Aldehydes & Ketones

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1   Introduction

Aldehydes and Ketones are organic compounds that are present in most foods and aromas. They are found commonly in nature and they exist in our bodies. Testosterone and progesterone are both ketones that exist in our bodies.

2 Theory

Aldehydes and Ketones are organic compounds that contain carbonyl groups $C{=}O$. They can be formed through the oxidation of primary and secondary alcohols. The carbonyl bond contains a σ bond and a π bond, which both contain two electrons each. Oxygen is more electronegative than carbon, meaning that the electrons in the double bond are more attracted to the oxygen atom. This bond is permanently polarised, resulting in a $\delta+$ charge on the carbon atom and a $\delta-$ charge on the oxygen atom. This affects the physical and chemical properties of aldehydes and ketones.
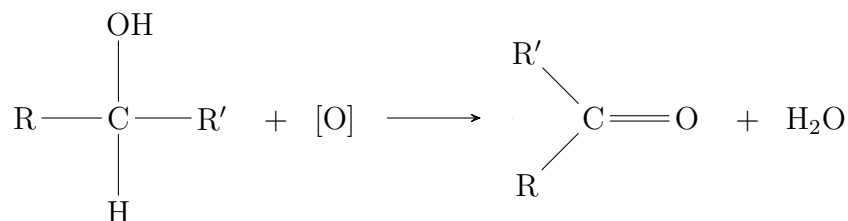
These are the general formulas for aldehydes and ketones:

Aldehyde   Ketone

Where R is a carbon chain of unspecified length or structure. As you can see, the aldehyde is formed through the partial oxidation of a primary alcohol:
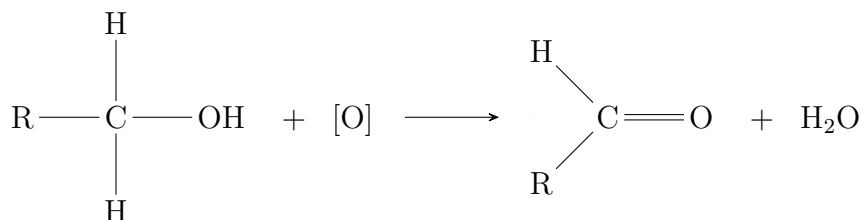

The ketone is formed through the oxidation of a secondary alcohol:

Aldehydes and ketones have higher boiling points than alkanes. This is due to the fact that the carbonyl groups have permanent dipole-dipole interactions, where alkanes only have Van der Waals weak intermolecular forces holding the molecules together. Alcohols, on the other hand have higher boiling points due to the fact that they can form hydrogen bonds.
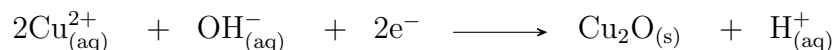
This means that upon oxidation, the boiling point reduces. Just like alkanes, straight chain aldehydes and ketones have higher boiling points than branched chain aldehydes and ketones since they cannot be packed closely together. Aldehydes and ketones can also dissolve in water, but the solubility decreases with increasing chain length. Aldehydes and Ketones can form hydrogen bonds with water molecules:
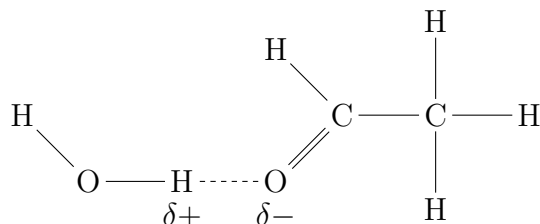
Van der Waals forces and dipole-dipole interactions exist between the carbonyl compounds and the water molecules. These interactions release energy, which supplies the energy needed to separate the water molecules from each other as well as the energy needed to separate the carbonyl compounds from each other, so that the hydrogen bonds can form, which supplies more energy. This interaction allows the carbonyl compounds to mix with water molecules.

