

I. Kinetics:

1. rates \rightarrow Formation (products) \swarrow
 \rightarrow Disappearance (reactants) \searrow

2. Initial rate:

The initial rate of disappearance of a reactant R is equal to the negative of the derivative of the curve $[R]=f(t)$ at $t=0$

$$r(R)_{t=0} = \left(-\frac{d[R]}{dt} \right)_{t=0}$$

The initial rate of formation of a product P is equal to the derivative of the curve $[P]=f(t)$ at $t=0$.

$$r(P)_{t=0} = \left(\frac{d[P]}{dt} \right)_{t=0}$$

3. Instantaneous rate: at instant t
def ...

4. Average rate:

The average rate of disappearance of a reactant R within the interval of time $\Delta t = t_2 - t_1$, is equal to the negative slope of the secant that belongs to the points M_1 and M_2 on the curve $[R]=f(t)$ of abscissa t_1 and t_2 respectively. $\bar{r} = -\frac{\Delta[R]}{\Delta t}$

The average rate of formation --- positive ---

5. Half life ($t_{1/2}$)

It is the time needed to disappear half of the initial amount of the limiting reactant.

It is the time needed to form half of the maximal amount of the product.

- Find initial value from given (search for limiting)
- Find maximal amount of product by S.R.

$$\frac{[P]}{\text{coeff}} = \frac{[R]_{\text{limiting}}}{\text{coeff}}$$

6. Kinetic factors that affect the rate:

- Temperature
- Concentration
- catalyst

7. Catalyst: is a chemical substance that accelerates (speeds up) the reaction but doesn't interfere in the reaction.
It is characterized by its activity and selectivity.

8. Relation:

$$[R]_{\text{remaining}} = [R]_{\text{initial}} - [R]_{\text{reacted}}$$

$$[R]_{\text{reacted}} = [R]_{\text{limiting}} \quad \text{acc. to S.R.}$$

Note:

$$n = \frac{m}{M}, \quad n = c \times v, \quad n = \frac{v}{V_m}$$

$$M = \frac{C_m}{C}, \quad f = \frac{m}{V}, \quad \text{mass concentration } C_m = \frac{m}{V}$$

$$\% \text{ by mass} = \frac{m_s}{m_t} \times 100$$

$$\% \text{ by volume} = \frac{V_s}{V_t} \times 100$$

$$\% \text{ yield} = \frac{m_{\text{exp}}}{m_{\text{theo}}} \times 100$$



www.tollablebenn.com

9. Dilution:

During dilution number of mole of solute (n_{solute}) is conserved

$$n_{\text{before dilution}} = n_{\text{after dilution}}$$

$$C_0 V_0 = C_1 V_1$$

a. Precautions: wash the glassware using distilled water and dry them well

b. Glassware:

- i. Liquid:
 - Volumetric pipet $\rightarrow V_0$
 - Volumetric flask $\rightarrow V_1$
- ii. Solid:
 - spatula
 - Spring balance
 - Volumetric flask
 -

c. Procedure:

- Take (V_0) from commercial solution s. using a volumetric pipet
- Pour this volume into a (V_1) volumetric flask
- Add water to the line mark
- Shake well to homogenize the solution

d. Dilution factor: (no. of times) $F = \frac{C_0}{C_1} = \frac{V_1}{V_0}$

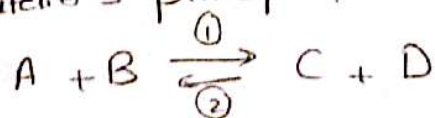
- Note: if given $V_0 = 20$ mL
choose the correct glassware:
- volumetric pipet 30 mL X
 - graduated pipet 30 mL ✓

II. Chemical Equilibrium:

- equilibrium constant $k_c = \frac{[P_1]^c \times [P_2]^d}{[R_1]^a \times [R_2]^b}$

- if Q is given, find k_c and compare:
 - if $k_c = Q \Rightarrow$ equilibrium
 - if $k_c \neq Q \Rightarrow$ not at equilibrium

- Le chatelier's principle:



$[C] \uparrow \Rightarrow$ According to Le chatelier equilibrium is shifted in direction 2 to $\rightarrow [C]$.

Note: Adding a catalyst increases the rate of the reaction in both directions in such a way that it enables the equilibrium to be attained more rapidly with no effect on the equilibrium state.

- Degree of dissociation α :

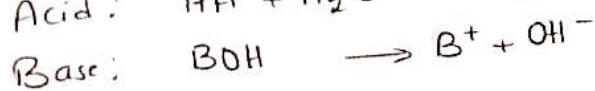
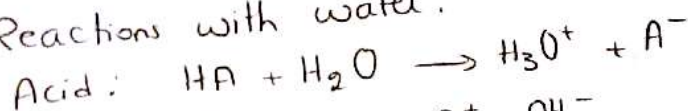
$$\alpha = \frac{\text{Quantity dissociated}}{\text{initial quantity}} = \frac{x}{n_0} = \frac{[]_{\text{diss}}}{[]_{\text{init}}}$$

$$\text{if (in \%)} \rightarrow \alpha = \frac{x}{n_0} \times 100$$

III. Strong Acid & Strong Base

- Acid : dissociates in water to give H^+ ions
- Base : dissociates in water to give HO^- ions

• Reactions with water :



