Acid Derivatives.

The compounds which are obtained by replacing the -OH of the carboxylic group by other atoms or groups such as $X^-, -NH_2, -OR$ and O-C-R are known as acid derivatives.

- R-C- group is common to all the derivatives and is known as acyl group and these derivatives are termed on as acyl compound.
 - The important derivatives are given below:

Group replacing – OH	Name	Structure
$(X = \overset{X}{F}, Cl, Br, I)$	Acyl halide	O R - C - X
$-NH_2$	Amide	$R - C - NH_2$
-OR'	ester	O $ $ $R - C - OR'$ $(R' may be R)$
LOOCR C	anhydride	O O O O O O O O O O O O O O O O O O O

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.

$$O \mid I \mid (L = X, NH_2, O - C - R \text{ or } OR)$$

The relative reactivities of various acyl compounds have been found to be in the following order:

Out of acid halides, the acid chlorides are more important ones.

The overall order of reactivity can be accounted for in terms of the following three factors:

(i) Basicity of the leaving group (ii) Resonance effects and (iii) Inductive effects.

- (i) **Basicity of the leaving group**: Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups are more reactive. Chloride ion is the weakest base while $-NH_2$ is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.
- (ii) **Resonance effect**: The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.

This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound.

However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of -Cl is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

(iii) *Inductive effect*: Higher the –*I* effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.

Acyl Halides

$$R - C \bigcirc O$$
 where R may be alkyl or aryl group.

Nomenclature: The common names as well as IUPAC names of the acid halides are derived by replacing ic acid by yl halide.

Acyl chloride	Common name	IUPAC name
HCOCI	Formyl chloride	Methanoyl chloride
CH ₃ COCI	Acetyl chloride	Ethanoyl chloride
CH ₃ CH ₂ COCI	Propionyl chloride	Propanoyl chloride
C ₆ H ₅ COCl	Benzoyl chloride	Benzoyl chloride

- (1) Methods of Preparation
- (i) From carboxylic acid: $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$ $3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$
- (ii) *Industrial method*: By distilling anhydrous sodium acetate

$$3CH_{3}COONa + PCl_{3} \xrightarrow{\quad \text{heat} \quad} 3CH_{3}COCl + Na_{3}PO_{3}$$

$$2CH_{3}COONa + POCl_{3} \xrightarrow{\quad \text{heat} \quad} 2CH_{3}COCl + NaPO_{3} + NaCl_{3}COCl + NaPO_{3} + NaCl_{3}COCl_{3} + NaCl_{3}COCl_{4} + NaPO_{3} + NaCl_{4}COCl_{5} + NaPO_{5}Coll_{5} + NaPO_{5}Coll_{$$

(iii) With thionyl chloride: $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

This is the best method because SO_2 and HCl are gases and easily escape leaving behind acyl chloride.

(2) **Physical properties:** The lower acyl chloride are mobile, colourless liquid while the higher members are coloured solids.

Acyl chloride have very pungent, irritating order and are strong lachrymators (tears gases)

The fume in air due to the formation of hydrochloric acid by hydrolysis.

They are readily soluble in most of the organic solvent. Acyl chloride don't form intermolecular hydrogen bonding. Therefore, their boiling points are lower than those of their parent acids.

(3) Chemical properties

$$\begin{array}{c|c}
C & C & C \\
R - C - Cl + : Nu^{-} \rightarrow R - C & Cl \rightarrow R - C + Cl^{-} \\
& Nu & Nu
\end{array}$$

$$Cl^- + H^+ \rightarrow HCl$$

(i) $Hydrolysis: CH_3COCl+HOH \rightarrow CH_3COOH+HCl$ Acetyl chloride Acetic acid

$$\begin{array}{c} C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + H_2O \\ \text{Benzoyl chloride} \end{array}$$

(ii) Reaction with alcohols (alcoholysis)

$$CH_3COCI + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCI$$
Ethyl acetate
$$C_6H_5COCI + C_2H_5OH \xrightarrow{\text{aq NaOH or}} C_6H_5COOC_2H_5 + HCI$$
Benzoyl chloride Ethyl alcohol Pyridine Ethyl benzoate

This reaction is called **Schotten Baumann reaction**.

(iii) Reaction with salts of carboxylic acid

$$CH_{3}COCl + CH_{3}COO^{-}Na^{+} \xrightarrow{Pyridine} CH_{3} \stackrel{O}{\underset{C-O-C-CH_{3}}{|I|}} C-O-C-CH_{3}$$
Acetic anhydride

(iv) **Reaction with benzene** (acylation): This reaction is called friedel craft reaction.

$$+ CH_3COC1 \xrightarrow{\text{Anhyd. }AlCl_3} + HCl$$

$$+ COC_6H_5$$

$$+ C_6H_5COC1 \xrightarrow{\text{Anhyd. }AlCl_3} + HCl$$

$$+ C_6H_5COC1 \xrightarrow{\text{Benzoyl chloride}} + HCl$$

$$+ C_6H_5COC1 \xrightarrow{\text{Benzophenone}} + HCl$$

(v) Reaction with ammonia or amines : $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$ Acetyl chloride Acetyl chloride

$$C_6H_5COCl + 2NH_3 \rightarrow C_6H_5CONH_2 + NH_4Cl$$
 Benzamide

However, acyl chlorides react with amines to form substituted amides.

$$CH_{3}COCl + H_{2}NC_{2}H_{5} \rightarrow CH_{3} C-NH-C_{2}H_{5}$$
 N-Ethyl acetamide
$$CH_{3}COCl + (C_{2}H_{5})_{2}NH \rightarrow CH_{3}CON(C_{2}H_{5})_{2} + HCl_{N, N-Diethyl acetamide}$$

(vi) **Reduction :**
$$CH_3COCl \xrightarrow{LiAlH_4 \text{ or} \atop NaBH_4} CH_3CH_2OH$$
 Ethanol (Primary alcohol)
$$CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$$

This reaction is called **Rosenmund reaction**.

