Reactants generally consist of two species:

$$\text{Substrate} + \text{Reagent} \rightarrow \text{Product}$$

1. One which is being attacked; it is called a substrate.
2. Other which attacks the substrate; it is referred to as a reagent. These two interact to form products.



Types of Reagents

Reagents are attacking species and are created by breaking of covalent bonds.

A covalent bond can get cleaved either by:-

(i)Heterolytic Cleavage

(ii) Homolytic Cleavage

(i):- heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with the more electronegative atom . After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a

$$H_3C-Br \longrightarrow H_3\overset{+}{C} + Br^{-}$$

negative charge. Thus, heterolytic cleavage of bromomethane will happen as follows as shown below.

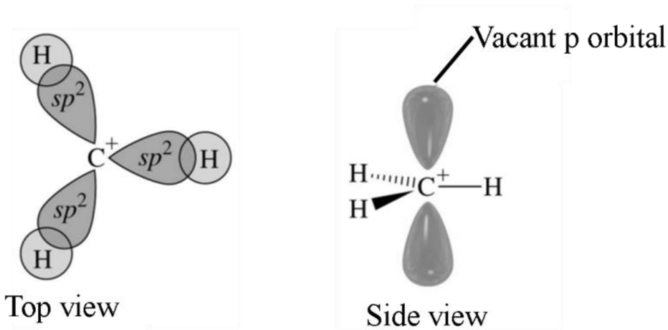
Carbocations

A species having a carbon atom possessing positive charge is called a carbocation (earlier called Carbonium ion). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilize the carbocations due to inductive and hyperconjugations effects.

The observed order of carbocation stability is:-

benzylic ~ 3° > Allylic ~ 2° > 1° > $CH_3^+ > Vinylic$

These carbocations have trigonal planar shape with positively charged carbon being *sp*^{2} hybridised. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons.



Carbanions

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. Such a carbon species carrying a negative charge on carbon atom is called *carbanion.* Carbanions are also unstable and reactive species. The carbanion exists in a sp3 hybridisation and trigonal pyramidal geometry.

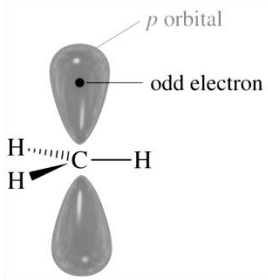
The observed order of carbanion stability is: $\mathbf{CH_3^-}$ **> 1° > 2° > 3°**

(ii) In **Homolytic** cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' 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. A homolytic cleavage can be shown as:-

$$R-X \xrightarrow{\text{Heat or Light}} \underset{\substack{\text{Alkyl}\\\text{Free radical}}}{\dot{R}} + \dot{X}$$

Carbon free radicals are also Sp_2 hybridized as shown in figure.

The observed order of free radical stability is: **Benzylic ~ Allylic > 3° > 2° > 1° > CH_3**



Nucleophiles and Electrophiles

A reagent that has an electron pair is called a nucleophile (Nu:) i.e., nucleus seeking and the reaction is then called nucleophilic. A reagent that takes away an electron pair is called electrophile (E^+) i.e., electron seeking and the reaction is called electrophilic.

During a polar organic reaction, a nucleophile attacks an electron deficient (relatively positive charge) centre of the substrate. Nucleophile may be neutral or negatively charge. All nucleophiles are Lewis base. Similarly, the electrophiles attack electron rich centre of the substrate. Electrophile may be neutral or positively charged. All electrophile are Lewis acids.

Examples of electrophiles:-

Electrophilic (Lewis Acids)		Nucleophile (Lewis Base)	
+ ve Change	Neutral	– ve change	neutral
H^+ (H_3O^+) l^+, Br^+, NO_2^+, RCH_2^+, NO^+	SO_3, BF_3 $AlCl_3$, $ZnCl_2$ $Becl_2$ $Fecl_3$ RMgX,	Cl^-, Br^-, I^- H^-, RNH^- OH^-, CN^-, N_3^- HSO_3^-, RCO^-	NH_3, RNH_2 ROH, ROR R_2NH, R_3N RMgX, RCL $LiAlH_4$

(D) Electron Displacement in Substance

(i) 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.

$$\underset{2}{\overset{\delta\delta^+}{CH_3}} \longrightarrow \underset{1}{\overset{\delta^+}{CH_2}} \longrightarrow \overset{\delta^-}{Cl}$$

Let us consider cholorethane (CH_2CH_2CL) in which the C-Cl bond is a polar covalent bond. It is polarized 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 point 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 $\delta\delta^+$ symbolizes 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 polarization of σ-bond caused by the polarization of adjacent σ-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 electro density to the attached carbon atom. Based on this ability, the substituents can be classified as electron-withdrawing or electron group relative to hydrogen. Halogens and many other groups such as nitro ($-NO_2$), cyano (-CN), carboxy (-COOH), ester (-COOR), aryloxy (-OAr, e.g. $-OC_6H_5$), etc. are electron-withdrawing group. On the other hand, the alkyl groups like methyl ($-CH_3$) and ethyl ($-CH_2-CH_3$) are usually considered as electron donating groups.

Strength of Various Atom and Groups

– I effect

$NO_2 > CN > F > COOH > CL > Br > I > OCH_3 > OH > C_6H_5$

+ I effect

$(CH_3)_2\,C > (CH_3)_3 > CH_3CH_2 > CH_3\ H$

Resonance

(1):- Whenever a molecule can be represented by two or more structure that are different only in arrangement of electrons – i.e. they have some arrangement of atoms (both structural and stereo) there is Resonance

(2):- When these structures are of about same stability (i.e. have same energy content), then resonance is important.

(3):- The actual molecular is a hybrid of all these structures and cannot be satisfactorily explained by any are of them. Each structure contributes to the hybrid.

(4):- The actual structure cannot be drawn as per Lewis structure and the lewis structures is not actual molecule.

(5):- The resonance hybrid is more stable than any of the contributing structures.

(6):- The contributing structures do not exist at all.

(7):- The contributing structures are called canonical forms.

Example Mule:- Mule is hybrid of Horse and donkey.

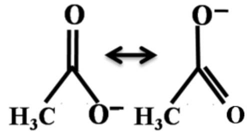
(a):- It does not mean that half mules are harse and other half donkey.

(b):- It also does not mean that some parts (say leg, ear etc) of mule, are of harse and other parts of donkey.

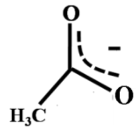
(c):- It sample means that Mule is an animal (Entirely different) which has some characteristics of horse and other of Donkey.

(d):- A Better example is Rhinoceros as a hybrid of Dragon and Unicorn. Because both dragon and Unicorn do not exist.

All contributing Structures of Resonance do not exist at all.

Example in chemistry:- 

Carboxylate ion $RCOO^-$. can be drawn as . The double headed arrow indicates that both structures are resonating structures of each other. The actual structure is neither. In actual structure the C – O bond length is same while in lewis



structure double bond is shorter than single bond like this and the minus charge is de-localised over both the oxygen atoms.