Applications of electronic effects:

Th1: Reaction intermediates

Reactive, shortlived, high energy, unstable species, those are formed in the course of organic reactions are called reaction intermediates.

Reaction intermediates generally formed after bond breaking and before bond formation.

A covalent bond can get cleaved by:

(i) Heterolytic cleavage (ii) Homolytic cleavage.

Homolytic fission of covalent bonds:

The bond may break in such a way that each fragment takes away one of the electrons of the bond. This process is called homolysis, produces fragments with unpaired electron called radicals.

$$A : \stackrel{\circ}{B} \rightarrow \underbrace{A \cdot + \cdot B}_{\text{Radicals}} \text{ Homolytic bond cleavage}$$

Heterolytic fission of covalent bonds:

The bond breaks in such a way that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital. This kind of cleavage called heterolysis, produces charged fragments or ions.

$$A \stackrel{(}{:} \stackrel{\flat}{B} \rightarrow A^* + : B^-$$
 Heterolytic bond cleavage

Heterolysis of a bond normally requires polarized bond.

$$\delta^{+}A : \stackrel{(}{B}{}^{\delta^{-}} \rightarrow A^{+} + : B^{-}$$

Polarisation of a bond usually result from different electronegatives of the atoms joined by the bond. The greater the difference in electronegativity, the greater the polarisation. In the given instance, atom B is more electronegative than A.



Section (A) : Carbanions

D1: A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion. Hybridisation: Hybridisation of carbanion may be sp³, sp² or sp. **Hvbridisation**

Example

sp³
$$\mathring{C}H_3$$
, $CH_3 - \mathring{C}H_2$, $CH_3 \mathring{C}HCH_3$, $(CH_3)_3 \mathring{C}$
sp² $H_2C = \mathring{C}H$, $CH_2 = CH - \mathring{C}H_2$, $\overset{\ominus}{\bigvee}$
sp $HC = \mathring{C}$

Stability of carbanion: Carbanions are stabilised by electron withdrawing effect as

(i) – I effect (ii) –M effect (iii) Delocalisation of charge

Carbanions are Lewis bases. In their reactions they seek a proton or some other positive centre to which they can donate their electron pair and thereby neutralize their negative charge.

$$- \overset{I}{\overset{\bullet}{\Gamma}} + \overset{\bullet}{\overset{H}{\overset{\bullet}{-}}} \overset{-}{\overset{\bullet}{\Lambda}} \xrightarrow{-} - \overset{I}{\overset{\bullet}{\overset{\bullet}{\Gamma}}} - H + :A^{-}$$
Carbanion Lewis acid



Examples of stability order:



Rearrangement: Generally carbanions do not undergo rearrangement.

Section (B) : Carbon free radicals

D2: Free radical: An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.

$$A \stackrel{(i)}{\to} \dot{B} \xrightarrow{\text{homolysis}} \dot{A} + \dot{B}$$
Radicals

It is generated in presence of sun light, peroxides or high temperature

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$$\begin{array}{c} \stackrel{}{\overset{}}{\overset{}} X \xrightarrow{h_{\upsilon}} \dot{R} + \dot{X} \\ \stackrel{}{\overset{}} or \\ \stackrel{}{\overset{}} Alkyl \\ free radical \end{array}$$

Note: (i) It is neutral species with odd e-.

(ii) It is paramagnetic in nature due to odd e-.

(iii) Rearrangement is not observed generally.

(iv) Carbon atom having odd electron is in sp² hybridised state

(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

(Stability order)

Stability of free radical: It is stabilised by resonance, hyperconjugation and + I groups. æ

Ex. (a)
$$\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H_-CH_3 < CH_3 - \dot{C}H_-CH_3$$

(b)
$$CH_3 - \dot{C}H_2 > CH_3 - CH_2 - \dot{C}H_2 > CH_3 - CH - \dot{C}H_2 > CH_3 - CH_3 - CH_2$$
 (Stability order)

(Due to resultant of inductive effect and hyperconjugation, both operates in same direction)

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(c)
$$(C_6H_5)_3C^{\bullet} > (C_6H_5)_2CH > C_6H_5 - CH_2 > CH_2 = CH - C - CH_3$$
 (Stability order)

Section (C) : Carbocations

D3: A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.
 Hybridisation: Carbocation may be sp² or sp hybridized.