(vii) Reaction with organocadmium compounds (formation of ketones)

$$\begin{aligned} 2CH_3COCl + (CH_3)_2Cd &\rightarrow 2CH_3COCH_3 + CdCl_2 \\ &\stackrel{\text{Dimethyl}}{\text{Cadmium}} & \text{Acetone} \\ 2C_6H_5COCl + (CH_3)_2Cd &\rightarrow 2C_6H_5COCH_3 + CdCl_2 \\ &\text{Acetophenone} \end{aligned}$$

(viii) Reaction with diazomethane

$$CH_{3} - C - CI + 2\overline{C}H_{2} - \overset{+}{N} \equiv N \rightarrow CH_{3} - \overset{-}{C} - \overset{+}{C}H - \overset{+}{N} \equiv N \xrightarrow{H_{2}O} CH_{3}CH_{2}C - OH$$

$$CH_{3} - C - CI + 2\overline{C}H_{2} - \overset{+}{N} \equiv N \rightarrow CH_{3} - C - \overset{+}{C}H - \overset{+}{N} \equiv N \xrightarrow{H_{2}O} CH_{3}CH_{2}C - OH$$

$$CH_{3} - C - CI + 2\overline{C}H_{2} - \overset{+}{N} \equiv N \rightarrow CH_{3} - C - \overset{+}{C}H - \overset{+}{N} \equiv N \xrightarrow{H_{2}O} CH_{3}CH_{2}C - OH$$

$$CH_{3} - C - CI + 2\overline{C}H_{2} - \overset{+}{N} \equiv N \rightarrow CH_{3} - C - \overset{+}{C}H - \overset{+}{N} \equiv N \xrightarrow{H_{2}O} CH_{3}CH_{2}C - OH$$

- (ix) Reaction with water: $CH_3COCl \xrightarrow{AgNO_3/H_2O} CH_3COOH + AgCl + HNO_3$
- (x) **Reaction with chlorine**: $CH_3COCl + Cl_2 \xrightarrow{\text{Red }P} Cl CH_2 CO Cl + HCl_{\text{Mono-}\alpha\text{-chloroacetyl chloride}}$
- (xi) Reaction with Grignard reagent

$$CH_3CO$$
 $CI + IMg$ $CH_3 \rightarrow CH_3COCH_3 + Mg$ CI

Methyl magnesium iodide

Acetone

- (xii) **Reaction with KCN** : $CH_3COCl + KCN \rightarrow CH_3COCN \xrightarrow{H_2O} CH_3COCOOH$ Acetyl cyanide Pyruvic acid
- (xiii) Reaction with Salicylic acid

$$\begin{array}{c}
OH \\
COOH
\end{array} + CIOCCH_3 \rightarrow
\begin{array}{c}
OOCCH_3 \\
COOH
\end{array} + HCI$$
Salicylic acid (Aspirin)

Acetyl salicylic acid (Aspirin)

- $(\text{xiv}) \ \textit{Reaction with ether}: \ CH_3COCl + C_2H_5OC_2H_5 \xrightarrow{ZnCl_2} CH_3COOC_2H_5 + C_2H_5Cl_{\text{Diethyl ether}} CH_3COOC_2H_5 + C_2H_5Cl_{\text{Ethyl acetate}}$
- (XV) Reaction with sodium peroxide (Peroxide formation)

$$\begin{array}{c|c} O & O & O \\ 2CH_3 - C - Cl + \stackrel{+}{Na}\stackrel{-}{O} - \stackrel{-}{ONa} \rightarrow CH_3C - O - O - C - CH_3 + 2NaCl \\ \text{Acetyl chloride} & \text{Acetyl peroxide} \end{array}$$

(XVi) Reaction with hydroxylamine and hydrazine

$$\begin{array}{c} CH_{3}COCl + H_{2}NOH \rightarrow CH_{3}CONHOH + HCl \\ & \text{Hydroxyl} \\ & \text{amine} \end{array} \\ CH_{3}COCl + H_{2}NNH_{2} \rightarrow CH_{3}CONHNH_{2} + HCl \\ & \text{Hydrazine} \end{array}$$

(4) Uses

- (i) As an acetylating agent.
- (ii) In the estimation and determination of number of hydroxyl and amino groups.
- (iii) In the preparation of acetaldehyde, acetic anhydride, acetamide, acetamilide, aspirin, acetophenone etc.

Acid Amides

$$R - C \stackrel{O}{\nearrow} NH_2$$
 where, $R = -CH_3, -CH_2CH_3, -C_6H_5$

Nomenclature

- ♣ In common system, -i.c., acid is replaced by amide.
- **★**In IUPAC system, *e* of parent hydrocarbon is replaced by amide.

Acyl amides	Common name	IUPAC name
HCONH ₂	Formamide	Methanamide
CH_3CONH_2 $C_2H_5CONH_2$ $C_6H_5CONH_2$	Acetamide Propionamide Benzamide	Ethanamide Propanamide Benzamide

The hydrogen atom of the acid may also be replaced by alkyl groups.

