• REACTION MECHANISM •

INTRODUCTION

Application of chemical kinetics in organic chemistry

Chemical Kinetics deals with the speed of a reaction and its mechanism, the stepwise changes in which reactants undergo in there conversion of product.

RATE OF CHEMICAL REACTION

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as **rate of reaction of that species**.

Rate = $\frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec.}} = \text{mol lit}^{-1} \text{ time}^{-1} = \text{mol dm}^{-3} \text{ time}^{-1}$

Rate is always defined in such a manner so that it is always a positive quantity. For a reaction

$$R \longrightarrow P$$

Rate =
$$\frac{\text{Total change in concentration}}{\text{Total time taken}} = \frac{\Delta c}{\Delta t} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

Relation Between the Rate of Reactions of Different Species Taking Part in a Chemical Reaction

We very well know that the rate of reaction of all the species taking part in a chemical reaction are not equal as evident from their stochiometric coefficients. The following example will make it clear

Ex.
$$N_2 + 3H_2 \rightarrow 2NH_3$$

rate of reacton of $N_2 = \frac{-d[N_2]}{dt}$

rate of reaction of
$$H_2 = \frac{-d[H_2]}{dt}$$

rate of reaction of $NH_3 = \frac{d[NH_3]}{dt}$

• From above we can have the following relation between the rate of reactions of different species

$$\frac{-d[N_2]}{dt} = \frac{-1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

The value of above expressions is also written as rate of the given reaction.

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* Remember that "Rate of Reaction" phrase has no meaning if a balanced equation is not given. Hence rate of reaction phrase is always used with a balanced chemical equation,

And for balanced chemical equation as given below, $aA + bB \rightarrow cC + dD$ rate of reaction means

Rate of reaction = $-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$

ORDER OF REACTION

Let there be a reaction $n_1 A + n_2 B \longrightarrow$ products.

Now, if on the basis of experiment, we find that

 $\mathbf{R} \propto [\mathbf{A}]^{\mathbf{p}} [\mathbf{B}]^{\mathbf{q}}$ Where p may or may not be equal to n, and similarly q may or may not be equal to n,.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p+q) is overall order of the reaction.

RATE LAW

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law.

It can only be established by experiments.

Rate ∝ (conc.)order

Rate = k (conc.)order Where k = Rate constant

Note : Value of k is a constant for a given reaction, depends only on temperature.

Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

TRANSITION STATE/ ACTIVATED COMPLEX

State in which partial dissociation and partial formation of bonds takes place is known as transition state. Transition state is unstable and cannot be isolated. Transition state is the highest energy state in a molecular collision that leads to reaction. Transition state must have energy equal to threshold energy.

Reaction profile

Chemical reaction involve the making and breaking of chemical bonds. Since different type of bonds have different bond strengths. The energy of the reacting system change in energy as a function of the progress of the reaction are known as reaction profile or energy diagram.





Elementary Reactions

These reactions take place in single step without formation of any intermediate



An elementary reaction the sum of stoichiometric coefficients is equal to order of the reactions.

Complex Reactions

Reaction which proceed in more than one steps. or having some mechanism. Complex reaction takes places in a sequence of a number of elementary reactions.



For complex reactions order is to be experimentally calculated Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.

MOLECULARITY

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction

 $aA + bB \longrightarrow products$

rate = $k[A]^{a}[B]^{b}$, where a + b = 1, 2 or 3.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning. Comparison between molecularity and order of reaction

Sr. No.	Molecularity of Reaction	Order of Reaction	
1	It is defined as the no. of molecules of reactant taking part in particular step	It is defined as the sum of the power of concentration terms that appear in the law	
2	It is always a whole number. It is can neither be zero nor fractional.	It may be zero, fractional or integer.	
3	It is derived from slowest step in the mechanism of reaction.	It is derived from rate expression.	
4	It is theoretical value.	It is experimental value.	



Activation Energy

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy (E_a) , or energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of E_a can be understood from the following diagram.



- $\Sigma H_{R} =$ Summation of enthalpies of reactants $\Sigma H_{P} =$ Summation of enthalpies of products
- $\Delta H = Enthalpy$ change during the reaction
- $Ea_1 = Energy$ of activation of the forward reaction $Ea_2 = Energy$ of activation of the backward reaction

Progress of reaction (or reaction coordinate) \longrightarrow

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur isknown as threshold energy.

 E_{a} = Threshold energy – Actual average energy

E_a is expressed in kcals mole⁻¹ or kJ mole⁻¹.

Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.

Factors affecting rate of chemical reaction

1. Effect of concentration : It is seen by rate law which is experimental

 $r = k[A]^m [B]^n$

2. Chemical nature of reactants : This is the point of detaled study in organic chemistry

3. Effect of Catalyst : Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.



4. Effect of temperature : rate of reaction is increases with temperature.

Rate determining step

The slowest step of the mechanism known as rate determining step of the reaction.Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction and generally using rate determine step (R.D.S). An organic reaction can be represented as

Reactant (substrate) + Reagent $\xrightarrow{\text{solvent}}$ Product



TYPES OF BOND DISSOCIATION

all reactions are initiated with bond dissociation. There are two types of bond dissociation. (a) HOMOLYTIC BOND DISSOCIATION

A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.

Ex. A–B \longrightarrow A[•] + B[•]

a homolytic bond dissociation generates radicals.

(b) HETROLYTIC BOND DISSOCIATION

A bond dissociation in which a bond pair electron is shifted to one atom only.

Ex., $A-B \longrightarrow A^{\oplus} + B^{\Theta}$

A hetrolytic bond dissociation always generate a cation and an anion.

TYPES OF REAGENTS

A reagent generates three type of attacking species. Which are nucleophile, electrophile and radical. (a) Electrophiles (b) Nucleophiles (c) Radicals

(a) **ELECTROPHILES**: Electrophiles are electron deficient species.