Hybridisation	Example
sp ²	$\stackrel{\Phi}{C}$ H ₃ , CH ₃ $\stackrel{\Phi}{C}$ H ₂ , CH ₃ $\stackrel{\Phi}{C}$ HCH ₃ , (CH ₃) ₃ $\stackrel{\Phi}{C}$
sp	$H_2C = \stackrel{\oplus}{C}H, HC = \stackrel{\oplus}{C}$

Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):



Carbocation Water (a Lewis acid) (a Lewis base)

Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of Neon.

Stability: Carbocations are stabilised by

(i) +M effect (ii) De

(ii) Delocalisation of charge (iii) Hyperconjugation

njugation (iv) +I effect

General stability order:

$$Ph_{3}C^{\oplus} > Ph_{2}\overset{\oplus}{C}H > Ph - \overset{\oplus}{C}H - R > CH_{2} = CH - \overset{\oplus}{C}H - R \gtrsim (CH_{3})_{3}\overset{\oplus}{C} \gtrsim Ph\overset{\oplus}{C}H_{2} > CH_{2} = CH - \overset{\oplus}{C}H_{2} \gtrsim (CH_{3})_{2}\overset{\oplus}{C}H > CH_{3} - \overset{\oplus}{C}H_{2} > \overset{\oplus}{C}H_{3} > CH_{2} = \overset{\oplus}{C}H \simeq \overset{\oplus}{C}H_{3}$$

Ex.

$$CH_{3} \rightarrow C^{\oplus} > CH_{3} \rightarrow C^{\oplus} > CH_{3} \rightarrow C^{\oplus} > CH_{3} \rightarrow C^{\oplus} > CH_{3} \rightarrow C^{\oplus} > CH_{2} > C^{\oplus} > CH_{3} \rightarrow C^{\oplus} > CH_{$$

t-Butyl carbocation has +I effect of three Me-groups and also Hyperconjugation effect which makes it most stable.

⊕ CH₂

$$H_{3} - CH_{3} - CH_{2} > CH_{2} = CH_{2}$$

Benzylic Ethyl cation Vinyl cation cation

In Benzyl cation, extensive resonance is seen which stabilises C^{\oplus} .

In Ethyl carbocation +I and hyperconjugation of Me-group stabilizes carbocation.

In vinyl carbocation stability decreases rapidly since carbon of (CH_2) is sp² hybridized which is slightly more electronegative hence acts as – I group which increases (+) charge density.

Rearrangement of carbocations:

Whenever an Intermediate carbocation is formed in reaction it may rearranges.

Only those carbocation will rearrange which can produce more stable species. It can be done either by (i) Shifting of H, alkyl, aryl, bond (1, 2 shifting)

- (ii) Ring expansion (more strained ring to less strained ring)
- (iii) Ring contraction

(i) Shifting of H, alkyl, aryl, (1, 2 shift)



(iii) Ring contraction:

(ii)

Note: Cyclopropylmethyl cation: In solvolysis of simple primary cylcopropylmethyl systems the rate is enhanced because of the participation by the σ -bonds of the rings. The ion that forms initially is an unarranged cyclopropylmethyl cation that is symmetrically stabilized, that is, both the 2, 3 and 2, 4σ -bonds help stabilize the positive charge. Cyclopropyl group stabilizes on adjacent positive charge even better than a phenyl group.



This special stability, which increases with each additional cyclopropyl group, is a result of conjugation between the bend orbitals of the cyclopropyl rings's and the vacant P-orbital of cationic carbon.



