

# ALKANOIC ACID/CARBOXYLIC ACID

- Contains carboxyl functional group  $\text{-COOH}$
- Two functional groups are contained in carboxyl- carbonyl ( $\text{C=O}$ ) and hydroxyl ( $\text{-OH}$ )
- Saturated aliphatic alkanolic acids have general formula  $\text{RCOOH}$  (where R can be hydrogen or alkyl)
- Higher members of alkanolic acids that occur in natural fat(ester) or oil are called fatty acids e.g. palmitic acid, stearic acid, lauric acid etc
- Alkanolic acids that contain two carboxyl group in its molecule are called Alkanedioic acid or dicarboxylic acid e.g. ethanedioic acid (oxalic acid), propane-1,3-dioic acid (malonic acid)

## NOMECLATURE OF ALKANOIC ACID

- IUPAC naming system takes after the names of the appropriate alkane
- Replace the ending '-e' in alkane with '-oic acid'
- Positions of the substitution are denoted by numbering the longest unbranched chain containing the carboxyl group e.g. 2-methylpropanoic acid  $(\text{CH}_3)_2\text{CHCOOH}$ , 2-phenylethanoic acid  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
- Names of aromatic acids are related to the appropriate hydrocarbon e.g. benzoic acid  $\text{C}_6\text{H}_5\text{COOH}$ , toluic acid  $\text{C}_6\text{H}_4(\text{CH}_3)\text{COOH}$

## **PHYSICAL PROPERTIES OF ALKANOIC ACIDS**

- **Lower members are liquids which completely miscible with water due to hydrogen bonding**
- **The higher members are waxy solids with decreasing water solubility**
- **The aromatic acids are crystalline solids sparingly soluble in water but have higher melting points than their aliphatic counterparts of comparable molecular weight**
- **They have higher boiling point and increased water solubility than alkanals because its hydrogen bonding occurs with the hydroxyl group and the carbonyl group**
- **Boiling points of alkanolic acid increases as their molecular weight increases**

**Class discussion: EXPLAIN THE RESONANCE EFFECT IN ALKANOIC ACID (ACIDITY)**

### **• PREPARATION OF ALKANOIC ACIDS**

**(A) Oxidation of alkanals and alkanals**

**(B) Hydrolysis of Cyanides/Nitrile**

**(C) Reaction of Grignard reagent with carbondioxide**

### **CHEMICAL PROPERTIES OF ALKANOIC ACID**

- **(I). Esterification (II). Reduction with  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  (iii). Decarboxylation (iv) Kolbe Electrolysis**

# DERIVATIVES OF ALKANOIC ACIDS

- Derivatives of alkanolic acid are formed by replacing the hydroxyl group (-OH) with X giving a general formula  $RCOX$  where

X = OR for Alkanoates (Esters)  
Acyl halides

X =  $NH_2$  for Amides

X = halogen for

X = -OOCR for anhydride

## METHODS OF PREPARATION OF ALKANOIC ACID DERIVATIVES

- Acyl halides and esters are prepared directly from alkanolic acid but others are prepared preferably from acyl halides by attack of a nucleophile

- (i) Acyl halides: prepared by reacting alkanolic acid with phosphorous halides ( $PX_5, PX_3, POX_3$ ) and thionyl halide ( $SOX_2$ )



- (ii) Amides: prepared by reacting ammonia or amines with acyl halides. At times substituted amides are also produced



- (III) Anhydrides: prepared by reacting two molecules of alkanolic acids with elimination of water molecule



- (IV) Alkanoates: prepared by reacting alkanolic acid with alkanols in the presence of concentrated mineral acids

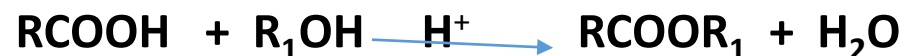


# ALKANOATES / ESTERS

- Produce by esterification reaction.
- Name by replacing the '-ic' from alkanonic acid by '-ate' preceding this the name of the alkyl or aryl group of the appropriate alkanol or phenol
- Examples of natural ester are fats and oils
- Simple esters are colourless liquids possessing pleasant fruity odour and used in scenting perfumes and flavouring food
- Ester of aliphatic carboxylic acids are soluble but their solubility decreases as molecular weight increases
- Esters of aromatic carboxylic acids are insoluble.

## PREPARATION OF ALKANOATES

- Fischer-Speier Esterification



- From Acid chloride or acid anhydride



## CHEMICAL PROPERTIES OF ALKANOATES

(I) Hydrolysis

(II) Reduction using  $\text{LiAlH}_4$  and ether

(III) Ammonolysis (Amide formation)

(IV) Reduction with Grignard Reagent



# CLASSIFICATION OF AMIDES

- Amides are classified as primary, secondary and tertiary

## PRIMARY AMIDES

- This contains  $\text{-NH}_2$  in its structure  $\text{RCONH}_2$  (that there is two hydrogen attached to N)
- They are named by changing the of the acid by dropping the “-oic acid” or “-ic acid” and adding “-amide”
- The carbonyl carbon is given the first location number and it is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain

$\text{HCONH}_2$  Methanamide (Formamide)

$\text{CH}_3\text{CONH}_2$  Ethanamide (Acetamide)