Ex. $\stackrel{\oplus}{H} \stackrel{\oplus}{\operatorname{Cl}} \stackrel{\oplus}{\operatorname{Br}} \stackrel{\oplus}{\operatorname{NO}}_{2}, \stackrel{\oplus}{\operatorname{CH}}_{3}$ (positively charged species), PCl₅, SO₂, SO₃ BH₃(species with vacant orbital at central

atom, carbenes) etc.

(b) NUCLEOPHILES : It is the electron rich species having atleast one unshared pair of electron. It can be neutral or negativetely charged it is always a lewis base.

Ex. CN^- , OH^- , Br^- , I^- , NH_3 , H_3O etc.

(c) **RADICALS** : It is electron deficient species with seven electrons around an atom.

Ex. $\dot{C}H_{3}$ C₂H₅, C₂H₅O, CH₃COO, X etc.

ELECTROPHILICITY

Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre. It participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile. Electrophilicity is a tendency of an electrophile to accept a pair of electrons.

NUCLEOPHILICITY

The tendency to give e⁻ pair to an electron deficient carbon atom is defined as nucleophilicity.

(i) Criteria for Nucleophilicity

1. The factors which increases e- density at 'donor atom increases nucleophilicity'.

2. The more polarisable donar atom is a better nucleophile. Therefore, large size of donor atom increases nucleophilicity.

(ii) Periodicity : Nucleophilicity decreases from left to right in a period.

 $:CH_{2}^{\Theta} > :NH_{2}^{\Theta} > :OH_{2}^{\Theta} > :F_{2}^{\Theta}$

... In a group, nucleophilicity increases from top to bottom due to increases in size of donor atom, but basicity decreases from top to bottom.

Acid strength : HI > HBr > HCl > HF Basic strength : $F^- > Cl^- > Br^- > I^-$ Nucleophilicity : $F^- < Cl^- < Br^- < I^-$



(iii) Steric effects on nucleophilicity

$$CH_{3} - C - O^{\ominus}$$

$$CH_{3} - C - O^{\ominus}$$

$$CH_{3}$$

$$CH_{3}$$

$$t$$
-butoxide

 $CH_3 - CH_2 - O^{\ominus}$

Stronger base, yet weaker nucleophile cannot approach the carbon atom so easily. weaker base, yet stronger nucleophile

Leaving group Ability/Nucleofugality

The best leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving group are good, which stabilise negative charge most effectively and weak base do this best, so weaker bases are always good leaving groups. A good leaving group always stabilize the transition state and lowers its free energy of activation and there by increases the rate of the reaction.

(a) Order of leaving ability of halide ion

$$\overset{\Theta}{I} > \overset{\Theta}{Br} > \overset{\Theta}{Cl} > \overset{\Theta}{F}$$
(b) Other good leaving groups are

Alkanesulphonate ion

Tosylate ion (OTs)

II O Alkyl sulphate ion CF₃SO₃

0-S-O-R

Triftlate ion (a super leaving group)

(c) Strongly basic ions rarely act as leaving group \rightarrow

$$\overset{\mathfrak{S}}{\underset{Nu}{\oplus}} \stackrel{\mathfrak{C}}{\underset{R}{+}} \stackrel{\mathfrak{C}}{\underset{R}{+}} \overset{\mathfrak{S}}{\underset{R}{+}} \stackrel{\mathfrak{S}}{\underset{R}{+}} \stackrel{\mathfrak{S}}{\underset{R}}{\underset{R}{+}} \stackrel{\mathfrak{S}}{\underset{R}{+}} \stackrel{\mathfrak{S}}{\underset{R}}{\underset{R}{+}} \stackrel{\mathfrak{S}}{\underset{R}}{\underset{R}}{}} \stackrel{\mathfrak{S}}{\underset{R}}{\underset{R}}{\underset{R}}{\underset{R}}{\underset{R$$

- (d) The weaker bases are better leaving groups.
- (e) The leaving group should have lower bond energy with carbon.
- (f) Negative charge should be more stable either by dispersal or declocalization.
- (g) Leaving group ability :

$$CH_{3}^{-} < NH_{2}^{-} < OH^{-} < F^{-}$$

$$R-COO^{-} > PhO^{-} > HO^{-} > RO^{-}$$

$$SH^{-} > OH^{-}$$

$$HO^{-} > RO^{-}$$



TYPES OF SOLVENTS

(a) Non polar

(b) Polar (i) polar protic (ii) polar aprotic

(i) Polar protic : A polar solvent which has acidic hydrogen.

(ii) Polar aprotic : A polar solvent which has no acidic hydrogen.



7. TYPES OF REACTIONS

In organic chemistry the following types of reaction are more important,

(I) Substitution reaction

(II) Elimination reaction

(III) Addition reaction

(IV) Rearrangement reaction



(I) Substitution Reaction

AROMATIC ELECTROPHILIC SUBSTITUTION REACTIONS

Like an alkene, benzene has clouds of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system still they are available to attack a strong electrophile to give a carbocation. This resonance-stabilized carbocation is called a sigma complex because the electrophile is joined to the benzene ring by a new sigma bond.

The sigma complex (also called an arenium ion) is not aromatic because the sp³ hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of thus first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

The overall reaction is the substitution of an electrophile $(\stackrel{\scriptstyle {\scriptstyle \oplus}}{\mathsf{E}})$ for a proton $(\stackrel{\scriptstyle {\scriptstyle \oplus}}{\mathsf{H}})$ on the aromatic ring: electrophilic aromatic substitution.