Q. Rearrange (if applicable) the following carbocations into more stable form:



	Carbon free radical	Carbocation	Carbanion
	Condi	Ctum	
Shape	trigonal planar	trigonal planar	Pyramidal
Hybridisation	sp ²	sp ²	sp ³
No. of electrons in outermost shell	7	6	8

D4: **Carbenes (Divalent Carbon intermediates) :**

There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :

 $CHCI_3 + HO^{\Theta} \xrightarrow{-HCI} : CCI_2$

$$\mathsf{CH}_2 I_2 \textbf{+} \mathsf{Zn} \xrightarrow[\Delta]{-\mathsf{ZnI}_2} : \mathsf{CH}_2$$

 $CH_2N_2 \xrightarrow{h_V \text{ or } \Delta} N_2\uparrow + : CH_2 \qquad \qquad CH_2 = C = O \xrightarrow{\Delta} : CH_2 + CO\uparrow$

Types of carbene	Singlet /C	Triplet – Ċ –
Shape	Bent	Linear
Hybridisation	sp ²	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

D5: Nitrenes: The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.

> R – N H – N

D6: **Benzyne :** The benzene ring has one extra C–C π bond in benzyne



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Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. Since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp² since the overlap between these sp² hybrid orbitals is not so much effective.

Section (D) : Basic strength

Th₂. Bases

- D7: (a) Arhenius base: Base is a substance that can donate (or loose) OH⁻ ions in H₂O.
- D8: (b) The Bronsted Lowry definition of acids and bases:

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :



D9: (c) The Lewis definition of acids and bases:

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

For example aluminiumchloride, reacts with ammonia in the same way that a proton donor does.



(d) Basicity (K_b):

$$\ddot{N}H_{3} + H_{2}O \longrightarrow H - \overset{I}{N^{+}}H + OH - \overset{I}{H}$$
$$K_{b} = \frac{[NH_{4}^{+}]}{[NH_{3}]}$$
$$pK_{b} = -\log K_{b}$$

Basicity order in periodic table:

(1) Basic strength decreases down the group,

(2) Basic strength decreases along the period because electron neagativity increases, so electron donor tendency decreases.

1.1 Aliphatic bases:

(1) On the basis of +I effect basic strength of amines should be $3^{\circ} > 2^{\circ} > 1^{\circ} > NH_3$

But this order is applicable only when the amines are in gaseous state or in case of non-polar aprotic solvent.

(2) Basic strength of nitrogeneous compound depends upon the hybridised state of nitrogen

$$\begin{array}{cccc} R-CH_2 - CH_2 - NH_2 > R - CH_2 - CH = NH > R-CH = CH-NH_2 > & R-C=N \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ & sp^3 (localised) & sp^2 (localised) & sp^2 (delocalised) & sp \\ (3) More electronegative atom (-I group) will decrease the basic strength & sp \\ \end{array}$$

 $CH_3-CH_2-CH_2-NH_2 > CH_2=CH-CH_2-NH_2 > H-C=C-CH_2-NH_2$

(4) Cyclic amines are more basic than acyclic amines of same nature

(5) Amidines are more basic in nature because their conjugate acid are more stable due to resonance.



Nitrogen (X) is more basic than nitrogen (Y).

Th3. Basic strength of aromatic amines and substituted anilines:

(a) Aniline:

Lone pair of aniline lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that it can get resonance stabilisation and hence, basic strength decreases. So, Aniline is a weaker base than NH₃.



(b) Pyridine (C₅H₅N) : 6-π electrons, aromatic



Lone pair of N in pyridine is localised so it is more basic than aniline.



Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



(d) Ortho substituted anilines :

Electron releasing groups (ERG) +M, HC, +I increases the $K_{\rm b}$ and Electron withdrawing groups (EWG) –m, –I decreases the $K_{\rm b}$

Steric effect of ortho-substituent in aniline (ortho effect) :



- (i) Ortho-substituted anilines are mostly weaker bases than aniline itself.
- (ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
- (iii) The small groups like $-NH_2$ or -OH do not experience (SIR) due to small size.