Therefore, the acid amides are classified:

- (1) Methods of preparation
- (i) Ammonolysis of acid derivatives

$$\begin{split} CH_3COCl + 2NH_3 &\rightarrow CH_3CONH_2 + NH_4Cl \\ (CH_3CO)_2O + 2NH_3 &\rightarrow CH_3CONH_2 + CH_3COONH_4 \\ Acetamide &Amm. \ acetate \\ C_6H_5COCl + NH_3 &\rightarrow C_6H_5CONH_2 + HCl \\ Benzoyl \ chloride &Benzamide \end{split}$$

(ii) From ammonium salts of carboxylic acids (Laboratory Method)

$$C\!H_{3}COO\!N\!H_{4} \xrightarrow{\quad Heat \quad} C\!H_{3}CO\!N\!H_{2} + H_{2}O$$

Note: * Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product (CH_3COOH) .

(iii) By partial hydrolysis of alkyl cyanide :
$$CH_3C \equiv N \xrightarrow{\text{Conc.}HCl} CH_3CONH_2$$
Acetamide

(iv) By heating carboxylic acid and urea
$$H_2N - C - NH_2 + R - C - OH \xrightarrow{\text{heat}} R - C - NH_2 + CO_2 + NH_3$$

- (2) Physical properties
- (i) **Physical state**: Formamide is a liquid while all other amides are solids.
- (ii) **Boiling points**: Amides have high boiling points than the corresponding acids.

Acetic Acid	Acetamide
b.p. 391 <i>K</i>	b.p. 494 <i>K</i>
Benzoic acid	Benzamide
b.p. 522 K	b.p. 563 <i>K</i>

The higher boiling points of amides is because of intermolecular hydrogen bonding

- (iii) Solubility: The lower members of amide family are soluble in water due to the formation of hydrogen bonds with water.
 - (3) Chemical properties

(i) **Hydrolysis**:
$$CH_3CONH_2 + H_2O \xrightarrow{Slowly} CH_3COOH + NH_3$$

 $CH_3CONH_2 + H_2O + HCI \xrightarrow{Rapidly} CH_3COOH + NH_4CI$
 $CH_3CONH_2 + NaOH \xrightarrow{Far more rapidly} CH_3COONa + NH_3$

(ii) Amphoteric nature (Salt formation)

It shows feebly acidic as well as basic nature.

$$CH_{3}CONH_{2} + HCl(\text{conc.}) \rightarrow CH_{3}CONH_{2}.HCl \\ \text{Acetamide hydrochloride} \\ \text{(only stable in aqueous solution)}$$

$$\begin{array}{ccc} 2CH_3CONH_2 + & HgO & \rightarrow (CH_3CONH)_2Hg + H_2O \\ & \text{Acetamide} & \text{Mercuric acetamide} \\ & \text{Oxide} & \end{array}$$

$$CH_3CONH_2 + Na \xrightarrow{\text{Ether}} CH_3CONHNa + \frac{1}{2}H_2$$
Sodium acetamide

(iii) **Reduction :**
$$CH_3CONH_2 + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2NH_2 + H_2O$$
Acetamide Ethylamine

$$C_6H_5CONH_2 + 4[H] \xrightarrow{Na/C_2H_5OH} C_6H_5CH_2NH_2 + H_2O$$
Benzamide

Benzylamine

(iv) **Dehydration:**
$$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3C \equiv N + H_2O$$
Acetamide heat Methyl cyanide

$$C_{6}H_{5}CONH_{2} \xrightarrow{P_{2}O_{5}} C_{6}H_{5}C \equiv N + H_{2}O$$
Benzamide
Phenyl cyanide
$$C_{6}H_{5}CONH_{2} \xrightarrow{SOCl_{2}} C_{6}H_{5}C \equiv N$$
Phenyl cyanide

(v) Reaction with nitrous acid

$$CH_{3}CONH_{2} + HONO \xrightarrow{NaNO_{2}/HCl} CH_{3}COOH + N_{2} + H_{2}O$$
Acetic acid

$$C_6H_5CONH_2 + HONO \xrightarrow{NaNO_2/HCl} C_6H_5COOH + N_2 + H_2O$$
Benzoic acid

(vi) *Hofmann bromamide reaction or Hofmann degradation*: This is an important reaction for reducing a carbon atom from a compound, i.e., $-CONH_2$ is changed to $-NH_2$ group.

$$\begin{array}{c} CH_3CONH_2 \xrightarrow{Br_2} CH_3NH_2 \\ \text{Acetamide} \end{array}$$
 Acetamide Acetamide Robin Methyl amine (p-)

This reaction occurs is three steps:

$$CH_{3} - C - NH_{2} + Br_{2} + KOH \rightarrow CH_{3}CONHBr + KBr + H_{2}O$$

$$CH_{3} - C - NHBr_{2} + KOH \rightarrow CH_{3}NCO + KBr + H_{2}O$$

$$CH_{3} - C - NHBr_{2} + KOH \rightarrow CH_{3}NCO + KBr + H_{2}O$$

$$CH_{3}NCO + 2KOH \rightarrow CH_{3}NH_{2} + K_{2}CO_{3}$$

$$Methyl amine$$

$$CH_{3}CONH_{2} + Br_{2} + 4KOH \rightarrow CH_{3}NH_{2} + 2KBr + K_{2}CO_{3} + 2H_{2}O$$