Step 1 : Attack of an electrophile on benzene ring forms the sigma complex



Resonance hybrid $[\sigma - complex]$ Arenium Ion





ELECTROPHILIC SUBSTITUTION REACTIONS

NUCLEOPHILIC SUBSTITUTION REACTION

In secondary alkyl halide both types of reactions S_N^1 or S_N^2 occurs, depending upon the nature of solvent :

(1) S_N^2 nucleophilic reaction : Mechanism and kinetics -

$$CH_3Br + OH \longrightarrow CH_3OH + Br Rate = K[CH_3Br][OH]$$

$$\begin{array}{ccc} C_{6}H_{13} & C_{6}H_{13} \\ H-C-Br \xrightarrow{I}{NaOH} & HO-C-H \\ CH_{3} & CH_{3} \end{array} \qquad (RI > RBr > RCl > RF) \\ Less energy is required to break RI bond. \end{array}$$

(-) 2-Bromo octane (Inversion of configuration).

An S_N^2 reaction proceeds with complete stereo chemical inversion.

 S_N^2 reaction decreases with stearic hindrance and increases by non protic solvent for example DMF and DMSO.

 S_N^2 reaction decreases in the presence of protic solvent like CH₃OH, C_2H_5 OH.

$$\begin{array}{cccc} H & H & Br & CH_{3} \\ H-C-Br > CH_{3}-C-Br > CH_{3}-C-CH_{3} > CH_{3}-C-Br \\ H & H & H \\ 37 & 1.0 & 2 \times 10^{2} & 8 \times 10^{4} \end{array}$$

 S_N^2 reactivity $1^\circ > 2^\circ > 3^\circ$

$$Rate - H\overset{\Theta}{O} + R - X \longrightarrow [H\overset{\Theta}{O} \dots R \dots N \overset{\delta}{X} \longrightarrow HO - R + \overset{\Theta}{X}(1.g)$$

& As the size of alkyl group increases then chemical reactivity towards S_N^2 decreases.

 $R-Br+C1 \xrightarrow{DMF} RC1 + Br$

Relative rate -
$$CH_3CH_2Br > CH_3CH_2CH_2Br > CH_3-CH-CH_2-Br > CH_3-CH_2-Br > CH_3-CH_2-Br > CH_3-CH_2-Br > CH_3-CH_2-Br > CH_3-CH_3-CH_3-CH_3 = CH_3 = C$$

Features of S_N2 Reaction

(i) Occurs mainly in 1° alkyl halide.

- (ii) Order of reaction is 2, but total step =1
- (iii) Speed of the reaction increases by non protic solvent ex. DMF and DMSO.
- (iv) Back attack of the nucleophile is there so that stereo chemical inversion occurs.
- (v) Elemental effect so that RI is maximum reactive.
- (vi) No carbocation, so no molecular rearrangement. Only transition state is formed.
- (vii) Kinetics of the reaction : rate ∞ [substrate] [nucleophile] rate = k[substrate] [nucleophile]

If the concentration of substrate in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is doubled. If the concentration of nucleophile is doubled the rate of reaction is also doubled. If the concentration of both are doubled then the rate of the reaction quadriples.



(viii) Energetics of the reaction



Figure : A free energy diagrams for S_N^2 reaction

- (ix) No intermediates are formed in the S_N^2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.
- (x) The stereochemistry of S_N^2 reactions \rightarrow As we seen earlier, in an S_N^2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as Walden inversion.

$$\overset{O}{\operatorname{Nu}} \overset{CH_3}{\underset{D^{\text{WW}}}{\overset{+\delta}{\underset{H}}}} \overset{-\delta}{\ell.g.} \overset{Inversion}{\underset{H}{\overset{\operatorname{Inversion}}}} \operatorname{Nu} \overset{CH_3}{\underset{H}{\overset{\bullet}}} + \overset{O}{\ell.g.}$$

Examples of S_N2 reactions of alkyl halide





(2) $S_N 1$ Substitution reaction

$$\begin{array}{ccc} CH_{3} & CH_{3} \\ H_{3}-C-Br+OH & \longrightarrow & CH_{3}-C-OH+Br \\ H_{3}-CH_{3} & CH_{3} \end{array}$$

Rate = K[RBr]

Slow: $R - X \longrightarrow \overset{\oplus}{R} + \overset{\Theta}{X}$

Fast: $\overset{\oplus}{R} + \overset{\Theta}{OH} \longrightarrow ROH$

Now nucleophilic attack can conceivably take place any time after the heterolysis and thus can involve any species from the initially formed ion pair to the free carbocation, attack on the free carbocation is random and yields the racemic modification. The anion clinge side of the carbocation and thus shields this side from attack; as result, back side attacks preferred to the extent, that attacks occurs before the ion pair has completely separated. Inversion of configuration competes with racemization.



Features of SN1 Reaction

- (i) Rate of reaction = K[RX]
 - Order = one, but occurs in two steps.
- (ii) Carbocation formation takes place so that molecular rearrangement may occur.
- (iii) Racemization takes place.
- (iv) Chemical reactivity $3^\circ > 2^\circ > 1^\circ$.
- (v) Elemental effect, so that RI are maximum reactive.
- (vi) Energetics of the $S_N 1$



Progress of reaction

Figure : Free energy diagram for the S_N^1 reaction.



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(vii) Stereochemistry of $S_N 1$ reaction : The over all reaction can be visualised with stereochemistry as followed



Properties	S _{N1}	S _N 2
Reactivity of halide leaving groups	RI > RBr > RCl > RF	RI > RBr > RCl > RF
Effect of structure	$R_3CX > R_2CHX > RCH_2X > CH_3X$ Rate is governed by stability of carbocation that is formed in ionization step.	$CH_3X > RCH_2X > R_2CHX > R_3CX$ Rate is governed by stearic effect (crowding in transition state).
Effect of solvent	Rate increases with increasing polarity of solvent.	Rate depends on both nature and concentration of nucleophile.
Effect of nucleophile	Rate of substitution is independent of both concentration and nature of nucleophile by its dielectric constant ε .	Polar aprotic solvents give fastest rates of substitution; solvent of Nu ¹ : is maximum and nucleophilicity is greatest.
Stereochemistry	Not stereospecific ; racemization accompanies inversion when leaving group is present at a stereogenic centre	Stereospecific; 100 percent inversion of configuration at reaction site. Nucleophile attacks carbon from side opposite bond to leaving group.

