PHYSICAL PROPERTIES OF ALDEHYDE AND KETONE:

a) Solubility: Lower aldehyde and ketone are soluble in water because they can form intermolecular H-bonding with water molecules.

$$R - C = O \cdots\cdots\cdots H - O$$

$$|\qquad\qquad\qquad\qquad |$$

$$H \qquad\qquad\qquad H \cdots\cdots O = C - R$$

$$|$$

$$H$$

But their solubility decrease with increase in molecular mass.

b) Boiling point : Aldehyde and ketone are polar compounds. Therefore ,there exits strong dipole –dipole interaction between there molecules .Hence they have higher boiling point than alkane of comparable molecular mass.

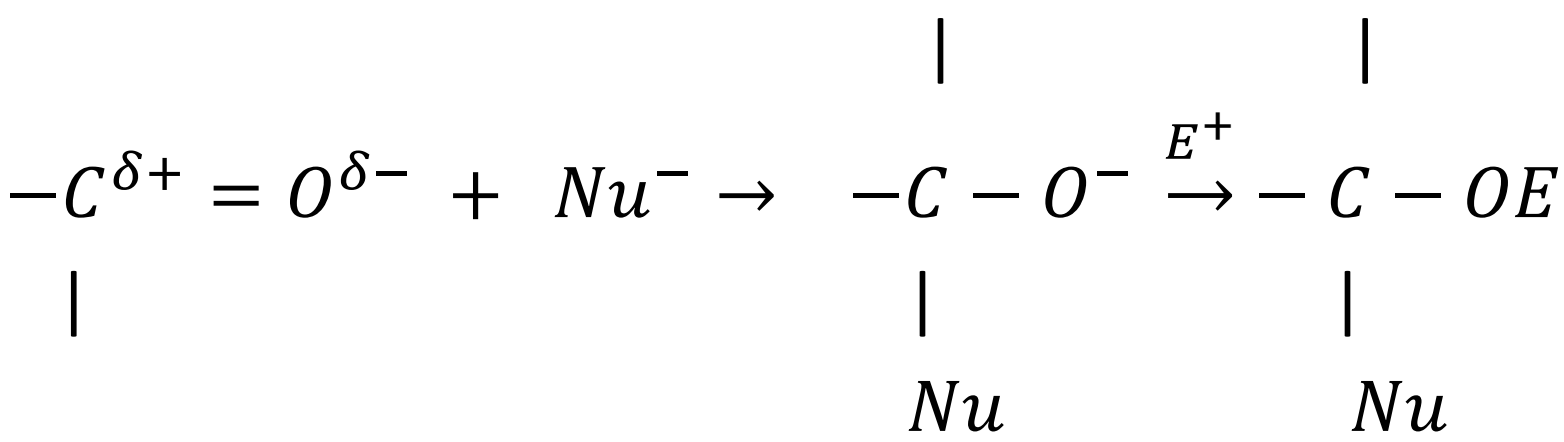
Compounds	molecular mass	boiling point
$CH_3CH_2CH_2CH_2CH_3$	72	36℃
$CH_3CH_2CH_2CHO$	72	76℃

But their boiling point is less than alcohol of comparable molecular mass because they are not able to form H- bonding between their molecules while alcohols are hydrogen bonded compounds.

Compounds	molecular mass	boiling point
$CH_3CH_2COCH_3$	72	80°C
$CH_3CH_2CH_2CH_2OH$	74	118°C

CHEMICAL PROPERTIES:

Due to presence of carbonyl group, the common reaction given by aldehyde and ketone is nucleophilic addition reaction because the carbonyl carbon is electron deficient and it becomes good attacking site for nucleophile. For this reaction, aldehydes are more reactive than ketones.



nucleophilic addition product

Reasons for high reactivity of aldehyde:

a) Inductive effect of alkyl group.

Alkyl groups are electron releasing group so they make carbonyl carbon less electropositive and therefore the carbonyl group becomes less reactive for the nucleophilic attack. In ketones, there are two alkyl groups with carbonyl carbon while in aldehydes,there is one alkyl group.Therefore,aldehydes are more reactive than ketones. Since the inductive effect increases with increase in number and size

Of the alkyl groups .Increase in inductive effect means decrease in reactivity. Therefore, lower aldehydes are more reactive than higher aldehydes.

b) Steric factor: In aldehyde, carbonyl carbon is attached to one bulky alkyl group whereas in ketones, the carbonyl carbon is attached with two bulky groups, which causes much steric hindrance for the attack by nucleophile. Thus reactivity of ketones get decreased.

$$H-C=O \quad > \quad R-C=O \; > \quad R-C=O$$
$$\quad\;\; | \qquad\qquad\qquad\;\; | \qquad\qquad\qquad\;\; |$$
$$\quad\;\; H \qquad\qquad\qquad\;\; H \qquad\qquad\qquad\;\; R$$

reactivity decrease

Some important nucleophilic addition reactions given by aldehydes and ketones:

A) Nucleophilic addition reactions.

a) Addition of hydrogen cyanide(HCN) : Aldehyde and ketone give cyanohydrin on reacting with HCN.

$$R-\underset{\displaystyle H}{\underset{|}{C}}=O \;+HCN \xrightarrow[H_2SO_4]{NaCN} R-\underset{\displaystyle CN}{\underset{|}{CH}}-OH$$

aldehyde cyanohydrin

$$CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O \;+\; HCN \;\rightarrow CH_3-\underset{\displaystyle CN}{\underset{|}{CH}}-OH$$

acetaldehyde cyanohydrin of acetaldehyde

Such cyanohydrin on hydrolysis gives $\alpha-$ hydroxy carboxylic acid which on strong heating, is dehydrated to α,β −unsaturated acid.

$$CH_3-CH-OH \xrightarrow[H_2O]{H^+} CH_3-CH-OH \xrightarrow{\Delta} CH_2=CH-COOH + H_2O$$

$$\begin{array}{lll} | & | & \text{propenoic acid} \\ CN & COOH & \alpha,\beta-unsaturated\ acid \end{array}$$

b) Addition of sodium bisulphit($NaHSO_3$): Both aldehyde and ketone form crystalline addition product when treated with a saturated solution of sodium bisulphite. This bisulphite addition product on heating with dil.acid or alkali ,regenerate original carbonyl compounds.

$$CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O + NaHSO_3 \rightarrow CH_3\underset{\displaystyle SO_3H}{\underset{|}{CH}} - O^-Na^+ \xrightarrow{proton\ trasfer} CH_3 - \underset{\displaystyle SO_3Na}{\underset{|}{CH}} - OH$$

acetaldehyde

acetaldehyde sodium bisulphite

$$CH_3 - \underset{\displaystyle SO_3Na}{\underset{|}{CH}} - OH + dilHCl \rightarrow CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O + SO_2 + H_2O + NaCl$$

The formation and decomposition of bisulphite addition product of aldehyde and ketone can be used for the separation and purification of carbonyl compounds from the non - carbonyl compounds.

c) Addition of Grignard reagent: Aldehydes and ketones react with Grignard reagent (RMgX) to form addition product which on hydrolysis gives different types of alcohol.

Formaldehyde or methanal gives primary alcohol on reacting with Grignard reagent.

$$RMgX + H - \underset{\displaystyle H}{\underset{|}{C}} = O \rightarrow H - \underset{\displaystyle R}{\underset{|}{CH}} - OMgX \xrightarrow[H_2O]{H^+} R - \underset{\displaystyle H}{\underset{|}{CH}} - OH + Mg(OH)X$$

methanal addition product $1° - alcohol$

Aldehydes other than formaldehyde give $2° - alcohol$.

Ketones give $3° - alcohol$.

$$R-C=O+RMgX \rightarrow R-CH-OMgX \xrightarrow[H_2O]{H^+} R-CH-OH$$

$$\begin{array}{ccc} | & | & | \\ H & R & R \end{array}$$

aldehyde — secondary alcohol

$$R-C=O+RMgX \rightarrow R_2-C-OMgX \xrightarrow{H^+/H_2O} R_2-C-OH$$

$$\begin{array}{ccc} | & | & | \\ R & R & R \end{array}$$

ketone — $3° - alcohol$

d) Addition of alcohol: Aldehyde (not ketone) react with alcohol in presence of dry HCl to form gem. dialkoxy compound which is known as acetal.

$$CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O \;\; + C_2H_5OH \xrightarrow{dry\ HCl} CH_3 - \underset{\displaystyle OC_2H_5}{\underset{|}{CH}} - OH \xrightarrow{C_2H_5OH} CH_3 - \underset{\displaystyle OC_2H_5}{\underset{|}{CH}} - OC_2H_5$$

ethanal — hemiacetal — acetal

1,1-diethoxy ethane

B) Nucleophilic addition followed by elimination reaction.

When aldehyde and ketone is treated with ammonia derivatives ($NH_2 - G$), organic compound containing $-\underset{|}{C} = N$ is formed.

$$-C^{\delta+}=O^{\delta-} \quad + \ddot{N}H_2 - G \rightarrow -C(H)(OH)-N-G \xrightarrow{-H_2O} -C=N-G$$

Carbonyl Compound

a) Addition of hydroxylamine($NH_2 - OH$)

Aldehyde and ketone give oxime on reacting with hydroxylamine.

$$CH_3 - C(H)=O \; + NH_2OH \; \rightarrow \; CH_3 - C(H)=N-OH \; + \; H_2O$$

Acetaldehyde Oxime(acetaldoxime)