CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Notes of Chapter - 11)

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Aldehyde, Ketones and Carboxylic Acid

Physical Properties of Aldehydes and Ketones

1. Boiling Point:

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to dipole-dipole interactions which results in weak molecular association. But their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

2. Solubility:

The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water. But the solubility decreases rapidly on increasing the length of alkyl chain.

3. Physical state:

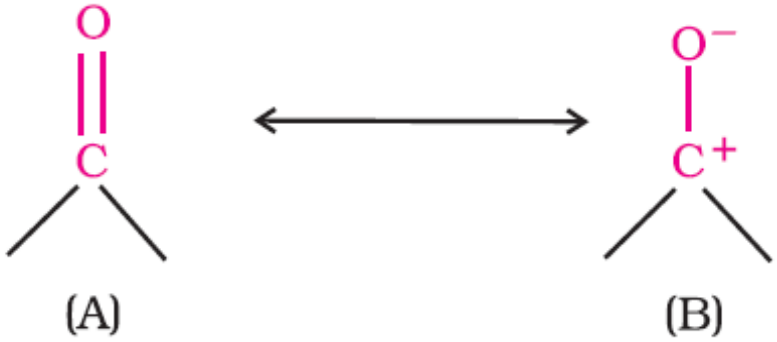
Methanal is a gas at room temperature, ethanal and acetone are volatile liquids and other aldehydes and ketones are liquid or solid.

Structure of the Carbonyl group

The carbonyl carbon atom is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon forms a π-bond with oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120^0.

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre.

The high polarity of the carbonyl group is explained on the basis of resonance as follows:

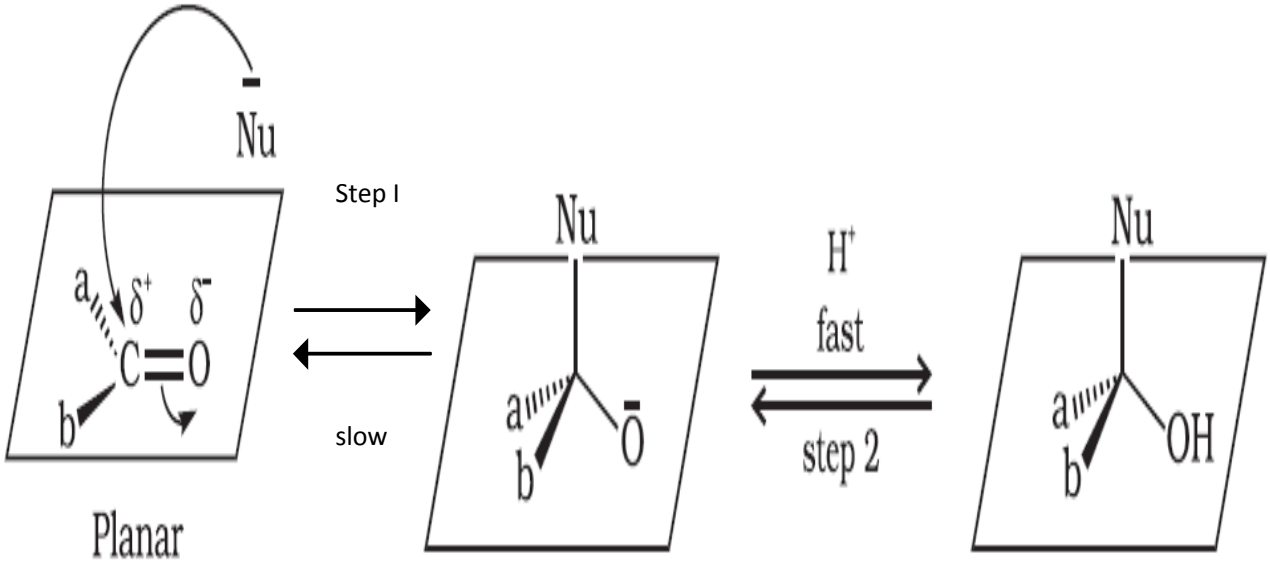


Chemical Reactions of Aldehydes and Ketones

Since aldehydes and ketones contain a carbonyl group, they undergo similar chemical reactions. The important reactions of aldehydes and ketones are:

1. Nucleophilic addition reactions:

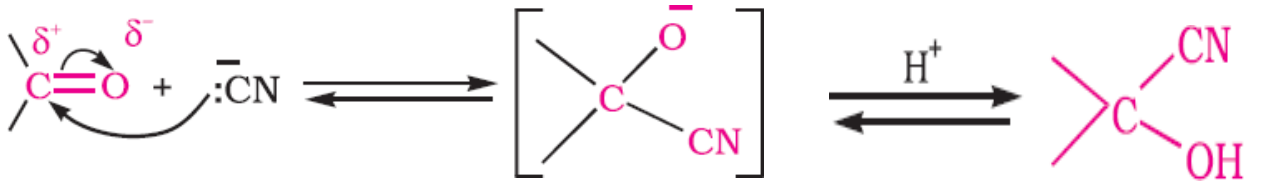
A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. As a result, the hybridisation of carbon changes from sp^2 to sp^3 and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the product.



Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two bulky alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes. Electronically, ketones are less reactive because of the electron releasing nature of the two alkyl groups reduces the electrophilicity of the carbonyl carbon.