Ex.
$$CH_3 - C - Br \xrightarrow{H_3O+acctone} CH_3 - C - OH + HBr$$
 (3° alkyl halide hence no S_{N^2} reaction)
 $CH_3 \xrightarrow{CH_3} CH_3$ CH_3
Ex. $CH_3 - C - CH_2 - Br \xrightarrow{CH_3OH/Ag'} CH_3 - C - CH_3$ (carbocation rearrangement)
 H OCH_3
Ex. $CH_3CHCH_3 \xrightarrow{Conc. HBr} CH_3CHCH_3$
 H OH Br
Isopropyl alcohol Isopropyl bromide
Ex. $CH_3 - C - CH_2 - OH \xrightarrow{Conc. HBr} CH_3 - C - CH_2 - CH_3$
 $Isopropyl alcohol Isopropyl bromide$



REACTION MECHANISM



(3) Bimolecular nucleophilic substitution with tetrahedral intermediate ($S_N 2$ Th)

Characteristic reaction of acid and it's derivatives (acid halide, anhydride, amid and ester). Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism. The incoming nucleophile adds to the carbonyl to form a tetrasubstituted intermediate with a tetrahedral carbon.



The tetrahedral intermediate formed when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative is not stable and cannot be isolated.

A pair of nonbonding electrons on the oxygen reforms the π bond, and either $\overset{\odot}{L}$ or Nu^{\ominus} is eliminated with its bonding electrons. Whether $\overset{\odot}{L}$ or Nu^{\ominus} is eliminated depends on their relative basicities. The weaker base is preferentially eliminated because the weaker the base, the better it is a leaving group.



Thus carboxylic acid derivative will undergo a nucleophilic acyl substitution reaction provided that the incoming nucleophile is a stronger base than the group that is to be replaced. If the incoming nucleophile and the group attached to acyl group in the starting material have similar basicities, the tetrahedral intermediate can expect either group with similar ease. A mixture of starting material and substitution product will result.

Condition for acyl nucleophilic substitution reaction

$$\begin{array}{ccc} O & O \\ \parallel & \Theta & \parallel & \Theta \\ R - C - L + Nu & R - C - Nu + L \end{array}$$

(i) L must be better leaving group than Nu^{\ominus} , i.e., basicity of Nu should be more than that of $\overset{\ominus}{L}$

(ii) Nu must be a strong enough nucleophilic to attack RCOL.

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(iii) Carbonyl carbon must be enough electrophilic to react with $\underset{Nu}{\ominus}$

$$\begin{array}{c|cccc} O & O & O & O \\ \parallel & \parallel & \parallel & \parallel & \parallel \\ \textbf{Reactivity order}: R - C - CI > R - C - O - C - R > R - C - OR > R - C - NH_2 \end{array}$$

Ex.
$$\begin{array}{c} O \\ \parallel \\ -C \\ -C \\ -OH + CH_3OH \\ -H^+ \\ -H^+ \\ -H^+ \\ -C \\ -OCH_3 + H_2O \\ OH \\ -H^+ \\ -H$$

Ex.
$$R \xrightarrow{\parallel} C = CI + OH \xrightarrow{-} R \xrightarrow{\parallel} C = OH + CI^{-}$$

 $O = OH + CI^{-}$
Ex. $C_{6}H_{5} \xrightarrow{-} C = OCH_{3} + NH_{3} \xrightarrow{-} C_{6}H_{5} \xrightarrow{-} C = NH_{2} + CH_{3}O^{-}$
 $O = OH^{-}$

Ex.
$$CH_3 - C - O - C - CH_3 + H_2O - H^+ \rightarrow 2 CH_3 - C - OH$$

(4) Bimolecular nucleophilic substitution in aromatic compound $(S_N 2 Ar)$

This reaction is characteristic reaction of arylhalides with ortho or para electron withdrawing substituent. The reaction mechanism can be visualised as :

Intermediate ion is stabilized by resonance.

Ex.

Free radical substitution reaction

Characteristic reaction of alkanes are **free radical substitution** reaction, these reactions are generally chain reactions which are completed in three steps :

(i) chain initiation	(ii) chain propagation.	(iii) chain termination		
Halogenation :	$R-H+X_2 = \frac{UV \text{ Light or temp}}{250^\circ - 400^\circ \text{C}}$	\longrightarrow R-X+HX		
Mechanism :				
(i) Chain initiation :	$X_2 \xrightarrow{\text{UV or temp.}} \dot{X} + \dot{X}$			
(ii) Chain propagation :	$\dot{X} + R - H \xrightarrow{rds} \dot{R} + HX$			
	$\vec{R} + X - X \longrightarrow R - X + \dot{X}$			
(iii) Chain termination :	$\dot{\mathbf{X}} + \dot{\mathbf{X}} \longrightarrow \mathbf{X}_2$			
	$\vec{R} + \vec{R} \longrightarrow R - R$			
	$\dot{R} + \dot{X} \longrightarrow R - X$			
Reactivity of X_2 : $F_2 > C_{12} > Br_2 > I_2$ Reactivity of $H : 3^{\circ}H > 2^{\circ}H > 1^{\circ}H$				
(a) $CH_3 - CH_2 - CH_3 - CH_3 - CH_3 - CH_2 - CH_3 + CH_3 - CH_2 - CH_$				
	(Major)			
(b) $CH_3 - CH_2 - CH_3 \xrightarrow{Br_2} heat 127^{\circ}C$	$CH_3 - CH_2 - CH_2 - Br + CH_3 -$	- CH – CH ₃		
nout, 127 C	(Minor)			
		Br (Major)		
	С	H,		
De		-		
(c) $CH_3 - CH - CH_3 \xrightarrow{BI_2}$ heat, 127°C	$H_3 - CH - CH_2Br + CH_3 - C$	-Br		
CH.	CH, C	H ₃		
	(Minor) (M	lajor)		