$$\widehat{\mathsf{C}} \approx \mathsf{R} - \overset{\ominus}{\mathsf{O}} \gtrsim \overset{\ominus}{\mathsf{O}} \mathsf{H} \gtrsim \mathsf{C} \mathsf{H}_3 \overset{\ominus}{\mathsf{O}} > \mathsf{C} \mathsf{O}_3^2 > \mathsf{Ph} \overset{\ominus}{\mathsf{O}} > \mathsf{R} \overset{\ominus}{\mathsf{S}} > \mathsf{R} \mathsf{C} \mathsf{O} \overset{\ominus}{\mathsf{O}} > \mathsf{O} \mathsf{C} \overset{\ominus}{\mathsf{N}} > \mathsf{H}_2 \mathsf{O} > \overset{\ominus}{\mathsf{C}} \mathsf{I}$$

Th4. Solvent effect in bases :

The trend is not regular in the aqueous state as evident by their pKb values given in Table.

Name of amine	pK₀	Name of amine	pКь
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Metheylmethanamine	3.27	Phenylmethanamine	4.70
N, N-Dimethylmethanamine	4.22	Aniline	9.38
Ethanamine	329	N-Methylaniline	9.30
N-Ethylethanamine	3.00	N,N-Dimethylaniline	8.92

Table : pKb Values of Amines in Aqueous Phase (Ref. NCERT)

In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion (Alkyl groups are hydrophobic and inhibits H bonding and solvation.), lesser will be the solvation and the less stabilised is the ion. The order of solvation of ions are as follows:



Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

On the basis of above two sequences, we can say that the basic strength of amines is the combined effect of inductive effect, steric hindrance and solvation.

$R_2NH > RNH_2 > R_3N > NH_3$	(if R = CH₃)	(1)
$R_2NH > R_3NH > RNH_2 > NH_3$	$(if R = C_2H_5)$	(2)

Th5. Reactions of bases :

(i) **Nature of aqueous solution:** Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.

 $RNH_2 + HOH \implies RNH_3OH^- \implies [RNH_3]^+ + OH^-$ 1° Amine

 $R_2NH + HOH \implies R_2 \overset{+}{NH_2OH^-} \implies [R_2NH_2]^+ + OH^-$

2º Amine

The aqueous solution of amines behave like NH₄OH and gives the precipitate of ferric hydroxide with ferric chloride.

 $3RNH_{3}OH + FeCI_{3} \longrightarrow Fe(OH)_{3} + 3RNH_{3}CI$

Brown ppt.

(ii) Aliphatic and aromatic amines form salt because of their basic nature:

 $RNH_2 + H_2O \longrightarrow RNH_3OH$

Alkylammoniumhydroxide

 $RNH_2 + HCI \longrightarrow RNH_3 CI$ Alkylammoniumchloride

 $RNH_2 + H_2SO_4 \longrightarrow (RNH_3)_2 SO_4^{-2}$

Similarly we get

 $C_6H_5NH_2 + H_2O \longrightarrow C_6H_5 \overset{+}{N}H_3 \overset{-}{O}H$

Aniliniumhydroxide

 $C_6H_5NH_2 + HCI \longrightarrow C_6H_5NH_3CI \text{ or } C_6H_5NH_2 : HCI$

Aniliniumchloride Anilinehydrochloride

Salts of amines are ionic compounds and hence water soluble.

Section (E) : Acidic strength

Th6. Acids

- D10: (a) Arhenius acid: An acid is a substance that can donate (or loose) a proton in H_2O .
- D11: (b) The Bronsted Lowry definition of acids and bases:

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :



Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion (H₃O⁺) and a chloride ion (CI⁻).

The molecule or ion that forms when an acid loses its proton is called the conjugate base of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the conjugate acid of that base.

(c) The Lewis definition of acids and bases D12:

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.



 $RCOOH + H_2O \implies RCOO^- + H_3O^+$

$$\begin{split} \mathsf{K}_{eq} &= \frac{[\mathsf{RCOO}^-] \quad [\mathsf{H}_3\mathsf{O}^+]}{[\mathsf{RCOOH}] \quad [\mathsf{H}_2\mathsf{O}]} \\ \mathsf{K}_a &= \frac{[\mathsf{RCOO}^-] \quad [\mathsf{H}_3\mathsf{O}^+]}{[\mathsf{RCOOH}]} \end{split}$$

 $pK_a = -\log K_a$

6.1 Relative acidity of hydrocarbons :

Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C-H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.