Mechanism:
$$R - C - NH_2 + Br_2 \xrightarrow{KOH} R - C - N - Br + KBr + H_2O \xrightarrow{H} N$$
-Bromamide

$$R - C - N - Br \xrightarrow{KOH} \begin{bmatrix} O \\ R - C - N - Br \end{bmatrix} K^+ + H_2O \xrightarrow{Unstable salt} K^+ + H_2O \xrightarrow{Unstable (acyl nitrene)} K^+ + KBr; \begin{bmatrix} R - C - N \\ R - C - N \end{bmatrix} \xrightarrow{Rearrangement (Intramolecular)} O = C = N - R$$

$$R - N = C = O \xrightarrow{2KOH} RNH_2 + K_2CO_3$$

$$R - N = C = O \xrightarrow{N} RNH_2 + K_2CO_3$$

$$NH_3/\Delta \xrightarrow{N} (-HOD)$$

$$NH_3/\Delta \xrightarrow{N} (-HOD)$$

$$NH_3/\Delta \xrightarrow{N} (-HOD)$$

$$NH_3/\Delta \xrightarrow{N} (-HOD)$$

Note: \blacksquare In this reaction a number of intermediates have been isolated; N-bromamides, RCONHBr; salts of these bromamides [RCONBr $^-$] K^+ ; Isocyanates, RNCO.

 $-ND_2 + K_2CO_3 + HOD \left\langle \bigcirc \right\rangle -NH_2 + 2HOD + K_2CO_3$

♠Nitrene rearranges to form isocyanate.

(vii) **Action with alcohol**:
$$CH_3CONH_2 + CH_3OH \xrightarrow{HCl} CH_3COOCH_3 + NH_4Cl \xrightarrow{70^{\circ}C} CH_3COOCH_3 + NH_4Cl \xrightarrow{methyl acetate}$$

(viii) Reaction with grignard reagent

OMgBr
$$CH_3 - Mg - Br + CH_3 - CONH_2 \rightarrow CH_4 + CH_3 - CONH - MgBr \xrightarrow{CH_3MgBr} CH_3 - \overset{|}{C} - NH - MgBr \xrightarrow{CH_3} CH_3 - \overset{|}{C} - NH - MgBr \xrightarrow{C} CH_3$$

$$\xrightarrow{H_2O/H^+} \left[\begin{matrix} OH \\ CH_3 - \begin{matrix} -C - NH_2 \\ CH_3 \end{matrix} \right] \xrightarrow{-NH_3} \left[\begin{matrix} O \\ CH_3 - \begin{matrix} -C - CH_3 \\ Acetone \end{matrix} \right]$$
Unstable

(4) Uses

- (i) In organic synthesis. The compounds like methyl cyanide, Methylamine and ethylamine can be prepared.
- (ii) In leather tanning and paper industry.
- (iii) As a wetting agent and as soldering flux.

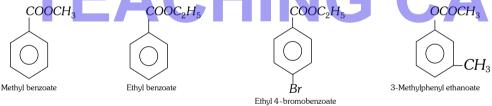
Amides such as dimethyl formamide (DMF), dimethyl acetamide (DMA) are used as solvents for organic and inorganic compounds.

These are the most important class of acid derivatives and are widely distributed in nature in plants, fruits and flowers.

Nomenclature: In common names and IUPAC system, change the suffix ic acid by ate.

Ester	Common name	IUPAC name	
HCOOCH ₃	Methyl formate	Methyl methanoate	
CH ₃ COOCH ₃	Methyl acetate	Methyl ethanoate	
CH ₃ COOC ₂ H ₅	Ethyl acetate	Ethyl ethanoate	
$CH_3COOC_6H_5$	Phenyl acetate	Phenyl ethanoate	
$CH_3CH_2CHCOOC_2H_5$ CH_3	Ethyl α -methyl butyrate	Ethyl 2-methylbutanoate	

The name of some aromatic esters are given below:



(1) Methods of preparation

(i) From carboxylic acid [Esterification]: Laboratory method.

* With diazomethane is the best method.

(ii) From acid chloride or acid anhydrides

$$CH_{3}CO \underbrace{Cl+H_{1}^{\dagger}OC_{2}H_{5}}_{\text{Acetyl chloride}} \rightarrow CH_{3}COOC_{2}H_{5} + HC1$$

$$CH_{3}CO \underbrace{CH_{3}CO}_{\text{CH}_{3}CO} O + CH_{3}CH_{2}OH \rightarrow CH_{3}COOCH_{2}CH_{3} + CH_{3}COOH$$

$$CH_{3}CO \underbrace{CH_{3}CO}_{\text{Ethyl acetate}} \rightarrow CH_{3}COOCH_{2}CH_{3} + CH_{3}COOH$$

$$CH_{3}CO \underbrace{CH_{3}CO}_{\text{Ethyl alcohol}} \rightarrow CH_{3}COOCH_{2}CH_{3} + CH_{3}COOH$$

$$CH_{3}CO \underbrace{Cl+H_{1}OC_{2}H_{5}}_{\text{Ethyl alcohol}} \rightarrow C_{6}H_{5}COOC_{2}H_{5} + HC1$$

$$C_{6}H_{5}CO \underbrace{Cl+H_{1}OC_{2}H_{5}}_{\text{Ethyl alcohol}} \rightarrow C_{6}H_{5}COOC_{2}H_{5} + HC1$$

$$C_{7}H_{1}CO \underbrace{Cl+H_{1}OC_{2}H_{5}}_{\text{Ethyl alcohol}} \rightarrow C_{6}H_{5}COOC_{2}H_{5} + HC1$$

$$C_{7}H_{1}CO \underbrace{Cl+H_{1}OC_{2}H_{5}}_{\text{Ethyl alcohol}} \rightarrow C_{6}H_{5}COOC_{2}H_{5} + HC1$$

$$C_{7}H_{1}CO \underbrace{Cl+H_{1}OC_{2}H_{5}}_{\text{Ethyl alcohol}} \rightarrow C_{6}H_{5}COOC_{2}H_{5} + HC1$$