• Strong Acid :

$$pH = -\log [H_3O^+]$$

$$pH = -\log C_a$$

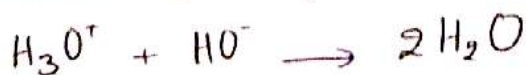
$$[H_3O^+] = 10^{-pH}$$

$$K_w = [H_3O^+][HO^-] = 10^{-14} = 10^{-pK_w} \Rightarrow pK_w = -\log K_w = 14$$

• Strong base :

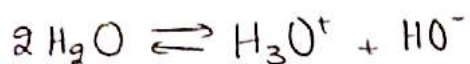
$$pH = pK_w + \log C_b \quad / \quad pH = 14 + \log [HO^-]$$

• Reaction between strong acid & strong base = neutralization reaction (complete - instantaneous - exothermic)



- Why do we perform dilution before titration?
 1. to immerse the electrodes of the pH meter (accurate measurement)
 2. Not to fill the buret several times to reach equilibrium (reducing error)
 3. Economic factor
 4. To reduce the effect of strong acid & strong base

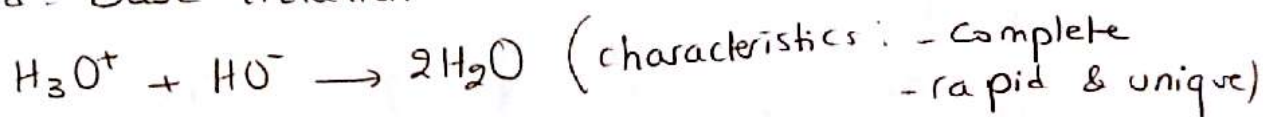
• Auto ionization of water:



$$K_w = \frac{[\text{H}_3\text{O}^+][\text{HO}^-]}{[\text{H}_2\text{O}]^2} \quad [\text{H}_2\text{O}] \rightarrow \text{constant}$$

$$\Rightarrow K_w = [\text{H}_3\text{O}^+][\text{HO}^-] = 10^{-14}$$

• Acid - base titration:



• Role of pH meter:

allows us to determine the volume of basic solution reacted to neutralize a certain volume of an acidic solution.

Note: Addition of distilled water to the titrated solution doesn't affect the equivalence point.

Titration: Addition of Base to Acid or Acid to Base to reach equivalence.

Base to Acid \Rightarrow Base in buret, acid in beaker

Acid to base \Rightarrow acid in buret, base in beaker

Glassware: buret - beaker - magnetic stirrer.

During titration reactants react in stoichiometric proportions

$$n_{\text{acid in beaker}} = n_{\text{base in buret}}$$

$$C_a V_a = C_b V_{bE} \quad (\text{we can calculate } V \text{ at equivalence point})$$

or graphically, using parallel tangent method we can detect the equivalence point.

Note: if the experiment is performed at high temp, then $t_{1/2} \downarrow$ since T is a kinetic factor

Note: if $f = 9 \text{ g/L}$

$$\Rightarrow m_t = 9 \text{ g}$$

$$v = 1 \text{ L} = 1000 \text{ mL}$$

if you are asked to prepare a solution of $v = 250 \text{ mL}$

then $9 \text{ g} \rightarrow 1000 \text{ mL}$
 $? \rightarrow 250 \text{ mL}$

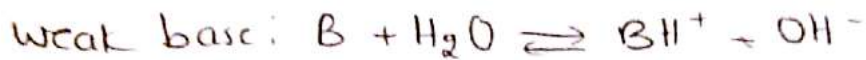
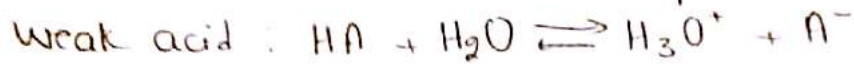
$$\frac{250 \times 9}{1000} = 2.25 \text{ g}$$

Procedure:

- weigh 2.25 g of powder using a digital balance
- put them in a volumetric flask (250 mL)
- Add water and agitate well to dissolve the powder in the flask
- Add water to the line mark

IV. Weak acid & weak base

- Reactions with water: (incomplete dissociation)



- as $k_a \uparrow \Rightarrow$ acid is stronger - conjugate base is weaker

$$\text{p}K_a = -\log k_a$$

$\Rightarrow \text{p}K_a \uparrow \Rightarrow$ acid is weakest, base is strongest

- if $k_r > 10^4 \rightarrow$ complete reaction
 $k_r < 10^4 \rightarrow$ incomplete reaction

$$k_a = \frac{[\text{B}][\text{H}_3\text{O}^+]}{[\text{A}]}$$

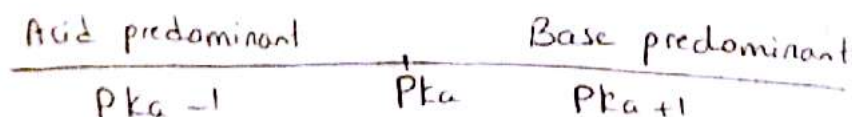
- if $k_r > 1 \rightarrow$ Forward direction
 $k_r < 1 \rightarrow$ backward direction
 $k_r = 1 \rightarrow$ no reaction

