ALDEHYDES, KETONES AND CARRBOXYLIC ACIDS CHEMICAL PROPERTIES OF CARBOXYLIC ACID

CHEMICAL PROPERTIES OF CARBOXYLIC ACID

1. Acidity of carboxylic acid: Acidity refers to the ease with which a substance donates a proton, resulting in the formation of an anion. The strength of an acid is determined by the disparity in stability between the acid and its corresponding anion.



Non-equivalent structures of Resonance hybrid

Equivalent structures of Resonance hybrid

Both the acid and its anion benefit from resonance stabilization, but the anion experiences significantly greater stabilization because it can generate two identical resonating structures.

- 2. Effect of substituents on Acidity: Any factor that provides more stability to the anion compared to the acid will enhance the acidity, while any factor that reduces the stability of the anion will lower the acidity of the carboxylic acid.
 - (a) Electron-withdrawing substituents enhance anion stability by dispersing the negative charge, thereby increasing the acidity of the carboxylic acid.
 - (b) Electron-releasing substituents increase the negative charge on the anion, reducing the stability of the carboxylate anion, and consequently decreasing the acidity of the acid.

Carboxylic acids are considered weak acids, and their carboxylate ions are strong conjugate bases. They exhibit slight alkalinity due to the hydrolysis of the carboxylate anion in comparison to other species. The order of acidity and basicity of their corresponding conjugate bases is as follows.

Acidity --RCOOH > HOH > ROH > CH = CH > NH₃ > RH

Basicity $--RCOO^- < OH^- < HC \equiv C^- < NH_2^- < R^-$



The impact of different numbers of substituents and their distances from the carboxyl group is demonstrated through the following examples.

(i) The influence of the number of substituents is evident in chloro-substituted acetic acids, where the acid strength follows the order provided below.

 $ClCH_2 - COOH < Cl_2CHCOOH < Cl_3CCOOH$

An increase in the number of chlorine substituents on the α -carbon atom of acetic acid intensifies the electron-withdrawing effect, leading to greater stability of the carboxylate ion. Conversely, when electron-releasing substituents are connected to the carboxylic group, the acid strength diminishes as the strength of electron release increases.

$$R \rightarrow CH_2 \rightarrow COOH > R \rightarrow CH \rightarrow COOH > R \rightarrow COOH \\ R \rightarrow COOH$$

(ii) The impact of the substituent's nature is exemplified by a range of halo acetic acids, and their acid strength can be ranked as follows.

(iii) Effect of the position of the substituent: The effect of the substituent decreases as its distance from —COOH group increases.



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Ortho Effect: The Ortho-substituted benzoic acid, regardless of whether the substituent is electron-withdrawing or electron-releasing, exhibits higher acidity compared to its para and meta isomers. This phenomenon is referred to as the ortho effect, and it arises from the combined effects of steric hindrance and intramolecular hydrogen bonding. This effect occurs whenever the opportunity arises to stabilize the carboxylate anion due to the proximity of the substituent. Groups such as -OH, -Cl, and -NO₂ provide even greater stabilization to the anion through direct interaction via intramolecular hydrogen bonding.





Order of acidic character

Reaction due to cleavage of --O--H bond as acid

(i) Reaction with active metals [alkali and alkaline metal]

$$R \xrightarrow{O} OH + Na \longrightarrow R \xrightarrow{O} ONa + H_2 (\uparrow)$$

(ii) Reaction with CaO

2R -COOH + CaO \longrightarrow (RCOO)₂Ca + H₂O

Chemistry

(iii) Reaction with Bicarbonates and Carbonates

Carboxylic acid reacts with carbonates and bicarbonates to liberate $\rm CO_2$ gas

$$R \xrightarrow{COOH} \xrightarrow{NaHCO_3} \xrightarrow{R} \xrightarrow{O} \\ R \xrightarrow{II} \\ CaCO_3 \\ CaCO_3 \\ CaCO_2 \\ CaC$$

REACTION INVOLVING CLEAVAGE OF -OH GROUP

Esterification

When carboxylic acid reacts with alcohol in the presence of conc. H_2SO_4 to form ester,

it is known as esterification

$$\begin{array}{c} R \longrightarrow C \longrightarrow OH + R \longrightarrow OH \\ 0 \end{array} \xrightarrow{\text{Conc. } H_2SO_4} \qquad R \longrightarrow C \longrightarrow OR + H_2O \\ 0 \\ 0 \\ 0 \end{array}$$

MECHANISM

The reactivity of alcohols in the formation of esters is significantly influenced by their structure. When there are bulkier substituents near the -OH group, the reaction proceeds more slowly. This observation holds true for acid-catalyzed reactions as well.

 $CH_3OH > CH_3CH_2OH > (CH_3)_2 CHOH > (CH_3)_3 COH$ H--COOH > $CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

Class-12th

Formation of acid chloride

$$R = COOH \xrightarrow{+ PCl_{5}} R = COCl + HCl + POCl_{3}$$

$$R = COOH \xrightarrow{+ SOCl_{2}} R = COCl + SO + HCl$$

$$C_{5}H_{5}N$$

$$R = COCl + SO_{3} + HCl$$

$$C_{5}H_{5}N$$

Formation of Acid Anhydride: When carboxylic acids are subjected to a dehydrating agent such as P_2O_5 , they undergo a reaction that leads to the formation of an anhydride through the elimination of a water molecule.