(iii) From alkyl halide:
$$C_2H_5Br + CH_3COOAg \rightarrow CH_3COOC_2H_5 + AgBr$$
 Ethyl bromide Silver acetate Ethyl acetate

(iv) From ether:
$$CH_3 - O - CH_3 + CO \xrightarrow{BF_3} CH_3COOCH_3$$

Methoxy methane Methyl acetate

(v) From Tischenko reaction :
$$CH_3 - C - H + O = C - CH_3 \xrightarrow{Al(OC_2H_5)_3} CH_3 - C - OC_2H_5$$

 O

(2) Physical properties

(i) **Physical state and smell**: Esters are colourless liquids (or solids) with characteristic fruity smell. Flavours of some of the esters are listed below:

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octyl acetate	Orange

- (ii) **Solubility**: They are sparingly soluble in water but readily soluble in organic solvents such as alcohol, ether etc.
- (iii) **Boiling points**: Their boiling points are lower than the corresponding acids because of the absence of hydrogen bonding. i.e., ethyl acetate $= 77.5^{\circ}C$.
 - (3) Chemical properties

(i)
$$Hydrolysis: CH_3COOC_2H_5 + H_2O \stackrel{\text{dil. acid}}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$
Ethyl acetate $CH_3COOC_2H_5 + NaOH \stackrel{\text{celtic acid}}{\rightleftharpoons} CH_3COONa + C_2H_5OH$
Ethyl acetate $CH_3COONa + C_2H_5OH$
Ethyl acetate $CH_3COONa + C_2H_5OH$

Hydrolysis of ester by alkalies (NaOH) is known as saponification and leads to the formation of soaps

Mechanism: It follows three steps:

Step I: The nucleophile, OH^- ion from the alkali attacks the carboxyl carbon to form an intermediate.

$$CH_3 - C + OH^- \rightarrow CH_3 - C - OC_2H_5$$

$$OC_2H_5 OH$$

Step II: The intermediate, then loses a molecule of ethoxide ion to form acetic acid as:

$$CH_3 - C - CH_5 \rightarrow CH_3 - C + OC_2H_5$$

OH

OH

OH

Step III: Ethoxide ion abstracts the acidic proton from acetic acid to form acetate ion.

Note: * This reaction is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

★The acid hydrolysis of esters is reversible.

(ii) Reaction with ammonia (ammonolysis) :
$$CH_3CO[OC_2H_5 + H]NH_2 \rightarrow CH_3CONH_2 + C_2H_5OH$$
 Ethyl acetate Acetamide

(iii) **Reduction**:
$$CH_3COOC_2H_5 + 4[H] \xrightarrow{\text{LiAlH}_4} 2C_2H_5OH$$

$$COOC_2H_5 \qquad CH_2OH \\ +4H \qquad \xrightarrow{\text{LiAlH}_4} \\ \text{or } Na/C_2H_5OH \qquad +C_2H_5OH$$

- Reduction in presence of Na/C_2H_5OH is known as Bouveault Blanc reduction.
- The catalytic hydrogenation of ester is not easy and requires high temperature and pressure. The catalyst most commonly used is a mixture of oxides known as copper chromate $(CuO.CuCr_2O_4)$.

Benzyl alcohol

$$\begin{array}{c}
O \\
R - C - OR' + 2H_2 \xrightarrow{CuO.CuCr_2O_4} RCH_2OH + R'OH
\end{array}$$

(iv) Reaction with PCl₅ or SOCl₂

Ethyl benzoate

$$CH_{3}COOC_{2}H_{5} + PCl_{5} \rightarrow CH_{3}COCl + C_{2}H_{5}Cl + POCl_{3}$$

$$CH_{3}COOC_{2}H_{5} + SOCl_{2} \rightarrow CH_{3}COCl + C_{2}H_{5}Cl + SO_{2}$$

$$Acetyl \ chloride Ethyl \ chloride$$

$$C_{6}H_{5}COOC_{2}H_{5} + PCl_{5} \rightarrow C_{6}H_{5}COCl + POCl_{3} + C_{2}H_{5}Cl$$

$$Ethyl \ benzoate Benzoyl \ chloride$$

(v) **Reaction with alcohols**: On refluxing ester undergoes exchange of alcohols residues.

$$R - C \xrightarrow{O} + R''OH \xrightarrow{H^+} R - C \xrightarrow{O} + R'OH$$

$$CH_3COOC_2H_5 + CH_3OH \rightarrow CH_3COOCH_3 + C_2H_5OH$$
Ethyl acetate
$$CH_3COOC_2H_5 + CH_3OH \rightarrow CH_3COOCH_3 + C_2H_5OH$$

- This reaction is known as alcoholysis or trans esterification.
- (vi) Reaction with Grignard reagents