(II) Elimination reactions

Elimination reactions, in which two groups are removed from a molecule, neither being replaced by another group, are the reverse of addition reactions. Usually they involve the loss of two substitutions from vicinal atoms resulting in the formation of a double or triple bond. Most commonly a proton is lost from one carbon whereas a nucleophile is lost from the adjacent carbon; these two carbon atoms are usually to as β -and α -carbons, respectively.

This type of elimination reaction is known β -elimination or 1, 2,-elimination reaction.

β-ELIMINATION REACTION

In analogy with substitution reaction, β -elimination reactions are divide into E_1 (Elimination, unimilecular) and E_2 (Elimination, biomolecular) reactions.

E, REACTION : THE BIOMOLECULAR MECHANISM

Many elimination reactions are successful only when carried out in the presence of a strong base. The formation of ethylene on the treatment of ethyl bromide with sodium ethoxide is an example of this type. The rate of alkene formation is proportional to the concentrations of ethyl bromide as well as that of sodium ethoxide.

$$CH_{3}CH_{2}Br + C_{2}H_{5}O^{1} \longrightarrow CH_{2} = CH_{2} + C_{2}H_{5}OH + Br^{1}$$

Two types of mechanism can be written both of which are in agreement with the kinetic data. In the first mechanism the base abstracts a proton from the β -carbon and simultaneously the leaving group departs from the α -carbon along with the pair of bonding electrons.

$$C_{2}H_{5}O \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{C_{2}H_{5}O} - \overset{\delta}{H} \xrightarrow{H} H \xrightarrow{C_{2}H_{5}O} - \overset{\delta}{H} \xrightarrow{H} H \xrightarrow{C_{2}H_{5}OH} + H \xrightarrow{C_{2}H_{5}OH} + H \xrightarrow{C_{2}H_{5}OH} + H \xrightarrow{H} H \xrightarrow{H}$$

 E_1 CB REACTION : Mechanism does operate under rather special circumstances 1, 1, 1 Trifluoro-2, 2 dichloroethane for instance, undergoes base-catalysed exchange of β -hydrogen atom with the solvent deuterium ethoxide faster than dehydrofluorination.

$$CF_{3}-CHCl_{2} \xleftarrow{C_{2}H_{3}OD}_{CF_{3}-CC} CF_{3} \xleftarrow{Fast}_{CF_{3}-CDCl_{2}} CF_{3}-CDCl_{2}$$

Mechanism

Step 2 :

 $-\mathbf{C} = \mathbf{C} -$

EDUBULL KEY POINTS

Remarks : First step consists of the removal of a proton, H, by a base generating a carbanion. In second step carbanion looses a leaving group to form alkene

Condition for the E₁CB

(i) substrate must be containing acidic hydrogens

(a) When the leaving group is strongly electronegative (i.e. exerts strong - I effect on β – H)

F,
$$\stackrel{\oplus}{\mathsf{NR}}_3$$
, $\stackrel{\oplus}{\mathsf{SR}}_2$

(b) Presence of EWG (-m) at $\beta - c$

$$(EWG) - CH_2 - L$$
; $-NO_2$, $> C = O, -C \equiv N$

(ii) poor leaving groups.

Ex.
$$CH_3 - CH - CH_2 - CHO \xrightarrow{NaOH} CH_3 - CH=CH-CHO$$

 $\downarrow \qquad OH$

Ex. Ph — CH₂ — CH₂ — CH₂
$$\xrightarrow{\text{OH}^-}$$
 Ph — CH = CH₂ + NR₃
 $\stackrel{\oplus}{\longrightarrow}$ NR₃

When the reaction is conducted in OD^{\ominus}/D_2O and a sample of reaction mixture is tested after some time interval, D-exchange is observed at $\beta - c$.

E, Reaction : The Unimolecular Mechanism

The main feature of this mechanism is that under the influence of solvation forces, the electron attracting group ("leaving group") breaks away along with the bonding electrons. The resultant carbonium ion subsequently loses a proton to the solvent or to some other proton acceptor.

The reaction thus has two stages of which the first is the rate-determining step and as a result the reaction rate depends only on the concentration of the first reactant.

Kinetics : Rate \propto [substrate] ; Rate = k [substrate]

Energetics : The free energy diagram for the E1 reaction is similar to that for the S_N 1 reaction.

Orientation in Elimination Reactions

The elimination reactions of unsymmetrical substrates usually yields mixtures of all possible products. There are two empirical rules governing the orientation in these reactions.

(a) The saytzeff Rule : It states that neutral substrates (alkyl halides or sulphonates) capable of forming a double bond in either direction of the chain preferably yield that alkene in which there is greater number of alkyl groups attached to the double bond. This rule applies to E1 reaction and to most of E2 reactions. The following examples are typical.

$$\begin{array}{ccc} C_2H_5O^1 + CH_3CH_2CHCH_3 & \xrightarrow{C_2H_5OH} & CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2\\ Br & (80\% \text{ of alkenes}) (20\% \text{ of alkenes}) + \text{ substitution product} \end{array}$$

The preferential formation of more substituted alkenes in the above reactions can be correlated with the relative stability of various alkenes. Calculations from heats of combusion and hydrogenation establish that the stability of a double bond is increases by alkyl substitution on the double-bonded carbon atoms. Thus the stabilities of alkenes follow the order :

 $R_2C = CR_2 > RCH = CR_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$

The greater stability of the more substituted alkene is sometimes explained on the basis of hyper conjugation.