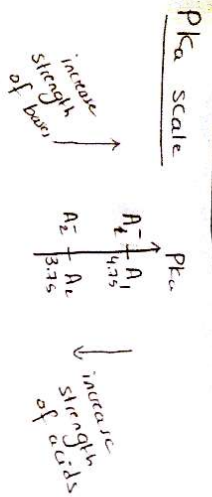
$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}]}{[\text{A}]}$$

if $[\text{B}] = [\text{A}] \Rightarrow \text{pH} = \text{p}K_a$ (half equivalence)

if $\text{pH} < \text{p}K_a - 1 \Rightarrow$ acid A is predominant
 $[\text{A}] > 10[\text{B}]$

if $\text{pH} > \text{p}K_a + 1 \Rightarrow$ base B is predominant
 $[\text{B}] > 10[\text{A}]$





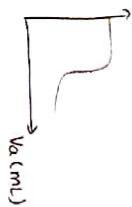
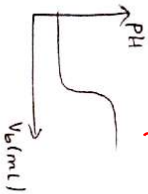
• K_r : acid/base reaction:

$$K_r = \frac{[B_1][A_2] \times [H_3O^+]}{[A_1][B_2][H_3O^+]} = \frac{K_{a1}}{K_{a2}}$$

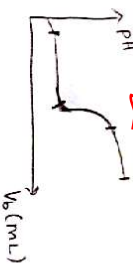
• Note: Complete = quantitative

• Note: Curves;

→ 3 parts with 1 inflection point ⇒ strong acid / strong base



→ 4 parts with 2 inflection points ⇒ weak acid / strong base



half equivalence = consumption of half of the amount of acids / base

$$PH = Pka \quad \text{and} \quad V = \frac{V_{BE}}{2} \quad (\text{Graphically})$$

at equivalence

$$n_a = n_b$$

$$C_a V_a = C_b V_{BE}$$

$$n_b = n_a$$

$$C_b V_b = C_a V_a$$

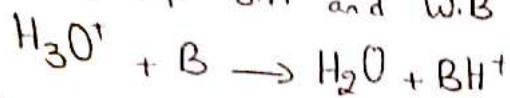
Note: For the reaction between weak acid and strong base, the PH at equivalence is > 7 .

For reaction between weak base and strong acid, PH < 7 at equivalence.

General Notes

- After dilution 10 times pH increases 1 unit in a strong acid
- If the rate of formation \downarrow as a function of time, then the kinetic factor that is responsible for this variation is the concentration because $[]$ of the limiting reactant \downarrow to 0 at the end of the reaction.

- Titration of S.A and W.B



$$K_R = \frac{[\text{BH}^+]}{[\text{H}_3\text{O}^+][\text{B}]} = \frac{1}{K_a} = 10^{\text{p}K_a} \quad 10^{\text{p}K_a} \geq 10^4 \\ \Rightarrow \text{p}K_a \geq 4$$

- Titration of S.B and W.A



$$K_R = \frac{[\text{A}^-]}{[\text{HA}][\text{HO}^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{K_a}{K_w}$$

$$K_R = 10^{14 - \text{p}K_a} \geq 10^4$$

$$\Rightarrow \text{p}K_a \leq 10 \Rightarrow \text{reaction complete}$$

- Effect of concentration (strong base - weak acid)

- with dilution $[] \downarrow$

- pH (initial) \uparrow

- $\frac{1}{2}$ eq is not affected

- jump decreases

- eq \downarrow but remains pH > 7 (basic)

- Effect of $[]$ (strong acid - weak base)

- with dilution $[] \downarrow$

- pH \downarrow

- $\frac{1}{2}$ eq doesn't change

- eq is affected

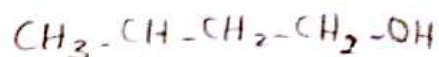
- jump \uparrow

• Alcohols

- OH (hydroxyl)

name: alkane \rightarrow alcohol

Primary: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$: 1-butanol



3-methyl-1-butanol

Secondary: $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$

4-ethyl-5-methyl-2-hexanol

Tertiary: $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}} - \text{CH}_3$: 2-methyl-2-propanol

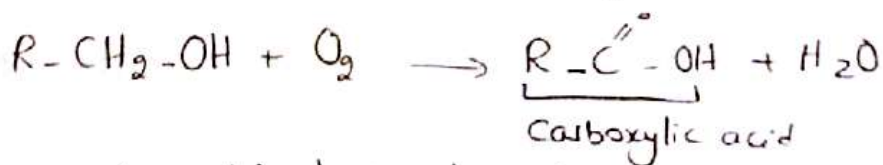
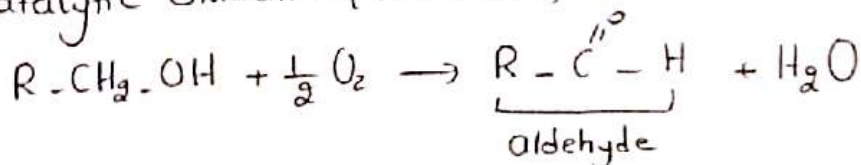
- Isomers: - positional \rightarrow position of F.G
- skeletal \rightarrow structure

The solubility of alcohol \downarrow as $C \uparrow$
Boiling pt \uparrow as n° of $C \uparrow$

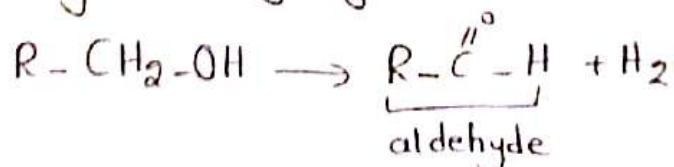
Reactions

1. Primary alcohols

a. Catalytic oxidation (exothermic)