(N) Reaction with Grighard reagents
$$CH_{3} - C - OC_{2}H_{5} + CH_{3}MgBr \rightarrow \begin{bmatrix} OMgBr \\ CH_{3} - C - OC_{2}H_{5} \\ CH_{3} \end{bmatrix}$$

$$O \qquad OMgBr \qquad O \\ CH_{3} - C - CH_{3} \leftarrow \begin{bmatrix} OMgBr \\ CH_{3} \end{bmatrix} - C_{2}H_{5}OMgBr$$

$$CH_{3} - C - CH_{3} \leftarrow \begin{bmatrix} OMgBr \\ CH_{3} \end{bmatrix} - C_{2}H_{5}OMgBr$$

$$CH_{3} - C - CH_{3} \leftarrow \begin{bmatrix} OMgBr \\ CH_{3} \end{bmatrix} - C_{2}H_{5}OMgBr$$

$$CH_{3} - C - CH_{3} \leftarrow \begin{bmatrix} OMgBr \\ CH_{3} \end{bmatrix} - C_{2}H_{5}OMgBr$$

(vii) Claisen condensation

$$CH_{3} - C - \underbrace{\begin{bmatrix}OC_{2}H_{5} + H\end{bmatrix}}_{\text{Ethyl acetate }} - CH_{2}COOC_{2}H_{5} \xrightarrow{C_{2}H_{5}O^{-}Na^{+}} + CH_{3} - C - CH_{2}COOC_{2}H_{5} + C_{2}H_{5}OH \xrightarrow{\text{Ethyl acetoacetate}} (g.\text{ketoester})$$

(viii) Reaction with hydroxyl amine

$$CH_{3} \xrightarrow{C} \xrightarrow{C} \xrightarrow{O} \xrightarrow{O} \xrightarrow{I} \xrightarrow{O} C_{2}H_{5} + H \xrightarrow{I} HNOH \xrightarrow{base} CH_{3} - C - NHOH + C_{2}H_{5}OH \xrightarrow{Hydroxyl} \xrightarrow{amine} Hydroxyl amine$$

(ix) $\pmb{Reaction \ with \ hydrazine: \ CH_3COOC_2H_5 + H_2NNH_2 \rightarrow CH_3CONHNH_2 + C_2H_5OH_3CONHNH_2 + C_2H_5OH_3C$

(x) $\pmb{Halogenation}: CH_3COOC_2H_5 + Br_2 \xrightarrow{-\text{Red P}} CH_2BrCOOC_2H_5 + HBr_{\alpha-\text{Bromoethyl acetate}}$

(xi) **Reaction with HI:** $CH_3COOC_2H_5 + HI \rightarrow CH_3COOH + C_2H_5OH$ Acetic acid Ethyl alcohol

- (4) Uses
- (i) As a solvent for oils, fats, cellulose, resins etc.
- (ii) In making artificial flavours and essences.

 (iii) In the preparation of ethyl acetoacetate.
- (5) General Tests
- (i) It has sweet smell.
- (ii) It is neutral towards litmus.
- (iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.

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(iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Acid Anhydride
$$CH_3CO > O$$
 or $(CH_3CO)_2O$

- (1) Method of preparation
- (i) From carboxylic acid

$$\begin{array}{c|c} O & O & O \\ R-C-\left[OH+H\right]O-C-R & \xrightarrow{\text{Quartz tube}} R-\frac{O}{C-O-C-R+H_2O} \\ \end{array}$$

$$C_6H_5CO[OH+H]OOCC_6H_5 \xrightarrow{P_4O_{10}} C_6H_5 \xrightarrow{P_4O_{10}} C_6H_5 + H_2O$$
Reproof: aphydride

(ii) From carboxylic acid salt and acyl chloride [Laboratory method]

$$CH_{3}COONa + CH_{3}COCl \xrightarrow{Py} CH_{3}COOCOCH_{3} + NaCl$$
 Acetic anhydride
$$C_{6}H_{5}COONa + C_{6}H_{5}COCl \xrightarrow{Py} C_{6}H_{5}COOCOC_{6}H_{5} + NaCl$$
 Benzoic anhydride

(iii) From acetylene

$$\begin{array}{c} CH \\ | | | \\ CH \end{array} + 2CH_3COOH \xrightarrow{HgSO_4} \begin{array}{c} CH_3 \\ | | \\ CH(OOCCH_3)_2 \end{array} \xrightarrow{\text{Distill}} CH_3CHO + \begin{array}{c} CH_3CO \\ CH_3CO \\ CH_3CO \end{array}$$
 Acetic anhydride

(iv) From acetaldehyde :
$$CH_3CHO + O_2 \xrightarrow[]{Cobalt} 2CH_3 - C - O - O - H \rightarrow (CH_3CO)_2O + H_2O = O_2O + O_3O + O_$$

- (2) Physical properties
- (i) **Physical state**: Lower aliphatic anhydrides are colourless liquids with sharp irritating smell. The higher members of the family as well as the aromatic acid anhydrides are solids in nature.
- (ii) **Solubility**: They are generally insoluble in water but are soluble in the organic solvents such as ether, acetone, alcohol, etc.
- (iii) **Boiling points**: The boiling points of acid anhydrides are higher than those of carboxylic acids because of the greater molecular size.
 - (3) Chemical Properties

(i) **Hydrolysis**:
$$CH_3 - C - O - C - CH_3 + H_2O \rightarrow 2CH_3COOH$$

Acetic anhydride Acetic acid

(ii) **Action with ammonia** :
$$(CH_3CO)_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$$
Acetamide Amm. acetate

(iii) Acetylation: Acetic anhydride react with compound having active hydrogen.