 $HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$

6.2 Acidity of phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol.

Groups which are -I, -m increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively + I and + m groups decreases acid strength.



Acid strength order : I > II > IV > V > IIIAns.

Sol. Step-1. III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).

Step-2. Since -I, -m group will increase acid strength, Nitrophenol will be most acidic followed by phenol,

Step-3. Amongst cresol and methoxyphenol, methoxyphenol has +M effect of -OCH₃ which increases e- density hence decrease acidic strength OH

Ex.



OH

CH.

Ans. Acid strengh order: I > III > II > IV

Step-1: Notice that CH₃ have +I effect so all methylphenols (cresols) are less acidic than phenol (I). Sol. Step-2: Now amongst cresols p- and o-CH₃ are increasing the e⁻ density due to their hyper conjugation but ortho isomer has viable +I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only +I works it as least e- density amongst the cresol.



Acid strength order: II > IV > III > IAns.

Step-1 : In nitrophenols -I effect of NO2 will help to increase acidic strength hence phenol is least acidic Sol. amongst all nitrophenols

Step-2 : Only -I effect is applicable in meta nitrophenol it will be number three. Now -o, -p have both -I and -m effect of NO₂ group over OH and in this particular case para isomer is more acidic than ortho since cular

H is trapped by NO₂ group.

Compound	Formula	рКа	Compound	Formula	рКа
o-Nitrophenol	0-02N-C6H4-OH	7.2	o-Cresol	o-CH ₃ –C ₆ H ₄ –OH	10.2
m-Nitrophenol	$m-O_2N-C_6H_4-OH$	8.3	m-Cresol	m-CH ₃ C ₆ H ₄ –OH	10.1
p-Nitrophenol	p-O ₂ N–C ₆ H ₄ –OH	7.1	p-Cresol	p-CH ₃ –C ₆ H ₄ –OH	10.2
Phenol	C ₆ H ₅ –OH	10	Ethanol	C ₂ H ₅ OH	15.9

Table : pK₂ values of some phenols and Ethanol (Ref. NCERT)

From the above data, you will note that phenol is million times more acidic than ethanol.

6.3 Acidity of carboxylic acids :

Conjugate base of carboxylic acid exists as two equivalent cannonical structures (A) and (B). This ion is resonance stablised and resonance hybrid structure is (C).



Electron withdrawing group (-M, -I effect) increases acidic nature. Electron releasing group (+M, +I effect) decreases acidic nature.

- **Ex.** (a) $F-CH_2-COOH > CI-CH_2COOH > Br-CH_2COOH > I-CH_2COOH$ CI CI
 - (b) $CI C COOH > CI CH COOH > CI CH_2COOH > CH_3COOH$
 - (c) HCOOH > CH_3COOH > CH_3-CH_2-COOH

The effect of the following groups in increasing acidicty order is $Ph < I < Br < CI < F < CN < NO_2 < CF_3$

[Ref. NCERT]

Thus, the following acids are arranged in order of decreasing acidity (based on pK_a values) : $CF_3COOH > CCI_3COOH > CHCI_2COOH > NO_2CH_2COOH > NC-CH_2COOH > FCH_2COOH > CICH_2COOH > BrCH_2COOH > HCOOH > CICH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3COO$

6.4 Comparison between two geometrical isomers :



Now $K_1^m > K_1^f$

Since the conjugate base is stabilised by intramolecular H bonding.

But $K_2^f > K_2^m$ Since in maleate ion, after donation of H^{\oplus} two $-COO^{\Theta}$ groups faces each other and makes system unstable. In fumarate ion this repulsion is minimised.

6.5 Acidic strength of substituted benzoic acids :

Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

HCOOH > PhCOOH >
$$C_6H_5 - CH_2 - C - \ddot{O} - H > CH_3 - C - \ddot{O} - H$$

Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

If electron donating group present at para position than it is always less acidic than benzoic acid.



Also it is less acidic then meta substituted benzoic acid.