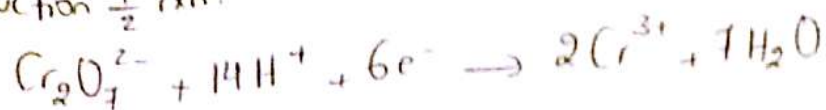


b. Catalytic dehydrogenation: (endothermic)

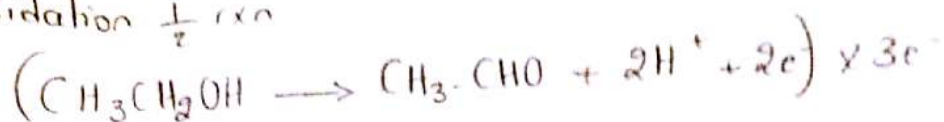


c. oxidation by oxidant: $(\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+})$
reduction

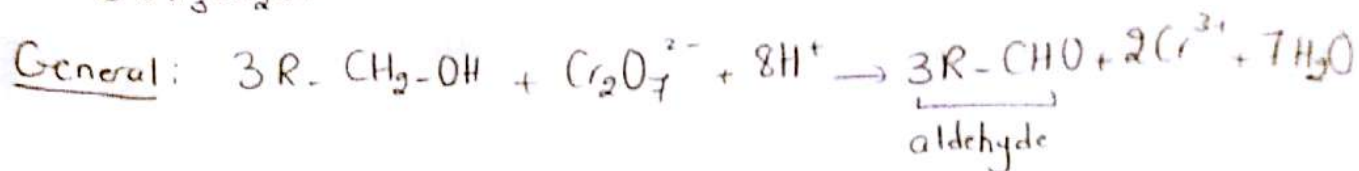
reduction $\frac{1}{2}$ rxn:



Oxidation $\frac{1}{2}$ rxn

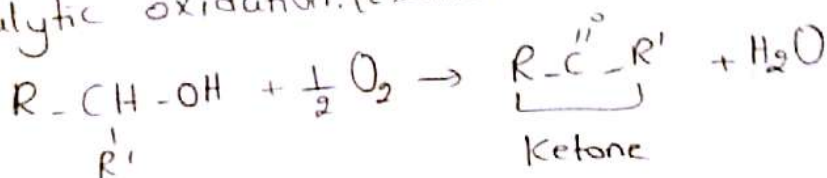


Overall rxn:

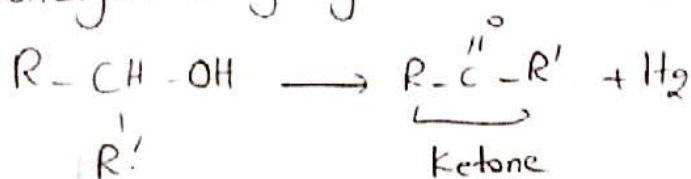


2. Secondary Alcohols

a. Catalytic oxidation: (exothermic)



b. Catalytic dehydrogenation (endothermic)

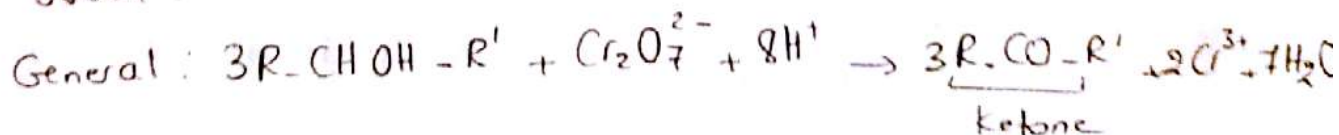


c. Oxidation by oxidant:

reduction —



overall . .



3. Tertiary Alcohols

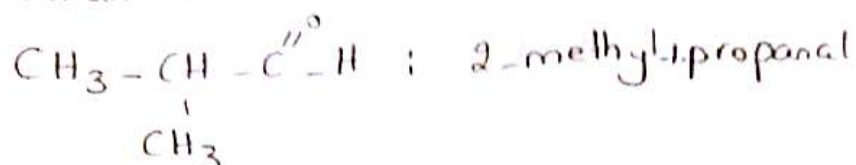
No reactions

- Esterification: formation of ester
 $\text{alcohol} + \text{acetic acid} \rightleftharpoons \text{ester} + \text{water}$
- $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^-$ (acts as a catalyst without changing yield)
 \rightarrow in large quantities, catalyst \rightarrow yield of esterification reaction, \uparrow rate
- Role of reflux heat, increases the T thus \uparrow the rate of esterification rxn (acts as dehydrating agent).
- Role of condenser, condenses the vapors that prevent the loss of components by condensing the vapor, hence minimizing loss upon heating
- $K_c = 4 \rightarrow 1^\circ$ alcohol \rightarrow yield = 66-67%
- $K_c = 2.0 \rightarrow 2^\circ$ alcohol \rightarrow yield = 60%
- $K_c = 0 \rightarrow 3^\circ$ alcohol \rightarrow yield smaller
- The yield of reaction is proportional to the experimental mass of ester. When part of this mass is lost the % of yield \downarrow .
- The temperature is a kinetic factor but doesn't shift equilibrium since it is an athermic reaction so it increases the rate of rxn in both directions and doesn't change the yield.
- Esterification reaction is:
 - athermic
 - incomplete
 - slow