$$\begin{split} &(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH \\ &\text{Ethyl alcohol} &\text{Ethyl acetate} \end{split}$$

$$&(CH_3CO)_2O + H_2NC_2H_5 \rightarrow CH_3CONHC_2H_5 + CH_3COOH \\ &\text{Ethyl amine} &N-\text{Ethyl acetamide} \end{split}$$

$$(CH_3CO)_2O + HN(C_2H_5)_2 \rightarrow CH_3CON(C_2H_5)_2 + CH_3COOH$$
 Diethylamine N,N-Diethyl acetamide

$$(CH_3CO)_2O + H_2NC_6H_5 \rightarrow CH_3CONHC_6H_5 + CH_3COOH$$
Aniline Acetanilide

$$(CH_3CO)_2O + \bigcirc OH \longrightarrow \bigcirc OOCCH_3 + CH_3COOH$$
Salicylic acid Acetyl salicylic acid (Aspirin)

- (iv) **Action of dry HCl**: $(CH_3CO)_2O + HCl \rightarrow CH_3COCl + CH_3COOH$
- (v) **Reaction with chlorine**: $(CH_3CO)_2O + Cl_2 \rightarrow CH_3COCl + CH_2CICOOH$ Acetyl chloride Monochloroacetic
- (vi) Reaction with PCl₅: $(CH_3CO)_2O + PCl_5 \rightarrow 2CH_3COCl + POCl_3$
- (vii) Friedel craft's reaction : $(CH_3CO)_2O + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCH_3 + CH_3COOH_6$ Benzene Acetophenone
- (viii) Reaction with acetaldehyde : $(CH_3CO)_2O + CH_3CHO \rightarrow CH_3CH(OOCCH_3)_2$ Acetaldehyde Ethylidene acetate
- (ix) **Reduction**: $(CH_3CO)_2O \xrightarrow{\text{LiAIH}_4} CH_3CH_2OH$ Ether Ethyl alcohol
- (x) **Action with ether:** CH_3CO $O.COCH_3 + C_2H_5 + O-C_2H_5 \rightarrow 2CH_3COOC_2H_5$ Ethyl acetate
- (xi) Action with N_2O_5 : $CH_3COOCOCH_3 + N_2O_5 \rightarrow CH_3 C O N_O$
- (4) Uses: Acetic anhydride is used
- (i) as an acetylating agent.
- (ii) For the detection and estimation of hydroxyl and amino group.
- (iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.

Urea or Carbamide
$$O = C < NH_2 \\ NH_2$$

Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $-NH_2$ groups.

$$O = C \xrightarrow{OH} \xrightarrow{OH} O = C \xrightarrow{NH_2} O = C \xrightarrow{NH$$

- Urine in 1773 by Roulle and hence the name urea was given.
- * It was the first organic compound synthesised in the laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.
 - * This preparation gave a death blow to Vital force theory.
 - # It is the final decomposition product of protein's metabolism in man and mammals and is excreted along with urine.
 - * Adults excrete about 30 grams of urea per day in the urine.
 - (1) Method of preparation
- (i) **From urine**: Urine is treated with conc. nitric acid where crystals of urea nitrate $CO(NH_2)_2$. HNO_3 are obtained.

$$2\text{CO(NH}_2)_2.\text{HNO}_3 + \text{BaCO}_3 \rightarrow 2\text{CO(NH}_2)_2 + \text{Ba(NO}_3)_2 + H_2O + CO_2$$
 Urea nitrate

- (ii) Laboratory preparation
- $\underset{\text{Potassium cyanate}}{2KCNO} + \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} \rightarrow \underset{\text{Ammonium cyanate}}{2NH_4CNO} + K_2SO_4$ (a) Wohler synthesis: $\begin{array}{c} NH_4CNO & \xrightarrow{\quad \text{Isomeric change} \quad} NH_2CONH_2 \\ \text{Ammonium cyanate} & \xrightarrow{\quad \text{On heating} \quad} NH_2CONH_2 \end{array}$
- * The solid residue is extracted with alcohol and the extract evaporated when the crystals of urea are obtained. It can be recrystalised from water.
 - (b) From phosgene or alkyl carbonate

$$O = C \underbrace{Cl}_{Cl} + 2NH_3 \rightarrow O = C \underbrace{NH_2}_{NH_2} + 2HCl$$
Carbonyl chloride
(Phosopene)

$$O = C \underbrace{Cl}_{Cl} + 2NH_3 \rightarrow O = \underbrace{CNH_2}_{NH_2} + 2HC1$$
Carbonyl chloride (Phosgene)
$$O = \underbrace{COC_2H_5}_{OC_2H_5} + 2NH_3 \rightarrow O = \underbrace{CNH_2}_{NH_2} + 2C_2H_5OH$$
Ethyl carbonate Urea

- (iii) Industrial method
- (a) By partial hydrolysis of calcium cyanide

$$CaC_2 + N_2 \xrightarrow{\text{heat}} CaCN_2 + C$$

of urea. $CaCN_2 \xrightarrow{H_2SO_4} H_2NCN \xrightarrow{H_2O} H_2NCONH_2$ Cyanamide (H_2O_2) (Urea)

or
$$CaCN_2 + H_2O + H_2SO_4 \xrightarrow{40^{\circ}C} NH_2CONH_2 + CaSO_4$$

(b) From carbon dioxide and ammonia

$$CO_2 + 2NH_3 \xrightarrow{150-200^{\circ}C} NH_2COONH_4 \xrightarrow{\text{heat (140^{\circ}C)}} NH_2CONH_2$$
Ammonium carbamate

(2) Physical properties: Urea is a colourless, odourless crystalline solid. It melts at 132°C. It is very soluble in water, less soluble in alcohol but insoluble in ether, chloroform.