3   Reactions of carbonyl compounds

One common way to distinguish the aldehydes and ketones is to observe whether they can be further oxidised or not. Fehling's solution, also known as Benedict's solution, is a solution that can be used to distinguish between aldehydes and ketones. It contains an aqueous alkaline solution which contains Cu^{2+} ions. This alone would produce a precipitate of copper(II) hydroxide. But this precipitation is prevented with the presence of 2,3-dihydroxybutanedioate ions, which forms a complex with the Cu^{2+} ions. If you were to warm an aldehyde with Fehling's solution, the solution would oxidise the aldehyde into a carboxylic acid, therefore reducing the Fehling's solution, giving a red-brown precipitate of copper(I) oxide. These are the half equations for the reaction:

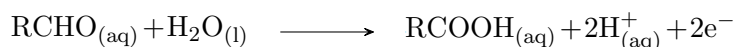$$2Cu^{2+}_{(aq)} \quad + \quad OH^-_{(aq)} \quad + \quad 2e^- \quad \longrightarrow \quad Cu_2O_{(s)} \quad + \quad H^+_{(aq)}$$

and:

$$RCHO_{(aq)} \quad + \quad H_2O_{(l)} \quad \longrightarrow \quad RCOOH_{(aq)} \quad + \quad 2H^+_{(aq)} \quad + \quad 2e^-$$

So by combining the two equations you can get this overall equation:

$$2Cu^{2+}_{(aq)} + RCHO_{(aq)} + OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Cu_2O_{(s)} + RCOOH_{(aq)} + 2H^+_{(aq)}$$
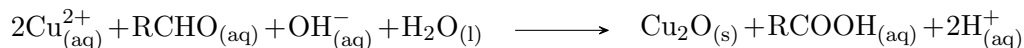
A ketone would not get oxidised by this reaction, meaning that the solution will stay blue. Another oxidation reaction test is the silver mirror test, using Tollen's Reagent. Tollen's Reagent is produced by dissolving silver nitrate in water and adding aqueous ammonia. Initially, silver(I) oxide is formed as a precipitate, but this dissolves upon the addition of ammonia, forming a complex diamminesilver(I) ion, $[Ag(NH_3)_2]^+$. When Tollen's Reagent is warmed gently with an aldehyde, the aldehyde gets oxidised and the silver(I) ions in the complex are reduced to form silver metal. If this reaction is carried out carefully, a silver mirror is formed from the inside of the test tube. If this reaction is not done carefully, a black precipitate forms. These are the half equations associated with the reaction:

$$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$$

and:

$$RCHO_{(aq)} + H_2O_{(l)} \longrightarrow RCOOH_{(aq)} + 2H^+_{(aq)} + 2e^-$$

So by combining the two equations you can get this overall equation:

$$2Ag^+_{(aq)} + RCHO_{(aq)} + H_2O_{(l)} \longrightarrow 2Ag_{(s)} + RCOOH_{(aq)} + 2H^+_{(aq)}$$
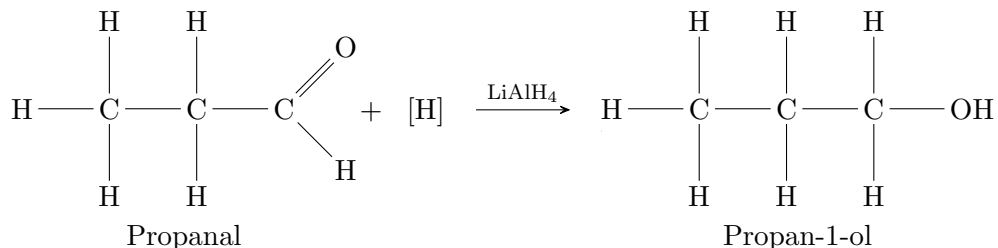
Obviously, as before, if a ketone is warmed with the same reagent, there is no reaction. The oxidation of aldehydes can be carried out by warming the aldehyde with a solution of potassium dichromate(VI) acidified with sulphuric acid. This is the full equation:

$$RCHO_{(l)} + Cr_2O_7^{2-}{}_{(aq)} + 8H^+_{(aq)} \longrightarrow RCOOH_{(aq)} + 4H_2O_{(l)} + 2Cr^{3+}_{(aq)}$$
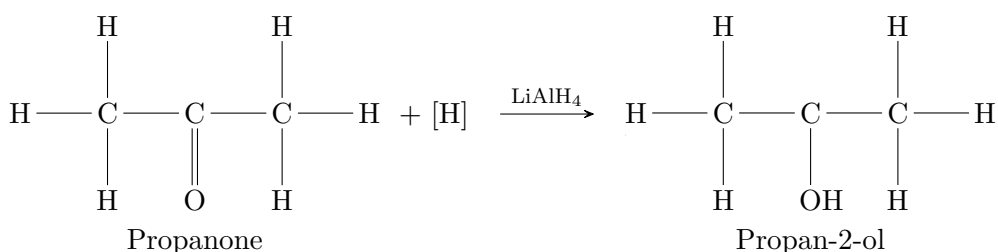
As before, there would be no reaction with any ketone.