• Aldehydes and Ketones

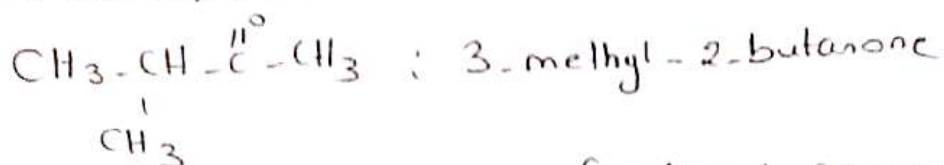
1. Aldehyde: $R-C(=O)-H$ ($C_nH_{2n}O$) $C(=O) \rightarrow$ carbonyl group

Alkane \rightarrow alkanal



2. Ketone: $R-C(=O)-R'$ ($C_nH_{2n}O$)

Alkane \rightarrow Alkanone



• aldehydes and ketones are functional isomers
aldehydes have no positional isomers

• boiling pt \uparrow as n° of C \uparrow
solubility \downarrow as n° of C \uparrow

• Aldehydes are more reactive than ketones

• Reactions

1. Addition Rxns

• Reaction with $NaHSO_3$: to identify presence of carbonyl group
(aldehyde / ketone)

• Reaction with DNPH: to separate aldehydes & ketones from
other substances (presence of carbonyl group)
it gives yellow orange precipitate

• Hydrogenation reaction:

Aldehyde + $H_2 \rightarrow$ primary alcohol

Ketone + $H_2 \rightarrow$ secondary alcohol

2. Mild oxidation of aldehydes:

1. Oxidation with $K_2Cr_2O_7$

Aldehyde \rightarrow Carboxylic acid

Color \rightarrow orange due to presence of $Cr_2O_7^{2-}$ (before)

\rightarrow green due to presence of Cr^{3+} (after)

2. Oxidation with ammoniacal silver nitrate (Tollen's reagent)

Before \rightarrow After

Colorless

Black

formation of silver

3. Oxidation with Fehling solution (basic)

Before \rightarrow after

blue

brick red precipitate

3. Mild oxidation of ketones

No change in color \rightarrow no reaction

• Schiff's reagent:

Aldehyde + Schiff's reagent \rightarrow pink color

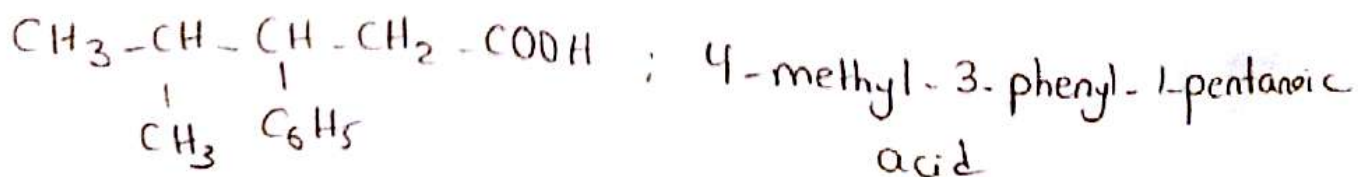
Ketone + Schiff's reagent \rightarrow no change

Note: Mild oxidation allows us to distinguish between aldehydes & ketones

• Carboxylic acid and derivatives

Carboxylic acid: $R-COOH$ ($C_nH_{2n}O_2$)

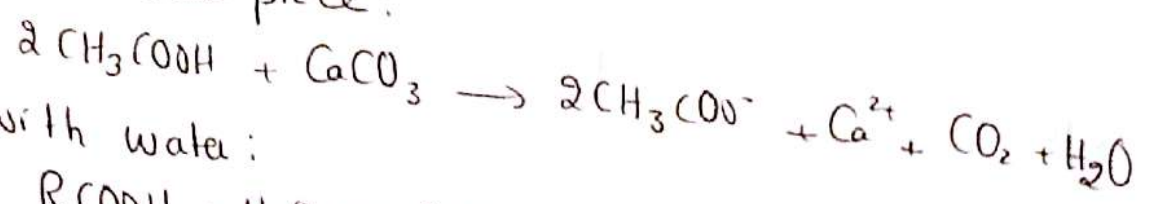
Alkane \rightarrow alkanic acid



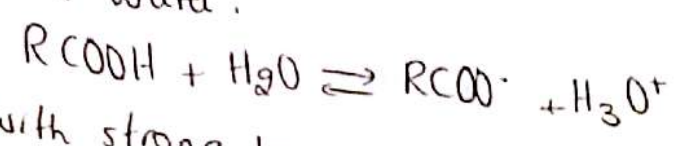
- As n° of C ↑ : boiling pt ↑, solubility ↓
- presence of H bond → boiling pt

Chemical reactions:

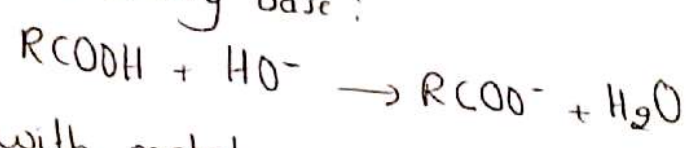
1. With marble piece:



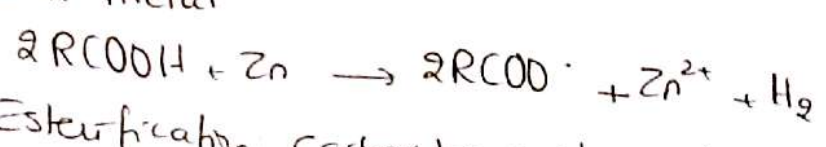
2. With water:



3. With strong base:



4. with metal

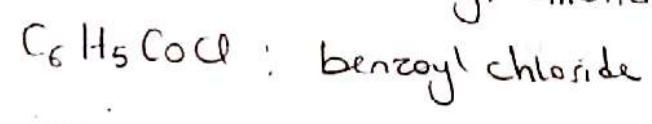
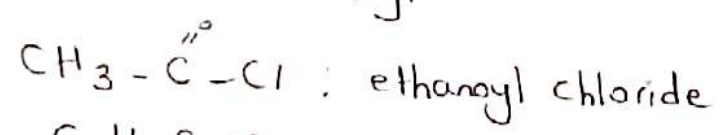


5. Esterification: Carboxylic acid + alcohol \rightleftharpoons ester + water

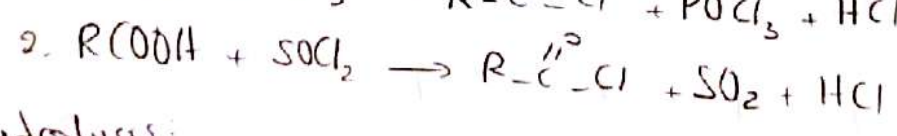
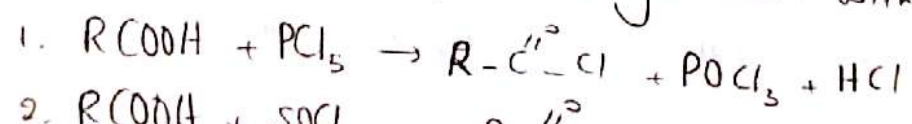
Derivatives (-OH is replaced by an atom)

1. Acylchlorides ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$: $\text{C}_n\text{H}_{2n-1}\text{OCl}$)

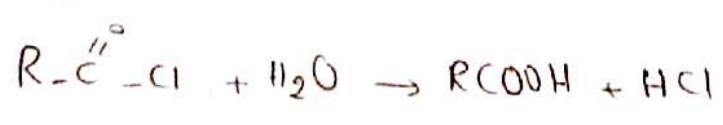
ethanoic → ethanoyl



• Obtained from rxn of carboxylic acid with PCl_5 or SOCl_2

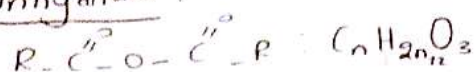


- Hydrolysis:

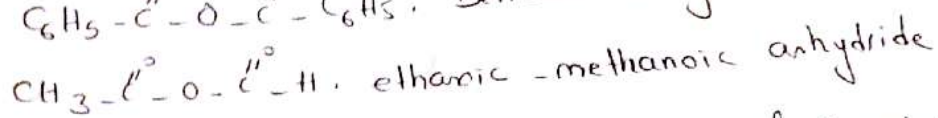
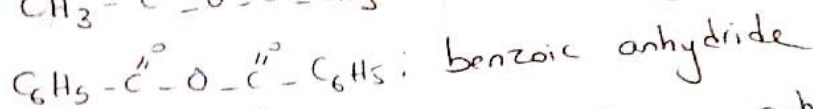
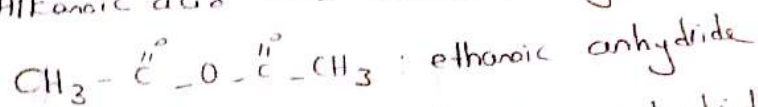


- Reaction is:
- fast
 - complete
 - exothermic
 - reactive

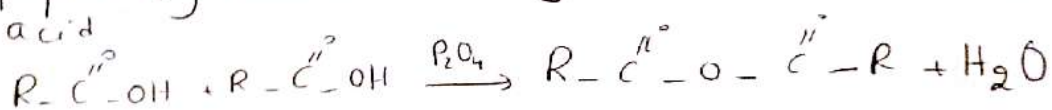
2. Anhydrides :



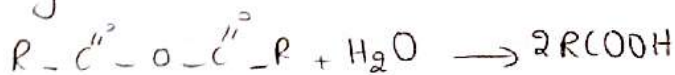
Alkanoic acid \rightarrow alkanic anhydride



- Prepared by intermolecular dehydration of 2 molecules of acid

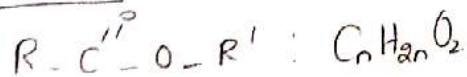


- Hydrolysis:

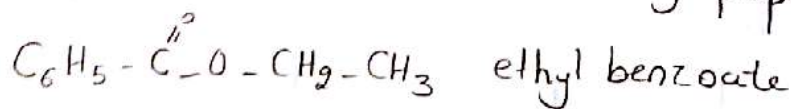
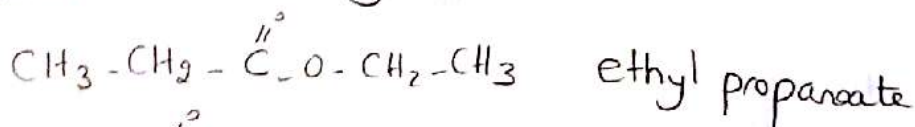