On the other hand if e⁻ withdrawing group is present at meta position then it is more acidic than benzoic acid.



Th7. Ortho effect :

D13. It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called ortho effect (which is combined effect of steric hindrance, crowding & electronic effect) in benzoic acid. However exceptions are seen.



Section (F) : Feasible reactions of acids and bases

Th8. Reaction of acid with salt:

(1)NaX ΗY NaY + HX + Salt of Weak acid Strong Acid

Remark: A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitates out as a solid. The weaker acid cannot displace the stronger acid from the salt.

- $2 \text{ NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ 1.
- $Na_2SO_4 + 2HCI \longrightarrow No reaction$ 2.
- $CH_3COONa + CH_3SO_3H \longrightarrow CH_3COOH + CH_3SO_3Na$ (feasible) 3.
- 4. $CH_3COONa + PhOH \longrightarrow PhONa + CH_3COOH$ (not feasible)

Section (G) : Tautomerism

Th9. Tautomerism

D14: **Definition**:

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hvdrogen.

These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

Conditions :

1. Usually present in the following functional groups



2. Basic need for its existence is attachment of these groups with the sp³ hybridised C-atom having atleast one hydrogen atom as -



To get tautomer of above structures α -hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as:



These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.





Ex.

Th10. Keto-enol tautomerisation :

10.1 (A) Base-catalyzed enolization :



Protonation of the carbanion by water on the α -carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

(B) Acid-catalyzed enolization :

Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the α -carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.



10.2 % Enol content in the carbonyl compounds :

(a) For monocarbonyl % Enol is very less

(b) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, hydrogen bonding etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(c) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.





(d) If active methylene group is more acidic then enol content will be more.

For example in acetyl acetone $(CH_3-C-CH_2-C-CH_3)$ enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group. (e) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

Th11. Racemisation and D-exchange :

Exchange of α -hydrogen from deuterium as well as racemization at the α -carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.



Th12. Other examples of tautomers (not to be done in class only for the reference of students)

(a) Imine-Enamine system :

Imine

 $R_2CH - CR = NR \implies R_2C = CR - NH - R$

Enamine

Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

(b) Nitroso-oxime system:

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.

 $\begin{array}{c} \mathsf{NO} \\ \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{NO} & \longrightarrow \\ \mathsf{Nitrosopropane} & \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH} = \mathsf{NOH} \\ \mathsf{Nitrosopropane} & \mathsf{Oxime} & \mathsf{CH}_3 - \mathsf{CH} - \mathsf{CH}_3 \\ \end{array} \xrightarrow{\mathsf{NO}}_{l} \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{NOH}}} \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{NOH}}} \mathsf{CH}_3 - \mathsf{CH}_3 - \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{NOH}}} \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{NOH}}} \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{NOH}}} \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{I}}} \mathsf{CH}_3 \\ \overset{\mathsf{I}}{\underset{\mathsf{I}}}$

Acetoneoxime

(c) Nitro-Acinitro system:

The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



Nitroform Acinitroform

The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.



(d) Lactam-Lactim system :



CHECK LIST

Definitions (D)			
D1 :	Carbanion		
D2 :	Free radicals		
D3 :	Carbocation		
D4 :	Carbenes (Divalent carbon intermediates)		
D5 :	Nitrenes		
D6 :	Benzyne		
D7 :	Arhenius base		
D8 :	Bronsted base		
D9 :	Lewis definition of acids and bases		
D10 :	Arhenius acid		
D11 :	Bronsted acid		
D12 :	Lewis definition of acids and bases		
D13 :	Ortho effect		
D14 :	Tautomerism		

Th1 :	Reaction intermediates	
Th2 :	Bases	
Th3 :	Basic strength of aromatic amines and	
	substituted anilines	
Th4 :	Solvent effect in bases	
Th5 :	Reactions of bases	
Th6 :	Acids	
Th7 :	Ortho effect	
Th8 :	Reactions of acids with salts	
Th9 :	Tautomerism	
Th10 :	Keto-enol tautomerisation	
Th11 :	Racemisation and D-exchange	
Th12 :	Other examples of tautomers	

Theories (Th)