Some important nucleophilic addition reactions of aldehydes and ketones are:

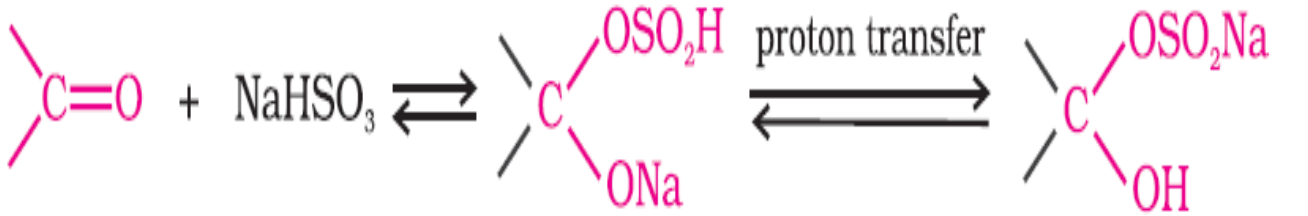
(a) Addition of hydrogen cyanide (HCN): Aldehydes and ketones react with hydrogen cyanide (HCN) in presence of a base to give cyanohydrins.



Intermediate Cyanohydrin

Aldehydes give aldehyde cyanohydrins and ketones give ketone cyanohydrins. The cyanohydrins are useful synthetic intermediates since it can be converted to carboxylic acids, amines, amides etc.

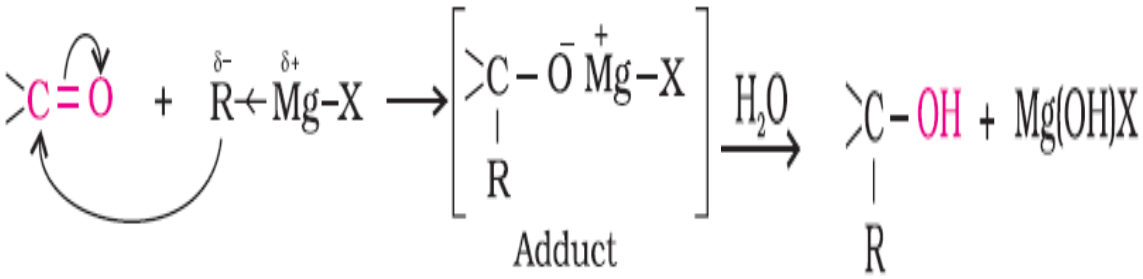
(b)Addition of sodium hydrogensulphite: Aldehydes and ketones add sodium hydrogensulphite to form the addition products (bisulphite adduct).



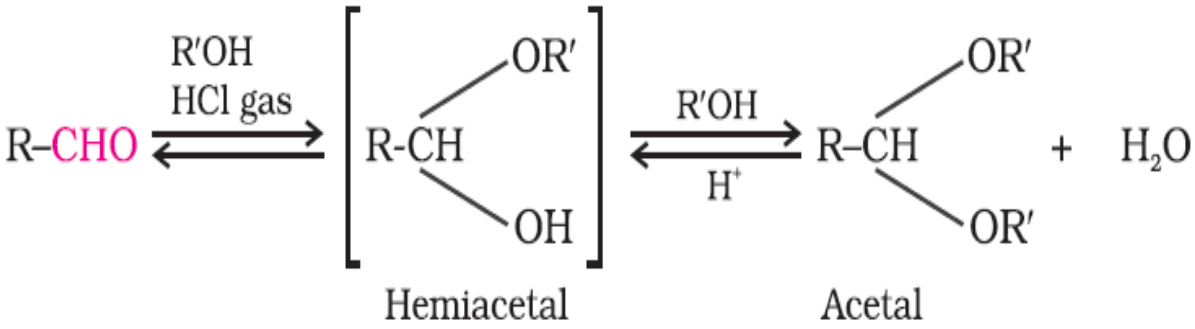
Bisulphite addition compound

The bisulphate adduct are water soluble and can be converted back to the original aldehyde or ketone by treating it with dilute mineral acid or alkali. Therefore, this reaction is used for the separation and purification of aldehydes and ketones.

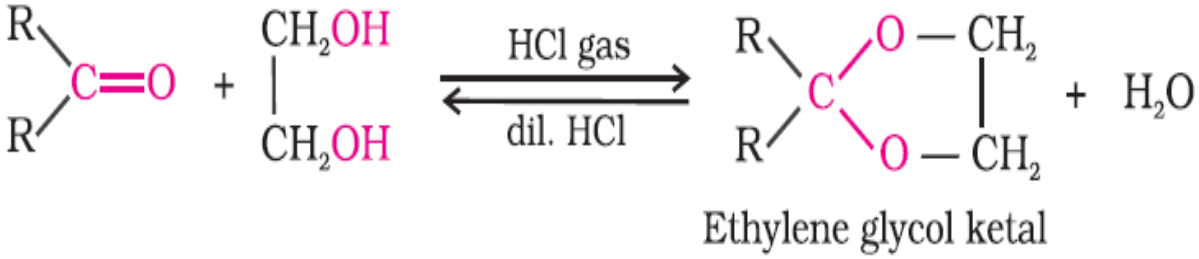
(c)Addition of Grignard reagents: Carbonyl compounds add Grignard reagent followed by hydrolysis, alcohols are formed. Formaldehyde gives primary alcohols, other aldehydes give secondary alcohols and ketones give tertiary alcohols.



(d)Addition of alcohols: Aldehydes react with monohydric alcohol in the presence of dry HCl to give alkoxyalcohol intermediate (known as hemiacetals), which further react with one molecule of alcohol to give a gem-dialkoxy compound known as acetal.



Ketones react with ethylene glycol in presence of dry HCl to form cyclic products known as ethylene glycol ketals. Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.



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