

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Notes of Chapter - 11)

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Aldehyde, Ketones and Carboxylic Acid

Properties of carboxylic acid:

Physical properties

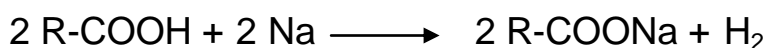
- 1. Physical state:** Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility.
- 2. Boiling point:** Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Most carboxylic acids exist as dimer in the vapour phase or in the protic solvents.
- 3. Solubility:** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. The simplest aromatic carboxylic acid, benzoic acid, is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Chemical properties:

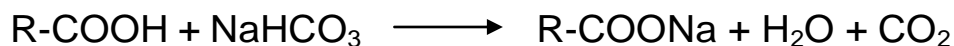
A. Reactions Involving Cleavage of O-H Bond:

1. Acidity:

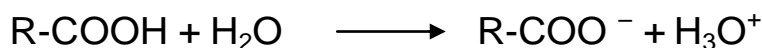
Reactions with metals and alkalis: Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate hydrogen gas.



Unlike alcohols and phenols, carboxylic acids react with sodium carbonates and bicarbonates and give brisk effervescence of carbon dioxide.



Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.



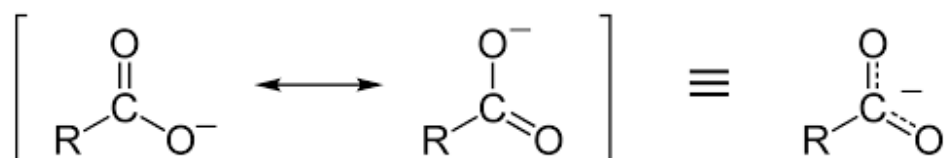
Due to the formation of hydronium ion in water, carboxylic acids are acidic in nature. The acidity of a substance is expressed in terms of pKa value, which is the negative logarithm of Ka
i.e. $\text{pKa} = -\log\text{Ka}$

Greater the value of Ka, smaller will be pKa and stronger will be the acid.

Comparison of acidic character

Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and many simple phenols. The higher acidity of carboxylic acids as compared to phenols can be explained as follows:

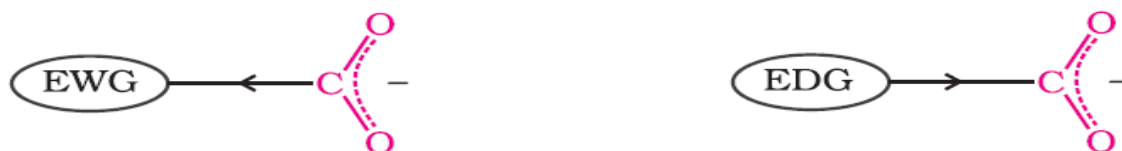
The carboxylate ion formed from the ionization of carboxylic acid is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. But the phenoxide ion formed from the ionization of phenol has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.



Also the negative charge is delocalized over two electronegative oxygen atoms in carboxylate ion, whereas it is less effectively delocalized over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Therefore carboxylate ion is more stable than phenoxide ion and hence carboxylic acids easily donate H^+ ion and form carboxylate ion. So it is more acidic.

Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups' increase the acidity of carboxylic acids by stabilising the carboxylate ion through delocalization of the negative charge by inductive and resonance effects. But electron donating groups decrease the acidity by destabilizing the carboxylate ion.

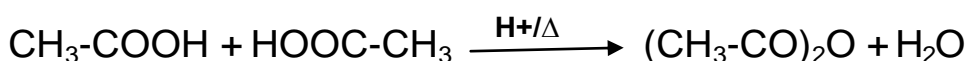
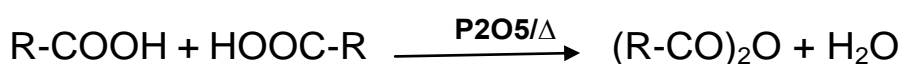


The effect of the following groups in increasing acidity order is
 $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid. This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

B. Reactions Involving Cleavage of C–OH Bond

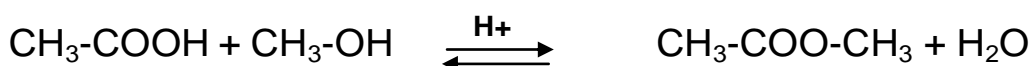
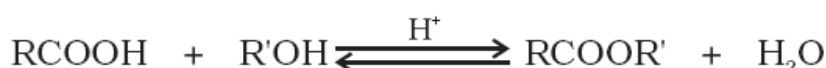
1. Formation of anhydride: Carboxylic acids on heating with mineral acids like H_2SO_4 or with P_2O_5 undergo dehydration to give acid anhydrides.



Acetic acid

acetic anhydride

2. Esterification: Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas, we get esters. This reaction is reversible and is known as esterification.



Acetic acid methanol

Methyl acetate
