CHM 102 ORGANIC CHEMISTRY I

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

C=O Carbonyl OH Hydroxyl R-COOH Carboxyl $R-CO_2H$ R-COOH $R-C(=O)-OH$ R-C=O Derivatives

3 reps of Carboxylic acid

Carboxylic acid is an organic acid that contains a carboxyl group (C(=O)OH) attached to an R. group.

R- referring to the alkyl, alkenyl, aryl or other group such as CH_3 eg amino acids and fatty acids.

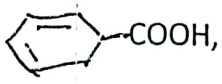
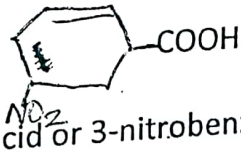
NOMENCLATURE

(i) Aliphatic carboxylic acids are named after the corresponding hydrocarbons from which the ending 'e' is dropped and –oic acid is added. Eg carboxylic acid derived from alkanes (paraffins and saturated hydrocarbons) are called alkanoic acid.

For instance H-COOH is methanoic acid- since it contains one carbon.

2, CH_3-COOH is ethanoic acid

3, $CH_3-C(CH_3)=C(Br)-COOH$ is 2-bromo-3-methyl-2-butenoic acid. It should be noted that the carbon atom of the carboxyl group is always numbered "1", since the carboxyl group is the most senior functional group.

(ii) Aromatic carboxylic acids are named as derivative of simplest molecule-benzene-carboxylic acid  , It's common name is benzoic acid, hence  is 3-nitrobenzenecarboxylic acid (or M-nitrobenzoic acid or 3-nitrobenzoic acid).

As in carboxyl compounds, Greek alphabets are sometimes used in naming, hence, $CH_3CH_2CH(NH_2)$-COOH is α-aminopropanoic acid, while $CH_3CH(Cl)CH_2$-COOH is β-chlorobutanoic acid. HOOC-CH_2CH-COOH is a dicarboxylic acid named 1,4-butanedioc acid or butane-1,4-dioic acid.

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

Solubility- Carboxylic acids are polar because they are both hydrogen-bond acceptors (the carbonyl –C=O) and hydrogen-bond donors (the hydroxyl –OH), they also participate in hydrogen bonding.

Boiling points- carboxylic acid tend to have higher boiling points than water, because of their greater surface areas and their tendency to form stabilized dimers through hydrogen bonds. For boiling to occur, either the dimer bonds must be broken or the entire dimer arrangement must be vapourized, increasing the enthalpy of evaporation requirements significantly.

Acidity- Carboxylic acids are **Bronsted-Lowry** acids because they are proton (H^+) donor. They are the most common type of organic acid. They are typically weak acids, meaning that they only partially dissociate into H_3O^+ cation and $RCOO^-$ anions in neutral aqueous solution.

Odour- Carboxylic acids often have strong sour odour. Esters of carboxylic acids tend to have fruity, pleasant odours and many are used in perfume.

Characterization- Carboxylic acids are readily identified as such by infrared spectroscopy. They exhibit a sharp band associated with vibration of the C=O carbonyl bond (V_c=O) between 1680 and 1725cm^{-1}. A characteristic V_0-H band appears as a broad peak in the 2500 to 3000cm^{-1} region. By ^1H NMR spectroscopy, the hydroxyl hydrogen appears in the 10-13ppm region, although it is often either broadened or not observed owing to exchange with traces of water.

The lower member of the alkanoic acid series C_1-C_2 are colourless liguids while the other higher members are coloursless solids- when pure.

All are soluble in alcohols and alkoxyalkanes (ethers).

Benzoic acid, as a result of its higher relative molecular mass and strong hydrogen bonds between its molecules, is a white crystalline solid, slightly soluble in cold water, but readily soluble in hot water- to give an acidic solution.

Lower members of the carboxylic acids are soluble in water to give weakly acid solutions.

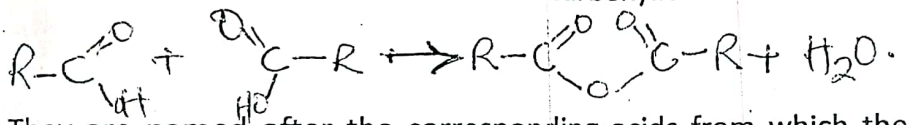
DERIVATIVES OF CARBOXYLIC ACIDS

Acid Halides (alkanoyl), Acid anhydrides, Alkyl alkanoates-Ester, ~~and~~ Acid amides and Amino acid.

ACID HALIDES- acid halides are derivatives of carboxylic acids R-COOH, formed by the replacement of the hydroxyl group, -OH by the halogen, X, to give RCOX. Saturated acid halides form homologous series with the general formula C_nH_{2n-1} OX. Their names have the characteristic ending "oyl halide".