Reaction is: - slower
- less reactive than acyl chlorides

3. Esters



Alkanoic acid \rightarrow Alkyl alkanoate



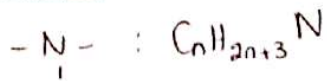
- Prepared by esterification reaction

- Hydrolysis:

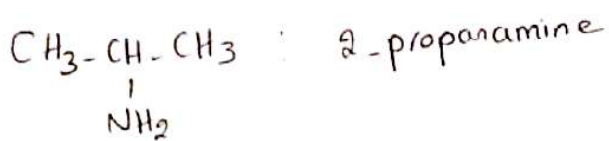
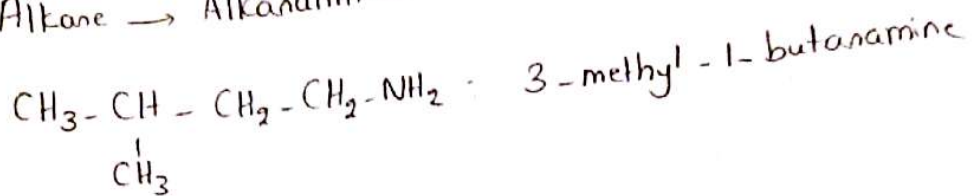


• Amines and α amino acids

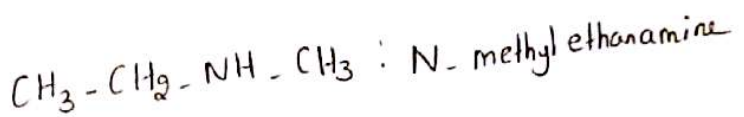
• Amine :



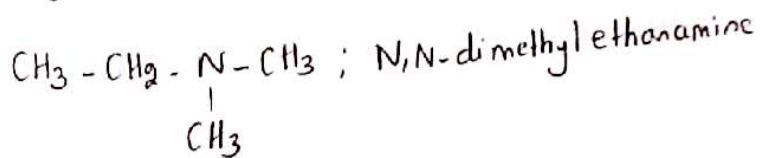
Alkane \rightarrow Alkanamine



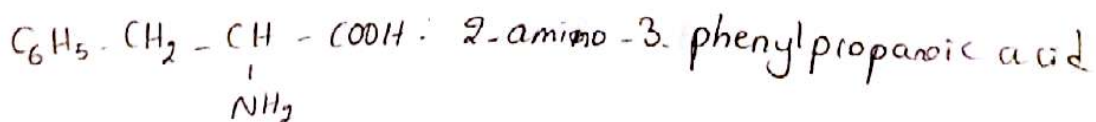
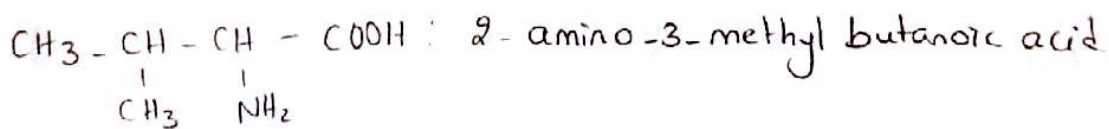
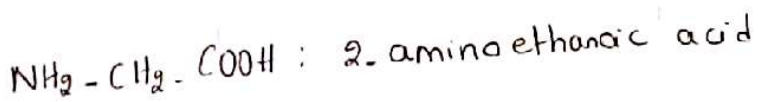
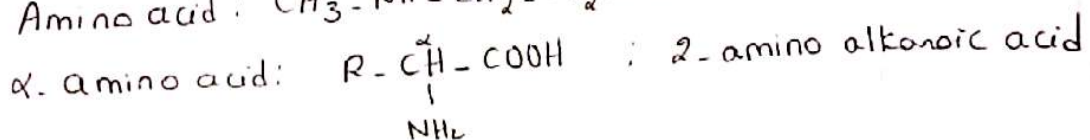
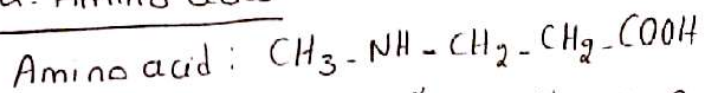
• Primary R-NH₂
Secondary R-NH



Tertiary R-N-R'
R''

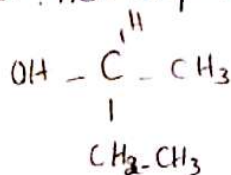


• α . Amino acids



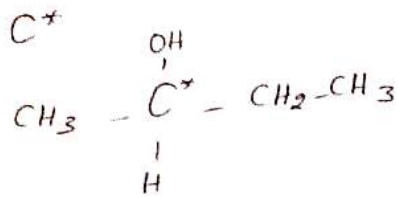
• Enantiomerism

Chiral : non-superimposable on its mirror image

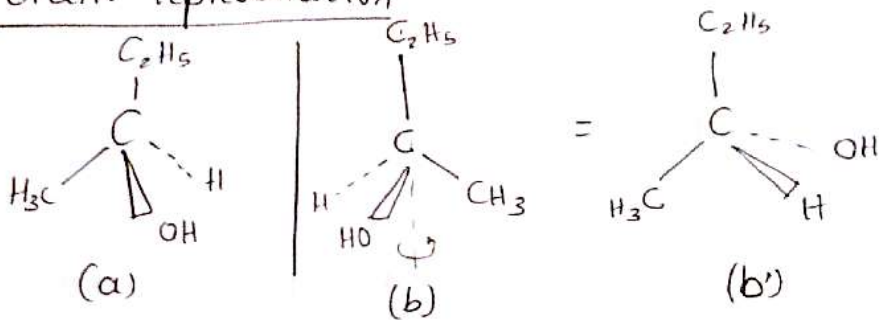


else it is achiral .