Formation of Amides

$$\begin{array}{c} 0 \\ \parallel \\ R - C - OH + MeNH_2 \end{array} \longrightarrow \begin{bmatrix} 0 \\ \parallel \\ R - C - \overline{O} \end{bmatrix} \begin{array}{c} \bigoplus \\ NH_3Me \end{array} \xrightarrow{heat} \begin{array}{c} 0 \\ -H_2O \end{array} \xrightarrow{Heat} \begin{array}{c} 0 \\ R - C - NH \\ \parallel \\ Me \end{array}$$

The lone pair of electrons on the nitrogen atom participates in resonance, resulting in the presence of a partial positive charge on the nitrogen atom.



As a result, the degree of hydrogen bonding increases, leading to higher boiling and melting points for amides compared to other types of acid derivatives.

REACTIONS INVOLVING – COOH GROUP

Schmidt Reaction:

Carboxylic acids, when combined with hydrazoic acid in the presence of concentrated H₂SO₄ at 90°C, result in the production of primary amines.

 $R - COOH + N_{3}H \xrightarrow{Conc.H_{2}SO_{4}} R - NH_{2} + N_{2} + CO_{2}$

MECHANISM



3. Soda lime Decarboxylation: When carboxylic acids are subjected to heating with soda lime (a mixture of NaOH and CaO), they undergo a transformation, resulting in the formation of an alkane with one fewer carbon atom than the original acid.

$$R---COOH \quad \frac{Soda \ lime}{\Delta} \rightarrow \quad R--H + CO_2$$

Hunsdicker Reaction:

$$R--COOH \xrightarrow{Ag_2O} R--COO^- Ag^+ \xrightarrow{Br_2} R--Br + AgBr + CO_2$$

MECHANISM

Reaction proceeds through free radical mechanism in various steps.

(i) Chain initiation



(iii)

 CH_3





 $\begin{array}{c} \text{CH3MgBr} & \oplus & \Theta \\ \hline \text{RCOOH} & \longrightarrow & \text{RCOO} & \text{MgBr} + & \text{CH}_4 \end{array}$ CH₃Li $\begin{array}{c} & \bullet \\ R & - \\ \hline & COO & Li + CH_4 \end{array}$

 CH_3

2 moles of organometallic compounds are needed to form ketone.

 CH_3

Acetone

Hell-Volhard-Zelinsky Reaction:

This is α -halogenation of a carboxylic acid.



Possible Mechanism for the reaction is

$$H_{3}C COOH \xrightarrow{PBr_{3}} H_{3}C COBr \xrightarrow{-Br_{2}} H_{3}C COBr \xrightarrow{H_{2}O} H_{3}C COOH$$

PBr₃ is employed with the aim of converting -OH groups into -Br groups, enhancing the acidity of the alpha-hydrogen atoms, which are then substituted with bromine atoms from Br₂.



This reaction progresses beyond mono-substitution and continues until all the alphahydrogen atoms have been replaced. The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.

Heating of β -keto acid:

$$\begin{array}{cccc}
0 & 0 \\
|| & || \\
C & -CH_2C & -OH \xrightarrow{100-150^{\circ}C} R & -CH_3 & -CO_2 \\
\beta & - \text{Keto acid} & \end{array}$$

There are two facts on which ease of decarboxylation depends.

(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.



This anion is much more stable than the anion formed by decarboxylation of an ordinary carboxylic acid anion.

(ii) When the acid undergoes decarboxylation, this process can occur through a sixmembered cyclic transition state. Upon heating alone or in the presence of a base, a β-keto acid experiences the swift elimination of CO₂.





Chemistry

(iii)



8. Reaction of α , β and γ halo carboxylic acid with aq. NaOH



Cyclization of γ haloacid

Heating of Dicarboxylic Acids:





Oxidation of Carboxylic acid at Alkyl Group:

Acid on treatment with mild oxidising agent such as H_2O_2 , is oxidized at the β position.



Oxidation can also occur at α carbon atom on treatment with oxidizing agent like selenium dioxide SeO₂.

$$RCH_{2}COOH + [0] \frac{seo_{2}}{\Delta} \rightarrow \alpha Keto acid$$

Abnormal Behaviour of Formic Acid: Formic acid exhibits distinct behavior compared to other carboxylic acids due to the presence of an aldehydic group.



Reaction with

(a) Tolle's reagents: Formic acid behaves as a reducing agent and reduces Tolle's reagent or Fehling solution. But others acid fails to do so.

H-COOH + Ag₂O → CO₂ + H₂O + 2Ag
$$\downarrow$$
 Silver mirror
H-COOH + 2CuO → CO₂ + H₂O + Cu₂O \downarrow Red ppt.

(b) Reaction with HgCl₂: Formic acid reacts with HgCl₂ to produce a white precipitate of Hg₂Cl₂, which can be transformed into a gray precipitate of mercury.

 $2HCOOH + HgCl_2 \longrightarrow CO_2 + Hg_2Cl_2 \downarrow + 2HCl$

white ppt.

Applications of Formic Acid:

- (i) Employed as an antiseptic.
- (ii) Utilized for fruit preservation.
- (iii) Involved in leather tanning.
- (iv) Used in dyeing wool and cotton textiles.
- (v) Serves as a coagulating agent for rubber.
- (vi) Applied in the hydrogenation of oil, often in the form of Ni-format.

Applications of Acetic Acid:

- (i) Found in vinegar, commonly as a 6-10% solution, used for culinary purposes and in pickle production.
- (ii) In its salt forms, it is employed in medicine and the paint industry.
- (iii) Used as a coagulant for the manufacture of rubber from latex and casein from milk.
- (iv) Aluminum and chromium acetates are used as mordants.
- (v) Essential in the production of dyes and perfumes.
- (vi) Functions as a solvent and laboratory reagent.