What is a Functional Group

substituent or moiety in a molecule that causes the molecule's characteristic chemical reactions.

Functional Groups - The Main Players





alkane

alkene

alkyne

·H





aldehvde

•• -N(H,R)₂

alcohol

ether



alkyl halide

thiol











amide

ketone

ester

carboxylic

acid

Carboxylic Acids and their Derivatives

Dr. Ghanshyam L Jadav Assistant professor Chemistry department

Table of content



INTRODUCTION

Name and History

Nomenclature

Name of acids and structure

Structure & Preparations

Structural arrangment preparation

Properties & Derivatives

Physical and Chemical Properties Derivatives INTRODUCTION carboxyl functional group, -COOH carbonyl group attached to a hydroxyl group

Classification

□aliphatic (RCOOH) or aromatic (ArCOOH) □higher members of aliphatic carboxylic acids (C12 – C18) known as **fatty acids**

Nomenclature

➢isolated from nature

common names end with the suffix –oic acid
Latin or Greek names of their natural sources

For example

Formic acid (HCOOH) was first obtained from red ants (Latin: formica means ant) Acetic acid (CH3COOH) from vinegar (Latin: acetum, means vinegar) Butyric acid (CH3CH2CH2COOH) from rancid butter (Latin: *butyrum*, means butter)

R. CLIMDAN **IUPAC!**

International Union of Pure and Applied Chemistry

-e in the name of the corresponding alkane with - oic acid the carboxylic carbon is numbered one The number of carboxyl groups are indicated by adding the multiplicative prefix, di, tri, etc. to the term oic

Structure	Common name	IUPAC name
НСООН	Formic acid	Methanoic acid
CH ₃ COOH	Acetic acid	Ethanoic acid
CH ₃ CH ₂ COOH	Propionic acid	Propanoic acid
CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Butanoic acid
(CH ₃) ₂ CHCOOH	Isobutyric acid	2-Methylpropanoic acid
НООС-СООН	Oxalic acid	Ethanedioic acid
HOOC -CH ₂ -COOH	Malonic acid	Propanedioic acid
HOOC -(CH ₂) ₂ -COOH	Succinic acid	Butanedioic acid
HOOC -(CH ₂) ₃ -COOH	Glutaric acid	Pentanedioic acid
HOOC -(CH ₂) ₄ -COOH	Adipic acid	Hexanedioic acid
HOOC -CH ₂ -CH(COOH)-CH ₂ -COOH	-	Propane-1, 2, 3- tricarboxylic acid





Structore of Carboxyl Group

Arrangment of Elements

The bonds to the carboxyl carbon lie in one plane and are separated by about 120

The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below





Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.

 \rightarrow RCOOH + $\overline{C1}$

 $\overline{OH/H_2O} \rightarrow RCOO^- + \overline{Cl} \xrightarrow{H_3O^+} RCOOH$

 $(C_6H_5CO)_2O \xrightarrow{H_2O} 2 C_6H_5COOH$ Benzoic anhydride

 H_2O

Benzoic acid

 $C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH$

Benzoic ethanoic

anhydride

RCOC

Hydrolysis from

acid derivatives

Benzoic acid

CH₃COOH

Ethanoic acid

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids

COOC ₂ H ₅	$\xrightarrow{H_3O^+}$	+		C_2H_5	ОН
Ethyl benzoate		Benzoic acid			
CH ₃ CH ₂ CH ₂ COOC ₂ H ₅ : Ethyl butanoate	NaOH	$CH_{3}CH_{2}CH_{2}COONa$ $H_{3}O^{+}$ $CH_{3}CH_{2}CH_{2}COOF$ Butanoic acid	H	+	C ₂ H ₅ OH

or cruphy



Physical Appearance and smell



due to their low volatility

State

02

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature. The higher acids are wax like solids. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



aprotic solvent

Hydrogen bonding of RCOOH with H₂O



Reactions of monocar oxylic acids

Salt formation
Decarboxylation
Halogenation – Hell Volhard Zelinsky Reaction

Salt formation

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogen carbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

 $\begin{array}{c} \hline \mathbf{OOOH} + 2Na \longrightarrow 2R \cdot \mathbf{COONa}^{\dagger} + H_2 \\ \text{Sodium carboxylate} \end{array}$

 $R-COOH + NaOH \longrightarrow R-COONa^{\dagger} + H_2O$

 $R-COOH + NaHCO_3 \longrightarrow R-COONa^+ + H_2O + CO_2$

Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

$$R-COONa \xrightarrow{NaOH \& CaO} R-H + Na_2CO_3$$

Heat

Halogenation – Hell Volhard Zelinsky Reaction

Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



a substituted acid.



The propionyl bromide produced then reacts again and again till the whole of acid is converted to asubstituted acid.