$\text{C}_6\text{H}_5\text{CONH}_2$  Benzamide

## SECONDARY AMIDES

- This contains -NH in its structure  $RCONHR'$  (that there is one hydrogen attached to N)
- They are named by using an upper case N to designate that the alkyl group is on the nitrogen
- Alkyl group attached to the nitrogen are named as substituents. The letter N used to indicate that they are attached to nitrogen
- $CH_3CH_2CONHCH_3$  N-methylpropanamide
- $CH_3CH_2CONHC_6H_5$  N-phenylpropanamide

## TERTIARY AMIDES

- This contains -N in its structure  $CONR'R''$  (that there is no hydrogen attached to N)
- They are named in the same way as secondary amides but two Ns
- $CONR_1R_2$
- $HCON(CH_3)_2$  N, N-dimethylformamide or N, N-dimethylmethanamide
- $CH_3CON(CH_3)C_2H_5$  N-ethyl-N-methylethanamide

# PREPARATION OF AMIDES

## FROM AMMONIUM SALT OF CARBOXYLIC ACID

- The carboxylic acid is first converted into ammonium salt which then produces amide on heating

- The ammonium salt is formed by adding solid ammonium carbonate to an excess acid



- When the reaction is completed, the mixture is heated and the ammonium salt dehydrates producing amide  $\text{CH}_3\text{COONH}_4 \xrightarrow{\text{heat}} \text{CH}_3\text{CONH}_2 + \text{H}_2\text{O}$

- The excess ethanoic acid is there to prevent dissociation of the ammonium salt before it dehydrates

## FROM ACYL CHLORIDE

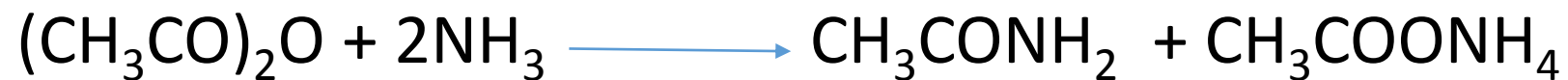
- Acylchloride is also known as acid chloride (RCOCl). The chlorine atom is very easily replaced by other atom or group like -NH<sub>2</sub> group to form an amide

- The acylchloride is added to a concentrated solution of ammonia in water but the reaction is exothermic and violet  $\text{CH}_3\text{COCl} + 2\text{NH}_3 \longrightarrow \text{CH}_3\text{CONH}_2 + \text{NH}_4\text{Cl}$



## FROM ACID ANHYDRIDES

- An acid anhydride is obtained when a molecule of water is removed from two carboxylic acid (-COOH group)
- The reaction of acid anhydrides are like those of acylchlorides except that a molecule of carboxylic acid is produced e.g. if ethanoic anhydride is added to concentrated ammonia solution, ethanamide and ammonium ethanoate is formed



## CHEMICAL REACTIONS OF AMIDES

### HYDROLYSIS OF AMIDES

- This is a nucleophilic acyl substitution.
- Amides hydrolyse to the parent carboxylic acid and the appropriate amine using a strong acid or base



## DEHYDRATION OF AMIDES

- Amides are dehydrated to form nitrile group (-CN)
- The dehydration is done by heating a solid mixture of the amide with phosphorus(V) oxide,  $P_4O_{10}$  ( $P_2O_5$ )



## REDUCTION REACTION

- Amides can be reduced to primary amines by reaction with lithiumaluminiumhydride( $LiAlH_4$ ) in dry ether at room temperature
- $RCONH_2 + 4[H] \xrightarrow{LiAlH_4/dry\ ether} RCH_2NH_2 + H_2O$

## HOFMANN DEGRADATION

- This is a reaction between an amide and a mixture of bromine and sodium hydroxide solution
- The amide group loses the  $-CO$  part and become a primary amine with one less carbon atom than the original amide had



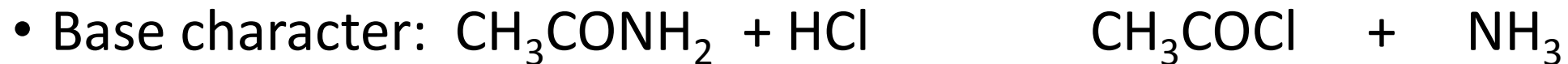
## REACTION WITH NITROUS ACID

- Amide react with nitrous acid to give carboxylic acids and nitrogen gas.
- Nitrous acid required is prepared in situ by reaction of sodium nitrite and hydrochloric acid



## AMPHOTERIC CHARACTER OF AMIDES

- Amides are feeble bases but are amphoteric in nature (that is they can behave as an acid and a base) due to resonance



# USES OF AMIDES

- Amides are used widely in industries in producing plastic, rubber, paper, colour in crayons, pencils and ink as well as in water and sewage treatment
- Acrylamide and polyacrylamide are the products most widely used in above industries. However, acrylamide is a carcinogen so it can be used only if the chemicals are not intended for consumption
  - I. Polyacrylamide is used in treatment of drinking water and sewage
  - II. Amides are used in paper industry, being used as a binder and for retention aid for fibres. It also retains colour pigment on paper
  - III. Acrylamide is used:
    - a) To stabilize soil and help keep free sand able to flow so that it can fill mould
    - b) As a coating on many household appliances and car parts with thermosetting acrylics
    - c) In the cosmetic industry to prepare soap, hair products and preshave lotion
    - d) For explosives, adhesives, printing inks, latex thickener and emulsion stabilizers.