All the oxidation reactions shown on page 2 are reversible, and are formally known as reduction reactions. Aldehydes are readily reduced to primary alcohols and ketones are readily reduced to secondary alcohols. Suitable reagents for these reactions are Lithium tetrahydridoaluminate ($LiAlH_4$) dissolved in dry ether, or Sodium tetrahydridoborate ($NaBH_4$) dissolved in ethanol.

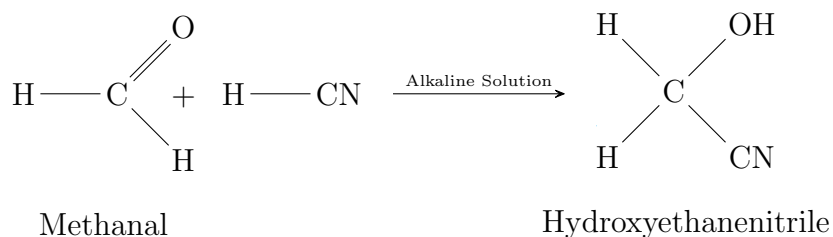These are the equations for the reduction reactions of propanal:

$$\text{Propanal} + [\text{H}] \xrightarrow{\text{LiAlH}_4} \text{Propan-1-ol}$$

and propanone:

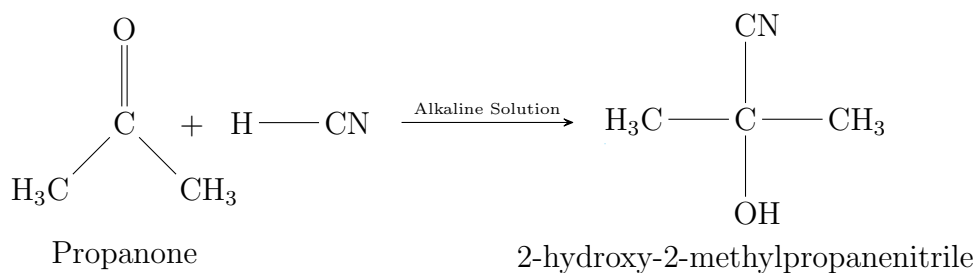$$\text{Propanone} + [\text{H}] \xrightarrow{\text{LiAlH}_4} \text{Propan-2-ol}$$

It is important to note that the reason for dissolving the Lithium aluminium hydride in dry ether instead of water, is due to the fact that water reacts quite voilently with $LiAlH_4$, even if it is water in the atmospheric moisture. $NaBH_4$ on the other hand is not as powerful a reducing agent as $LiAlH_4$, but it is much easier to handle in the lab.

Aldehydes and ketones undergo addition reactions with hydrogen cyanide, producing hydroxynitriles, otherwise known as cyanohydrins. The hydrogen cyanide molecules add across the carbonyl group as shown below:

$$\text{Methanal} + \text{H}\!-\!\text{CN} \xrightarrow{\text{Alkaline Solution}} \text{Hydroxyethanenitrile}$$

and for ketones:

$$\text{Propanone} + \text{H}\!-\!\text{CN} \xrightarrow{\text{Alkaline Solution}} \text{2-hydroxy-2-methylpropanenitrile}$$

This reaction requires the presence of potassium cyanide in cold, alkaline solution. In aqueous solution, the following acid-base equilibrium is established:
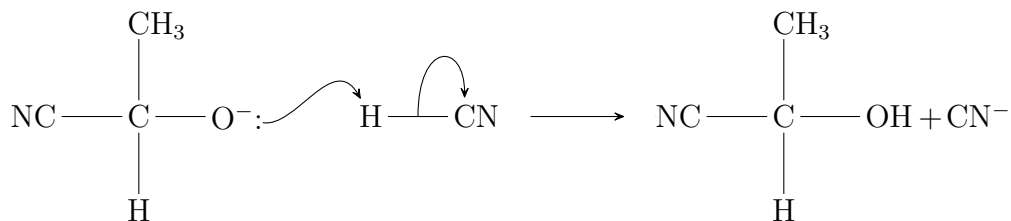
$$K^+_{(aq)} \;+\; CN^-_{(aq)} \;+\; H_2O_{(l)} \;\rightleftharpoons\; K^+_{(aq)} \;+\; HCN_{(aq)} \;+\; OH^+_{(aq)}$$
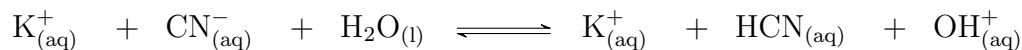
The backward reaction is favoured more than the forward reaction. This means that there is more $CN^-_{(aq)}$ formed. This is the nucleophile required for attacking the carbon atom with the carbonyl group attached to it. This is the mechanism of the reaction:

Step 1:
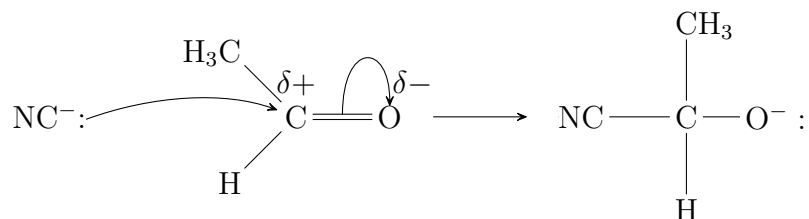
Step 2:

In the first step, the incoming nucleophile (CN^-) has a lone pair of electrons. The nucleophile attacks the central carbon atom, displacing the pair of electrons in the double bond, pushing them to the oxygen atom. This gives the oxygen atoma negative charge. In the second step of the mechanism, the negatively charged oxygen atom acts as a base and accepts a donated proton from the hydrogen cyanide molecule to make the final product. This particular reaction produces a chiral molecule as it has 4 different groups attached around the central carbon. If we look at carbonyl carbon, we can see that it is a planar molecule. This means that CN^- can attack from either above or below the plane of the molecule, with each possibility having the same probability. This in turn means that both enantiomers of the final product are formed in equal quantities, producing a racemic mixture.
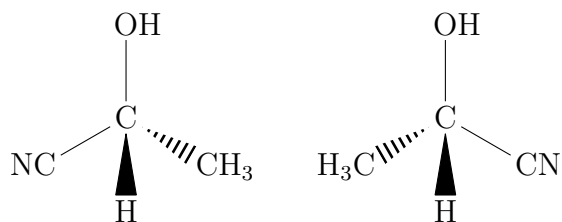
Consider the following reaction:
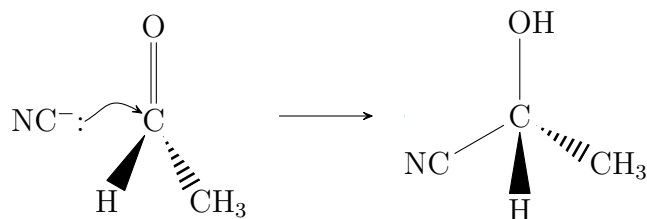

producing one enantiomer, and:
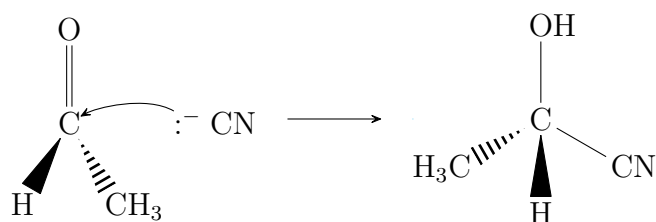
producing the other enantiomer. Seeing these two molecules side by side, we can easily see that these are enantiomers:

Brady's reagent otherwise known as (2,4-dinitrophenylhydrazine) is a red-orange solid, usually supplied as wet so as to reduce the chances of an explosion occuring. This is the skeletal formula:
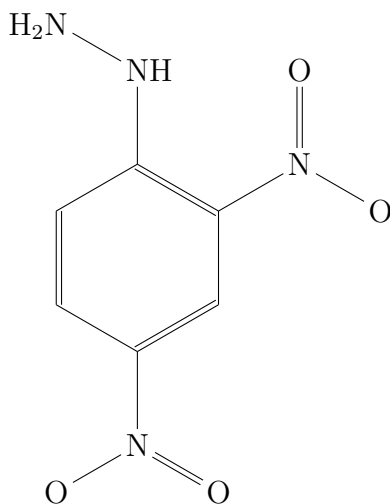
Aldehydes and Ketones react with Brady's Reagent to form a crystalline solid which is either yellow, orange, or red. These solids are called 2,4-dinitrophenylhydrazine derivatives. The reagent's hydrazine group reacts with the carbonyl group in a condensation reaction that forms water. Consider the following reaction:
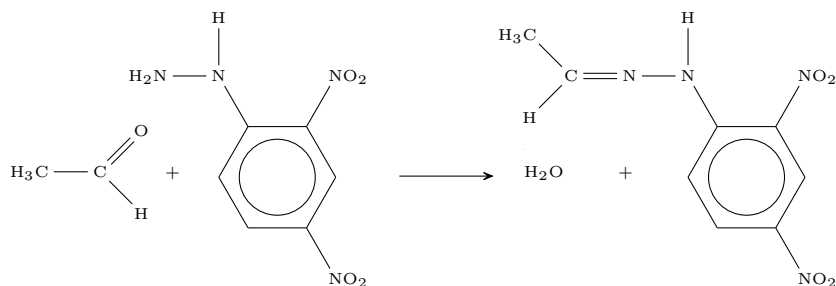
The derivative produced can be removed by filtration and purified by recrystallisation. These compounds have charecteristic melting temperatures which can be refereenced in most data books. This table shows the temperatures for the derivatives of some carbonyl compounds.