Carboxylic acid derivatives

> ACETYL CHLORIDE ANHYDRIDE AMIDES ESTERS







Reactions of Acetyl Chloride

Hydrolysis of Acetyl Chloride

 $CH_{3}COC1 + H_{2}O \longrightarrow CH_{3}COOH + HC1$ Acetyl chloride $C_{6}H_{5}COC1 + H_{2}O \longrightarrow C_{6}H_{5}COOH + HC1$

Benzoyl chloride

Mechanism



Reaction with alcohol



Mechanism


Reaction with Ammonia (Ammonolysis)

An acid chloride reacts with ammonia to form an amide. $CH_3COCL + NH_3 \longrightarrow CH_3CONH_2 + HCl$ Acetyl chloride Acetamide $C_6H_5COCl + NH_3 \longrightarrow C_6H_5CONH_2 + HCl$ Benzoyl chloride Benzamide

Mechanism



Reaction with Amines

An acid chloride reacts with an amine (primary or secondary) to form substituted amide

 $\begin{array}{rcl} CH_3COCI + C_2H_5NH_2 \longrightarrow & CH_3CONHC_2H_5 + HCl \\ Acetyl chloride & & N-Ethylacetamide \end{array}$

 $CH_3COC1 + (C_2H_5)_2NH \longrightarrow CH_3CON(C_2H_5)_2 + HC1$ Acetyl chloride N,N-Diethylacetamide

Reduction

When reduced with hydrogen in the presence of 'poisoned' palladium catalyst, they form aldehydes. This reaction is known as Rosenmund reduction.



They reduced with LiAlH₄ to form ethyl alcohol.





The compounds derived by the loss of a water molecule between two molecules of a carboxylic acid are called Acid anhydride or simply Anhydrides



By Reaction of acid halide with salt of a carboxylic acid

NaCl

 $CI + CH_3^{-}COO^{-}Na^{+}$

Reactions Anhydrides

Hydrolysis

Acid anhydrides get hydrolysed by water to give acids



By Reaction of acid halide with salt of a carboxylic acid



Hydrolysis

Acid anhydrides get hydrolyzed by water to give acids.

 H_2O

Alcoholysis (Reaction with alcohol)



Ammonolysis (Reaction with Ammonia)

• Ammonia react with acetic anhydride to give Acetamide



Reaction with Amines



Reduction

 Acid Anhydrides on reduction with reducing agent LiAlH4 or Na/alcohol, produces alcohols



Amides

By the action of Ammonia on acid chlorides: By the action of Ammonia on Anhydrides: By heating ammonium carboxylate.





Amides

• By the action of Ammonia on Anhydrides:



Amides



Hydrolysis Hydrolysis of amides produces acid $CH_3-CONH_2 + H_2O + HCI \longrightarrow CH_3-COOH + NH_4CI$

Reaction with nitrous acid (NaNO2 HCl)

Amides on reaction with nitrous acid produces Carboxylic acid

 $CH_3-CONH_2 + O = N - OH - CH_3-COOH + N_2 + H_2O$ Nitrous acid • Reduction of amides in presence of reducing agent like LiAIH4, produces Amines



Dehydration

Ha



CH₃-CN Acetonitrile



Amide on reaction with bromine and sodium hydroxide solution produces a amine.

 Amide on reaction with bromine and sodium hydroxide solution forms isocyanate which on hydrolysis and decarboxylation produces amine

Hoffman's degradation of amides



Fischer Esterification Mixture of carboxylic acid and alcohol heated in presence of sulphuric acid is known ad Esterification and is reversible in nature.

 $CH_3COOC_2H_5 + H_2O$

Esters

$CH_3COOH + HO-C_2H_5$

Mechanism

• Protonation of carbonyl oxygen followed by nucleophilic attack by alcohol.



From acid chloride and Anhydrides on reaction with alcohol





Hydrolysis

Ester when heated with water in presence of acid catalyst give the parent carboxylic acid and alcohol

 $H_3C - C - OC_2H_5 + H_2O \implies H_3C - C - OH + HO-C_2H_5$ Ethyl acetate

Hydrolysis in base

- On hydrolysis with aq. NaOH forms sodium salt of carboxylic acid and a alcohol.
- Kinetic studies revealed that basic hydrolysis of an ester is a bimolecuare reaction and it follows second order kinetics (B_{AC}^2 mechanism)



Reaction with Ammonia

Esters on reaction with ammonia produces
amides and alcohols

 CH_3 - $COOC_2H_5$ + $H-NH_2$ \sim CH_3 - $CONH_2$ + CH_3 - CH_2OH Ethyl acetate Ammonia



Ester of an alcohol can react with another lower alcohol in the presence of a mineral acid, to form the ester of second alcohol. The interchange of alcohol portions of the ester is called Transesterification

Transesterification

 $CH_3-COOC_2H_5 + CH_3-OH \xrightarrow{H^+} CH_3-COO-CH_3 + C_2H_5OH$ Ethyl acetate