Crystal structure: In solid urea, both nitrogen atoms are identifications

This indicates that C-N bond in urea has some double bond character.

- (3) Chemical Properties
- (i) **Basic nature** (Salt formation): It behaves as a weak monoacid base $(K_b = 1.5 \times 10^{-14})$. It forms strong acid.

$$NH_2CONH_2 + HNO_3 (conc.) \rightarrow NH_2CONH_2.HNO_3$$
Urea nitrate

$$2N\!H_2CO\!N\!H_2 + H_2C_2O_4 \rightarrow (N\!H_2CO\!N\!H_2)_2H_2C_2O_4$$
 Oxalic acid Urea oxalate

Due to resonance stabilization of cation, the negatively charged oxygen atom is capable of coordination with one proton.

$$H_2N$$
 C
 H_2
 H_2
 H_2
 H_2
 H_2N
 H_2
 H_2N
 H_2
 H_2

Note: * An aqueous solution of urea is neutral.

(ii) Hydrolysis:
$$O = C$$

$$NH_2 + H OH$$

$$Aq. alkali \text{ or acid} OH$$

$$OH$$

$$Carbonic acid$$

$$CO_2 + H_2O$$

$$NH_2CONH_2 + 2NaOH \rightarrow 2NH_3 + Na_2CO_3$$

An enzyme, urease, present in soyabean and soil also brings hydrolysis.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$
Ammonium carbonate

(iii) **Action of heat**:
$$NH_2CO\underbrace{NH_2 + H}_2HNCONH_2 \xrightarrow{heat} NH_2CONHCONH_2 + NH_3$$
 Biuret

Urea is identified by the test known as biuret test. The biuret residue is dissolved in water and made alkaline with a few drops of *NaOH*. When a drop of copper sulphate solution is added to the alkaline solution of biuret, a violet colouration is produced.

when heated rapidly at $170^{\circ}C$, polymerisation takes place:

(iv) Reaction with nitrous acid

$$\begin{array}{c|c} O \mid N \mid OH \mid & \\ H_2 \mid N \mid CO \mid N \mid H_2 + 2HNO_2 \xrightarrow{\quad NaNO_2 + HCl \quad} & H_2CO_3 \\ HO \mid N \mid O & & \downarrow \\ H_2O + CO_2 & & \end{array} + 2N_2 + 2H_2O$$

(v) Reaction with alkaline hypohalides

$$NaOH + Br_2 \rightarrow NaOBr + HBr$$

 $NH_2CONH_2 + 3NaBrO \rightarrow N_2 + 2H_2O + CO_2 + 3NaBrO$

(vi) Reaction with acetyl chloride or acetic anhydrides

$$NH_2CONH_2 + CH_3COC1 \rightarrow NH_2CONHCOCH_3 + HC1$$
Acetyl chloride
$$NH_2CONH_2 + (CH_3CO)_2O \rightarrow NH_2CONHCOCH_3 + CH_3COOH$$
Acetyl urea
$$Acetyl urea$$
Acetyl urea
$$Acetyl urea$$
Acetyl urea

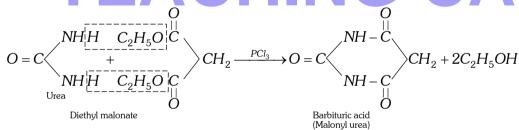
(vii) Reaction with hydrazine

$$\text{(viii) } \textit{Reaction with ethanol: } H_2NCO[\underbrace{NH_2+H_1}_{\text{Ethanol}}]OC_2H_5 \xrightarrow{\text{heat}} H_2NCOOC_2H_5 + NH_3$$

(ix) Reaction with chlorine water :
$$O = C$$
 $+ 2Cl_2 \rightarrow O = C$ $+ 2HCl$ $+ 2Cl_2 \rightarrow O = C$ $+ 2HCl$ $+ 2Cl_2 \rightarrow O = C$ $+ 2HCl$ $+ 2Cl_2 \rightarrow O = C$ $+ 2HCl$ Dichloro urea

- (x) **Dehydration**: $NH_2CONH_2 + SOCl_2 \rightarrow H_2N C \equiv N + SO_2 + 2HCl + H_2O$
- (xi) Reaction with fuming sulphuric acid

$$NH_2CONH_2 + H_2SO_4 + SO_3 \rightarrow 2NH_2SO_3H + CO_2$$
(xii) Formation of cyclic ureides



(xiii) Reaction with formaldehyde

$$O = C$$

$$NH - H C_{2}H_{5}O - CO$$

$$+ CH \rightarrow O = C$$

$$NH - CH_{3}$$

$$+ CH_{3}$$

$$+$$

$$CH_2 = O + NH_2CONH_2 \xrightarrow{HCl} CH_2(OH)NHCONH_2 \xrightarrow{CH_2 = O} Monomethylol \ urea$$

 $\begin{array}{ccc} CH_2(OH)NHCONH(OH)CH_2 & \xrightarrow{heat} & Resin \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\$

(4) Uses

- (i) Mainly as a nitrogen fertilizer. It has 46.4% nitrogen.
- (ii) In the manufacture of formaldehyde-urea plastic and semicarbazide.
- (iii) As animal feed.
- (iv) For making barbiturates and other drugs.
- (v) As a stabilizer for nitrocellulose explosives.

(5) General Tests

- (i) When heated with sodium hydroxide, ammonia is evolved.
- (ii) When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.
 - (iii) Its aqueous solution with concentrated nitric acid gives a white precipitate.
- (iv) On adding sodium nitrite solution and dil. HCl (i.e., HNO₂) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.

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