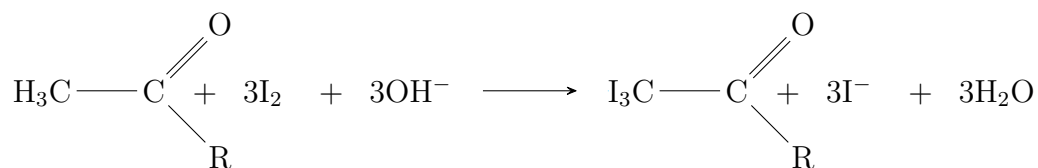| Carbonyl compound	Melting temperature of 2,4-dinitrophenylhydrazone/°C
Methenal	166
Ethanal	168
Propanal	155
Butanal	126
Benzaldehyde	237
Propanone	126
Butanone	115
Pentan-3-one	156

Brady's Reagent is used to identify the presence of a carbonyl group, and it is also used to identify the structure of the specific carbonyl compound reacted with it. The positive test for a carbonyl group tested against Brady's Reagent is that either a yellow, orange, or red precipitate forms. The carbonyl compound can be identified given data of the melting temperatures of the derivatives. other compounds such as hydroxylamine, hydrazine, or dinitrohydrazine, fow example can be used to form derivatives. We use 2,4-dinitrophenylhydrazine derivatives since they are less soluble and can therefore crystallise out more easily.

The triiodomethane reaction is a reaction with carbonyl compounds, specifically carbonyl compounds next to a methyl group. Specifically, the reaction only takes place with molecules of these forms.

$$\underset{\displaystyle H_3C - C}{}\overset{\displaystyle O}{\underset{\displaystyle R}{\big\|}} \qquad \qquad H_3C - \overset{\displaystyle OH}{\underset{\displaystyle H}{C}} - R$$
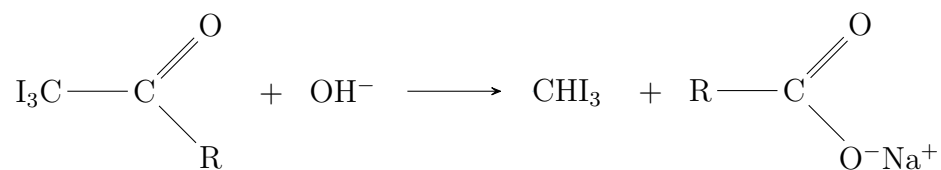
Where R is representative of hydrogen atom or a carbon chain of undefined length and structure. When R is just a hydrogen atom, we can see that only two molecules of such form undergo the reaction: ethanal and ethanol. Ethanal is the only aldehyde that undergoes the reaction, and ethanol is the only primary alcohol to undergo the reaction. The reaction is carried out by warming the test sample with iodine in alkaline solution of Sodium Hydroxide, which produces a two stage reaction:

Step 1:

$$H_3C - \overset{O}{\underset{R}{C}} \;+\; 3I_2 \;+\; 3OH^- \longrightarrow I_3C - \overset{O}{\underset{R}{C}} \;+\; 3I^- \;+\; 3H_2O$$

Step 2:

$$I_3C - \overset{O}{\underset{R}{C}} \;+\; OH^- \longrightarrow CHI_3 \;+\; R - \overset{O}{\underset{O^- Na^+}{C}}$$

The triiodomethane formed is an insoluble yellow precipitate with a characteristic smell. The methyl alcohol reacts the same way after being oxidised to form a methyl ketone (or in the one specific case, ethanal), to then react as shown above. This reaction is also known as the iodoform reaction.