ALDEHYDES, KETONES and CARBOXYLIC ACIDS

SYNOPSIS:

* General formula for carbonyl compounds: $C_nH_{2n}O$.
* In carbonyl group, the hybridisation of carbon atom is sp^2.
* In aldehyde the functional group is –CHO.
* In aldehydes one of the two available valencies of carbonyl group carbon is satisfied by H atom and another by H atom or C atom of aryl or alkyl group. Due to this the aldehyde group becomes chain terminating group.
* Aldehydes are named after the carboxylic acids which they form on oxidation.
  In the common system ketones are named by mentioning the alkyl groups in alphabetical order and then giving the suffix ketone. If both the alkyl groups are same then the prefix 'di' - is used for alkyl group.
* When Propyne is passed through an aqueous solution of 40% H_2SO_4 in presence of 1% $HgSO_4$ (catalyst) at 60^0C, Acetone is obtained. This is a <u>hydration</u> reaction.
* In this reaction, $BaSO_4$ acts as a catalytic poison and lowers the activity of the catalyst.
* $BaSO_4$ acts as poison and prevents the reduction of aldehyde to alcohol.
* Small amount of quinoline and sulphur is added to poison the catalyst in Rosenmund's reduction.
* Ketones can't be prepared by this method.
* The carbon - oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. This polarity of carbonyl group due to resonance leads to two active centres i.e. a positive centre (electrophilic) on the carbon atom, and a negative centre (nucleophilic) on the oxygen.
* If the nucleophile is strong it will readily attack the carbonyl carbon, and the product is subsequently protonated by the solvent or by the added acid
* **Reactivity:** Aldehydes are more reactive towards nucleophilic attack than ketones for both steric and electronic reasons.
* The presence of alkyl group increases the crowding near carbonyl group. Thus larger alkyl groups hinder the approach of nucleophile to carbonyl carbon and decreases the reactivity.
  Order of reactivity: HCHO > R-CHO > RCOR
* **Electronic effect:** Alkyl groups, phenyl groups reduce the electrophilicity and electron with drawing groups increase the electrophilicity of the carbonyl group.
  Ex: $NO_2CH_2CHO > ClCH_2CHO > CH_3CHO > CH_3CH_2CHO$.

* Generally among ketones, those with smaller alkyl groups are more reactive than those with bigger alkyl groups.
* **Action of ammonia:** Acetaldehyde forms acetaldehyde ammonia and acetone forms diacetone ammonia with ammonia.
* Acetals and ketals are hydrolysed with aqueous mineral acids give corresponding aldehydes and ketones respectively.
* **"Addition of Grignard reagents"** to aldehydes and ketones form an addition product. This addition product formed is hydrolysed to alcohols.
* Aldehydes and ketones differ slightly in their oxidation reactions. Acetaldehyde is easily oxidised to acetic acid that contains same number of carbon atoms as that in acetaldehyde with common oxidising agents like nitric acid, potassium dichromate, potassium permanganate etc. Mild oxidising agents like Ag^{+} and Cu^{2+} also oxidise acetaldehyde to acetic acid in alkaline medium. Acetone gets oxidised only with strong oxidising agent like potassium dichromate but nto with mild oxidising agents Ag^{+}, Cu^{2+} etc. Oxidation of acetone involved carbon - carbon bond cleavage and the carboxylic acid (acetic acid) formed contains less number of carbon atoms than those in ketone.
* In this reaction we may use X_2/K_2CO_3, X_2/KOH, X_2/Na_2CO_3, $CaOCl_2$, $X_2/Ca(OH)_2$, NaOX etc.
* The reaction is an oxidative cleavage of aldehydes and ketones having atleast one methyl group linked to the carbonyl carbon atom.
* The methyl group is converted to haloform, and the residual part is converted to salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound.
* Compounds containing CH_3CH (OH)-group also undergo haloform reaction as they produce CH_3CO-group on oxidation.
* Paraldehyde is pleasent smelling liquid with boiling point 128^0c. It is used as a hypnotic drug.
* Acetaldehyde when treated with conc. H_2SO_4 at 0^0c gives metaldehyde.
* Metaldehyde is a cyclic tetramer, which is a white solid with m.p. -246^0C. It is used as a solid fuel.
* Fehling's solution is obtained by mixing equal volumes of solution -1 with solution - 2.
* Para Rosaniline Hydrochloride is a pink coloured solution.
* When SO_2 gas is passed through Para Rosaniline Hydrochloride, it becomes colourless. It is schiffs reagent.
* Acetaldehyde restores the pink colour when reacts with schiffs reagent by absorbing SO_2 gas
* Acetone does not give Tollen's, Fehling's, and Benedict's test because Ag^{+}, Cu^{+2} are mild oxidizing agents.