Eg CH_3COCl is ethanoylchloride while $CH_3CHCOBr$ is 2-bromopropanoyl bromide.

ACID ANHYDRIDES- are generally written as $(RCO)_2O$ (where R=Alkyl or aryl). Their names come from the assumption that they are formed by the loss of a water molecule between two ~~molecule between two~~ molecules of a carboxylic acid.



They are named after the corresponding acids from which the ending "acid" is replaced by "anhydride" eg the simplest alkanoic anhydride is ethanoic anhydride, $CH_3COOCOCH_3$. (methanoic acid does not form an anhydride).

ALKYL ALKANOATES (ESTERS)- Esters are group of compounds generally written as RCOOR', where R can be H, Alkyl or aryl group, and R' can be alkyl or aryl group. Saturated aliphatic esters (alkanoates form homologous series with the general formula $C_nH_{2n+1}COOC_nH_{2n+1}$ or $C_xH_{2x}O_2$. Note RCOOR is same as R'OCOR. Their names are derived from the alcohols (alkanols, R'OH) and the carboxylic acids (alkanoic acids, RCO_2H) from which they are formed. The alkanol portion, R', is named first as alkyl, the alkanoic acids portion RCOO is then named as alkanoate. In fact, from the name of an ester, it is very easy to name the alcohol and the carboxylic acid from which it was formed.

Eg 1) $HCOOCH_3$ is methylmethanoate: from methanol CH_3OH and methanoic acids HCOOH.

2) $CH_3CH_2CO_2CH_2CH_3$ is ethylpropanoate; from ethanol, CH_3CH_2OH and propanoic and $CH_3CH_2CO_2H$.

3) $(CH_3)_3CCOOCH(CH_3)_2$ is 1-methylethyl-2-2-dimethylpropanoate; from propan-2-ol and 2-2-dimethylpropanoic acid. Cyclic esters are called **Lactones.**

ACID AMIDES- Acid amides are organic compounds containing Carbon, Hydrogen, Oxygen and Nitrogen. They are regarded as derivatives of carboxylic acids RCOOH, formed by the replacement of the hydroxyl group -OH by amino group $-NH_2$ to give $RCONH_2$.

Amides can also be described as monoalkanoyl or monoacyl derivatives of ammonia, NH_3; Primary amines, RNH_2 and secondary amines, R_2NH. Tertiary amines do not form amides.

Saturated aliphatic amides form a homologous series with the general formula $C_nH_{2n+1}ON$. The first member in the series, n=1 has the molecular formula CH_3ON, and Structural formula $HCONH_2$. The next member n=2 has molecular formula C_2H_5ON, and structural formula CH_3CONH_2 etc. Their names have the characteristic ending amide. Eg

$H-C(=O)-NH_2$ is methanamide,

$C_6H_5-C(=O)-NH_2$ is Benzenecarboxamide an aromatic amide.

$CH_3CH_2CH_2-C(=O)-NHCH_3$ is N-ethylbutanamide and

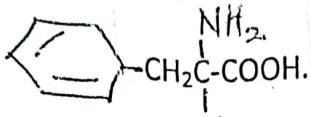
$CH_3-C(=O)-N(CH_3)_2$ is N,N-dimethylethanamide- both are N-substituted amides. The grouping

$-C(=O)-N(H)-$(-CONH) is called amide bond.

AMINO ACIDS- Amino acids are organic compounds that contain a basic amino group , $-NH_2$ and an acidic carboxyl group –COOH in the same molecule. In short, simple amino acids are bifunctional compounds. There are various kinds of amino acids, however, those that occur naturally in all living cells and are essential part of our diet is 2-amino acids (α-amino acids)- that is, those in which the amino group and carboxyl group are attached to the same carbon atom. The general form of the naturally occurring amino acid is $R-C(NH_2)(H)-COOH$. The simplest amino acid, R=H, is aminoethanoic acid, Popularly called **glycine** $H-C(NH_2)(H)-COOH$

The next in the series $R=CH_3$, is 2-aminopropanoic acid called **Alanine** $CH_3-C(NH_2)(H)-COOH$

When R is $(CH_3)_2CH-$, the amino acid is 2-amino-3-methylbutanoic acid called **Valine**

$(CH_3)_2CH-\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}-COOH$. An example of an aromatic amino acid is 3-phenyl-2-aminopropanoic acid called, **Phenylalanine** 

While **serine** is 2-amino-3-hydroxy-propanoic acid $HOCH_2-\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}-COOH$.

All naturally occurring amino acids, except aminoethanoic acid (glycine) have asymmetric α-carbon atoms and hence optically active. (Asymmetric carbon is attached to four atoms or groups all of different kinds).