Hofmann Rule : Suggests usually less substituted products if leaving group are positively charged **(b)** $(NR_3, SR_2$ etc.) and fluorine, Actually more acidic β -hydrogen is abstracted to produce alkene.

(i)
$$CH_{3} - CH_{2} - CH_{2} - NH_{3} - CH_{2} - CH_{2} - H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} + CH_{2} = CH_{2} + H_{2}O$$

(ii) $CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{3} - CH_{3} - CH_{2} - C$

The reaction in which reagent adds to a multiple bonds to give less unsaturated or completely saturated product, are known as addition reactions. e.g.

Hofmann product

$$C = C \left(\xrightarrow{A-B} \right)^{A} C = C \left(\xrightarrow{A-B} \right)^{A} C = C \left(\begin{array}{c} A \\ C \end{array} \right)^{A} C = C \left(\begin{array}(\begin{array}{c} A \\ C \end{array} \right)^{A} C = C \left(\begin{array}(\begin{array}{c} A \\ C$$

Ex.

(i)
$$CH_2 = CH_2 \xrightarrow{H_2} CH_3 - CH_3$$

(ii) $CH_3 - CH = CH_2 \xrightarrow{H_2} CH_3 - CH_3 - CH_1 - CH_3$

(iii)
$$CH_3 - CH = CH_2 \xrightarrow{HBr}_{Peroxide} CH_3 - CH_2 - CH_2$$

(iv)
$$CH_2 = CH_2 \xrightarrow{H-OH}_{H^{\oplus}} CH_2 - CH_2$$

(v)
$$CH_2 = CH_2 \xrightarrow{H_2O+Cl} HOCl \to CH_2 - CH_2$$

Mechanism of addition reaction

Mechanism of addition reactions can be classified in following ways :

- Classification based on the type of attacking reagents. (A)
- Classification based on the fashion of addition. **(B)**

Addition by cationic attack (Electrophilic addition)

(i)
$$CH_2 = CH_2 \xrightarrow{H^{\textcircled{O}}} CH_2 - CH_2 \xrightarrow{Cl^{\textcircled{O}}} CH_2 - CH_2 \xrightarrow{H_1} CH_2 - CH_2$$

(ii)
$$CH_2 = CH_2 \xrightarrow{\oplus} CH_{3} \xrightarrow{\oplus} CH_2 - CH_2 \xrightarrow{\oplus} CH_3 \xrightarrow{\oplus} CH_2 - CH_3 \xrightarrow{\oplus} CH_2 - CH_2 \xrightarrow{\oplus} CH_2 - CH_2 \xrightarrow{\oplus} CH_2 - CH_2 \xrightarrow{\oplus} CH_3 \xrightarrow{\oplus} CH_2 \xrightarrow{\oplus} CH_2 \xrightarrow{\oplus} CH_3 \xrightarrow{\oplus} CH_3$$

Addition by free radical attack

(i)
$$CH_2 = CH_2 \xrightarrow{Br} CH_2 - CH_2 \xrightarrow{H-Br} CH_2 - CH_2$$

(ii)
$$CH_3 - CH = CH_2 \xrightarrow{Br'} CH_3 - CH - CH_2 \xrightarrow{H-Br} CH_3 - CH_3 - CH_2$$

(iii)
$$CH_3-C$$
 CH \xrightarrow{Br} $CH_3-\dot{C} = CH$ $\xrightarrow{H-Br}$ $CH_3-\dot{C} = CH$

(vi)
$$\xrightarrow{Br} \xrightarrow{Br} \xrightarrow{Br} \xrightarrow{Br} \xrightarrow{H-Br} \xrightarrow{H}$$

Addition by anionic attack (nucleophilic addition)

(i)
$$CH_3 - C - H \xrightarrow{\circ} CH_3Mg^{\circ}CI \rightarrow CH_3 - C - H \xrightarrow{H^{\oplus}} CH_3$$

(ii)
$$CH_3-C-H \xrightarrow{CN} CH_3-C-H \xrightarrow{H^{\oplus}} CH_3-C-H \xrightarrow{H^{\oplus}} CH_3-C-H$$

(iii)
$$CH_3 - C - H \xrightarrow{AIH_3^{\odot}} CH_3 - C - H \xrightarrow{H^{\oplus}} CH_3 - C - H \xrightarrow{H^{\oplus}} CH_3 - C - H$$

H H H

(iv)
$$CH \equiv CH \xrightarrow{Hg^{2'}} CH = CH \xrightarrow{-CN} CH = CH \xrightarrow{-Hg^{2'}} CH = CH \xrightarrow{-Hg^{2'}} CH = CH \xrightarrow{-Hg^{2''}} CH = CH \xrightarrow{-H$$

REACTION MECHANISM

It is the example of nucleophilic addition reaction catalysed by $\mathrm{Hg}^{\scriptscriptstyle 2+}$

(v)
$$CH_3-C-H \xrightarrow{N \in H_H} CH_3-CH-N \in H_H \xrightarrow{\Theta} CH_3-CH-N-H \xrightarrow{H^{\oplus}} CH_3-CH-N-H \xrightarrow{H^{\oplus}} CH_3-CH-N-H \xrightarrow{H^{\oplus}} CH_3-CH-N-H \xrightarrow{H^{\oplus}} CH_3-CH-N-H$$

(vi)
$$CH_2 = CH = CH = O \xrightarrow{CI^{\Theta}} CH_2 - CH = CH = O \xrightarrow{H^{\oplus}} CH_2 - O \xrightarrow{H^{\oplus}} CH$$