• Asymmetric carbon: attached to four different atoms



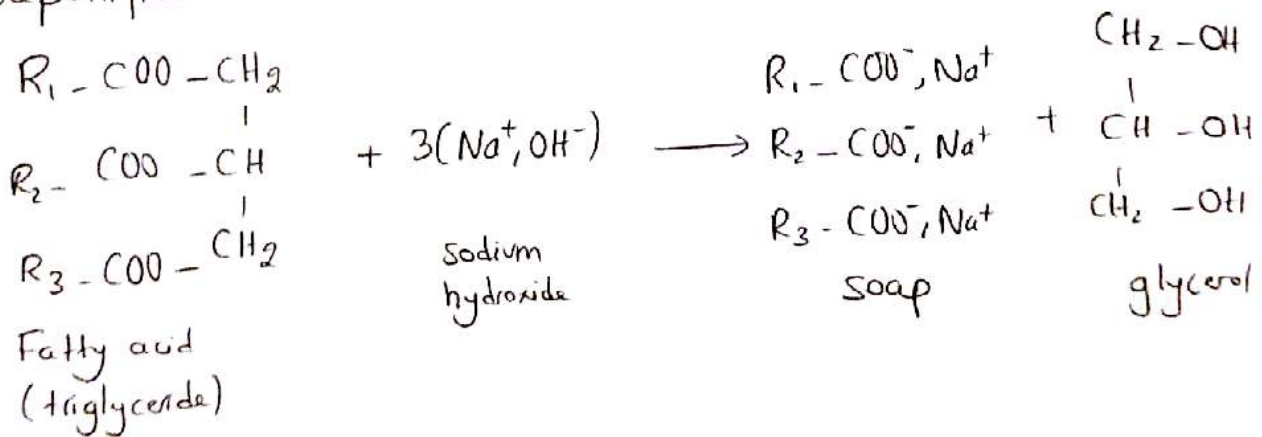
Cram representation



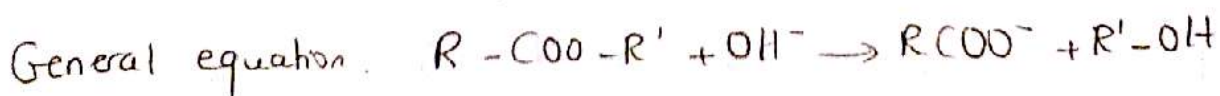
(a) & (b) are enantiomers = mirror images
 (b) & (b') are identical = rotating 180°

• Soaps and detergents

Saponification reaction:



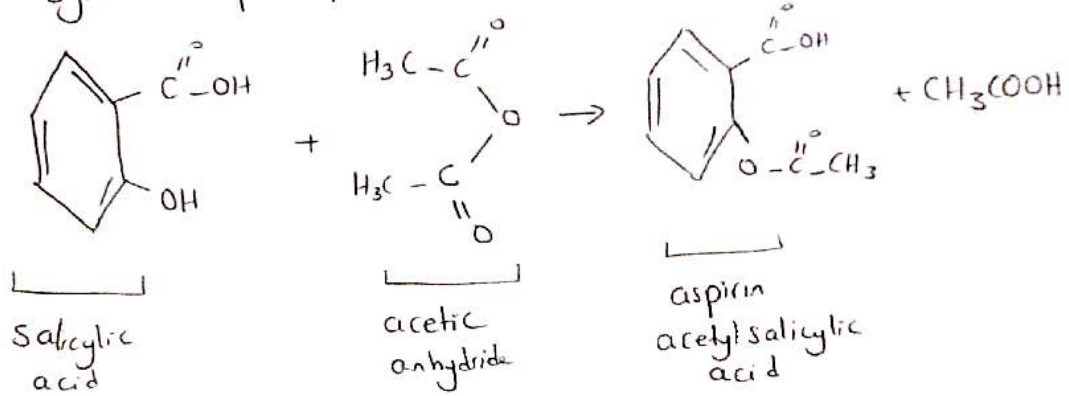
- Characteristics:
- at high T
 - Soaps are hard from NaOH
 - Soaps are soft from KOH



- Reaction is:
- Complete
 - Slow
 - at 80°C to ↑ its rate

Current Medicinal Drugs

- Drugs → therapeutic purposes
- Analgesic → relieves pain
- Hemisynthesis of aspirin:



Don't forget to read the detailed explanation on C.B.

**TOLLAB
LEB NEN**

www.tollablebnen.com

Fly in the plane of ambition
Land in the airport of success
The luck's yours, the wish
is mine ;
May your future always
shine

Good Luck

Soukainah Rashid