CCI

Addition by carbene attack

(i)
$$CH_2 = CH_2 \xrightarrow{:CH_2} CH_2 - CH_2$$

(ii)
$$CH_3 - CH = CH - CH_3 \xrightarrow{cc_{cl}} CH_3 - CH - CH - CH_3$$

(iii)
$$\bigcirc$$
 :c $<^{Cl}_{Cl}$ \bigcirc C $<^{Cl}_{Cl}$ \bigcirc \bigcirc \bigcirc

Addition by molecular attack

(i)
$$CH_2 = CH_2 \xrightarrow{Cl_2} CH_2 - CH_2 \xrightarrow{Cl_2} CH_2 - CH_2 \xrightarrow{Cl_2} CH_2 - CH_2 \xrightarrow{Cl_2} CH_2 - CH_2$$

(ii)
$$CH = CH \xrightarrow{Cl_2} CH = CH \xrightarrow{Cl^{\Theta}} CH = CH \xrightarrow{Cl^{\Theta}} CH = CH \xrightarrow{Cl^{\Theta}} H \xrightarrow{Cl^{\Theta}} CH = CH \xrightarrow{Cl^{\Theta}} H$$

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(iii)
$$CH_2 = CH_2 \xrightarrow{H-BH_2} CH_2 \xrightarrow{BH_2} CH_2 \xrightarrow{BH_2} CH_3 - CH_2$$

(iv)
$$CH \equiv CH \xrightarrow{H-BH_2} CH \equiv CH \xrightarrow{H} CH \equiv CH$$

$$(\mathbf{v}) \qquad \overset{\mathrm{CH}_2}{\underset{\mathrm{CH}_2}{\Vdash}} + \overset{\mathrm{O}}{\underset{\mathrm{O}}{\twoheadrightarrow}} \overset{\mathbb{O}}{\underset{\mathrm{O}}{\circledast}} \xrightarrow{\mathrm{CH}_2-\mathrm{O}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{O}}{\longrightarrow}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{O}}{\longrightarrow}} \overset{\mathbb{CH}_2-\mathrm{OH}}{\underset{\mathrm{CH}_2-\mathrm{OH}}{\longrightarrow}} \overset{\mathrm{CH}_2-\mathrm{OH}}{\underset{\mathrm{CH}_2-\mathrm{OH}}{\longrightarrow}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{OH}}{\longrightarrow}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{OH}}{\amalg}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{OH}}{\longrightarrow}} \overset{\mathbb{O}}{\underset{\mathrm{CH}_2-\mathrm{O$$

(IV) REARRANEMENT REACTION

It may be defined as the reaction involving reshuffling of the sequence of atom to form a new structure : **Beckmann rearrangement**

In this reaction ketoxime reacts with $H_2SO_4(conc.)$ to give a product by alkyl migration.

Bayer-villiger rearrangement

The reaction involve the oxidation of ketone to ester by the treatment with peracids such as peracetic acid, perbenzoic acid, pertrifluro acetic acid, etc. In this case best migratory group migrate to electron deficient oxygen.

$$\begin{bmatrix} \overset{\oplus}{OH} & OH \\ H \\ CH_3 - C - O - \langle \bigcirc \rangle \langle \longleftrightarrow \rangle CH_3 - \overset{OH}{C} - O - \langle \bigcirc \rangle \end{bmatrix} \xrightarrow{-H^{\oplus}} CH_3 - C - O - \langle \bigcirc \rangle$$

Migratory order : $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_{3}^{\circ}$

$$CH_3-O-\langle O \rangle -> CH_3-\langle O \rangle -> \langle O \rangle -> Cl-\langle O \rangle -> O_2N-\langle O \rangle -$$

Acid-catalysted decomposition of cumene hydroxide

Benzylic acid rearrangement

$$\underbrace{\bigcirc}_{C-C=O}^{O} \xrightarrow{\text{KOH}} \underbrace{\bigcirc}_{C-C=O}^{Ph} \xrightarrow{Ph}_{O} \xrightarrow{Ph}_{O$$

Fries rearrangement

The phenyl esters on treatment with anhydrous $AlCl_3$ undergo fries rearrangement to give o - and p - hydroxy ketones.

Claisen rearrangement

This is the rearrangement of allyl aryl ether to allyl phenols. No catalyst is required and it occurs when the substrate is heated alone to about 200°C or in some inert solvent like diphenyl ether. Allyl group migrates to ortho-position and if ortho-position is already occupied, para-isomer is obtained.

1. Rate determining step

The slowest step of the mechanism known as rate determining step of the reaction.Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction and generally using rate determine step (R.D.S). An organic reaction can be represented as

Reactant (substrate) + Reagent — solvent → Product

Homolytic bond dissociationEx. $A-B \longrightarrow A^{\circ} + B^{\circ}$ Hetrolytic bond dissociationEx. $A-B \longrightarrow A^{\oplus} + B^{\ominus}$

2. Types of Reagents

A reagent generates three type of attacking species. Which are nucleophile, electrophile and radical. (a) Electrophiles (b) Nucleophiles (c) Radicals (a) Electrophiles : Electrophiles are electron deficient species.

Ex. $\stackrel{\oplus}{H} \stackrel{\oplus}{\operatorname{Cl}} \stackrel{\oplus}{,\operatorname{Br}} \stackrel{\oplus}{,\operatorname{NO}_2}, \stackrel{\oplus}{\operatorname{CH}}_3$ (positively charged species), PCl₅, SO₂, SO₃ BH₃(species with vacant orbital at central atom, carbenes) etc.

(b) Nucleophiles : It is the electron rich species having atleast one unshared pair of electron. It can be neutral or negativetely charged it is always a lewis base.

Ex. CN^{-} , OH^{-} , Br^{-} , I^{-} , NH_3 , H_2O etc.

(c) Radicals : It is electron deficient species with seven electrons around an atom.

Ex. $\dot{C}H_3$, C_2H_5 , C_2H_5O , CH_3COO , X[•] etc.

3. Nucleophilicity

The tendency to give e⁻ pair to an electron deficient carbon atom is defined as nucleophilicity.

Leaving group Ability/Nucleofugality

(a) Order of leaving ability of halide ion

$$\Theta$$
 Θ Θ Θ O

(b) Other good leaving groups are

Tosylate ion (OTs)

Alkanesulphonate ion

Alkyl sulphate ion

Triftlate ion (a super leaving group)

(c) Strongly basic ions rarely act as leaving group \rightarrow

$$\overset{\Theta}{\text{Br}} + \overset{\Theta}{\text{R}} - \overset{\Theta}{\text{OH}} \quad \overrightarrow{\text{X}} \quad \text{R} - \text{Br} + \overset{\Theta}{\text{OH}} \text{ (strong base / poor leaving group)}$$

$$\Theta$$
 Nu + CH₃ - CH₃ \rightarrow CH₃ - Nu + Θ (It is not a leaving group)

Nu:
$$^{\Theta}$$
 + R $^{\Theta}$ - X $^{\Theta}$ - Nu - R + X $^{\Theta}$
Leaving group

(d) The weaker bases are better leaving groups.

- (e) The leaving group should have lower bond energy with carbon.
- (f) Negative charge should be more stable either by dispersal or declocalization.
- (g) Leaving group ability :

1.
$$CH_3^- < NH_2^- < OH^- < F^-$$

$$2. \qquad R-COO^{-} > PhO^{-} > HO^{-} > RO^{-}$$

3.
$$SH^- > OH^-$$

4. Types of solvents

- (a) Non polar
- (b) Polar (i) polar protic (ii) polar aprotic
- (i) Polar protic : A polar solvent which has acidic hydrogen.
- (ii) Polar aprotic : A polar solvent which has no acidic hydrogen.

5. Types of Reactions

In organic chemistry the following types of reaction are more important,

- (I) Substitution reaction
- (II) Elimination reaction
- (III) Addition reaction
- (IV) Rearrangement reaction

Nucleo	philic	Substitution	Reaction
1 ucico	philite	Substitution	iteaction

Properties	S _{N1}	S_{N^2}
Reactivity of halide	RI > RBr > RCl > RF	RI > RBr > RCl > RF
leaving groups		
Effect of structure	$R_3CX > R_2CHX > RCH_2X > CH_3X$	$CH_3X > RCH_2X > R_2CHX > R_3CX$
	Rate is governed by stability of	Rate is governed by stearic effect
	carbocation that is formed in	(crowding in transition state).
	ionization step.	
Effect of solvent	Rate increases with increasing	Rate depends on both nature and
	polarity of solvent.	concentration of nucleophile.
Effect of nucleophile	Rate of substitution is independent	Polar aprotic solvents give fastest
	of both concentration and nature	rates of substitution; solvent of Nu ¹ :
	of nucleophile by its dielectric	is maximum and nucleophilicity is
	constant ε .	greatest.
Stereochemistry	Not stereospecific ; racemization	Stereospecific; 100 percent inversion
	accompanies inversion when	of configuration at reaction site.
	leaving group is present at a	Nucleophile attacks carbon from side
	stereogenic centre	opposite bond to leaving group.

 S_N^1 reactivity $3^\circ > 2^\circ > 1^\circ$

 S_N^2 reactivity $1^\circ > 2^\circ > 3^\circ$

6. Condition for acyl nucleophilic substitution reaction

Reactivity order :
$$R - C - CI \ge R - C - O - C - R \ge R - C - OR \ge R - C - NH_2$$

Saytzeff Rule : It states that neutral substrates (alkyl halides or sulphonates) capable of forming a double bond in either direction of the chain preferably yield that alkene in which there is greater number of alkyl groups attached to the double bond. This rule applies to E1 reaction and to most of E2 reactions. The following examples are typical.

$$CH_{3} \xrightarrow{CH_{3}} CH_{2}CH_{3} \xrightarrow{H,O} CH_{3} \xrightarrow{CH_{3}} CH_{2}CH_{2}CH_{3} \xrightarrow{CH_{3}} CH_{2}CH_{2}CH_{3} \xrightarrow{CH_{3}} CH_{2}CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

 $\begin{array}{ccc} C_2H_5O^1 + CH_3CH_2CHCH_3 & \xrightarrow{C_2H_3OH} & CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2\\ Br & (80\% \text{ of alkenes}) (20\% \text{ of alkenes}) + \text{ substitution product} \end{array}$

Hofmann Rule : Suggests usually less substituted products if leaving group are positively charged ($\stackrel{\oplus}{NR_3}, \stackrel{\oplus}{SR_2}$ etc.) and fluorine, Actually more acidic β -hydrogen is abstracted to produce alkene.

(i)
$$CH_3 - \overset{H}{\underset{H}{C}} - CH_2 - \overset{H}{\underset{H_3}{N}} CH_2 - \overset{H}{\underset{H_9}{C}} CH_2 - \overset{H}{\underset{H_9}{C}} H \longrightarrow CH_3CH_2CH_2N - CH_3 + CH_2 = CH_2 + H_2O$$

(ii)
$$CH_3 - CH_2 - CH_1 - CH_2 \xrightarrow{KOH}_{C_2H_3OH} CH_3 - CH_2 - CH = CH_2 1$$

F

Free radical substitution reaction : Characteristic reaction of alkanes are **free radical substitution** reaction, these reactions are generally chain reactions which are completed in three steps :

(i) chain initiation (ii) chain propagation (iii) chain termination

Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$ Reactivity of $H : 3^{\circ}H > 2^{\circ}H > 1^{\circ}H$

