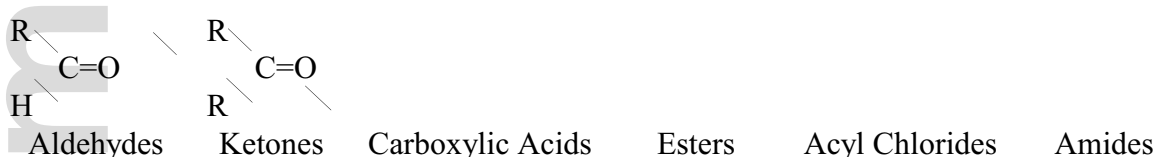


Chemistry of Carbonyl Compounds

Aldehydes & Ketones

(Alkanals and Alkanones)

There are a number of important homologous series in which the compounds contain C = O functional group they are:



In addition to its own properties the carbonyl group has a considerable effect on adjacent groups. In this unit we will be concerned with the chemistry of aldehydes, (alkanals), and ketones, (alkanones).

Nomenclature of Aldehydes & Ketones

Some aldehydes and ketones have been known for a long time and their trivial names are widely used. The IUPAC nomenclature replaces the suffix **-ane** of alkane in the case of aldehyde, by **-al** (alkanal) and **-one** (alkanone) for ketones. The location of the carbonyl group must be specified with a number preceding the suffix **-one**, except in cyclic ketones, where it is assumed to occupy the number 1 position.

Methanal (Formaldehyde)	Cyclohexanone	Propanone (Acetone)
Ethanal (Acetaldehyde)	Benzaldehyde (benzenecarbaldehyde)	Alkylphenylketone (Ex: acetophenone or phenylethanone)

Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, is used in small quantities in flavourings, (flavour of almonds) and perfumes.

Methanal, HCHO , the aqueous solution is known as “formalin”, and is used to preserve biological specimens, to sterilise surgical instruments, and is used as a fungicide and disinfectant. Methanal was the first polymer synthesized in 1907; and is also used to make ‘Bakelite, Formica’ for heat insulation, example: handles for pots and pans and electrical insulation and the explosive cyclonite.

Vanillin is used in flavouring chocolate.

The aldehyde 2-methylundecanal, $\text{CH}_3(\text{CH}_2)_8\text{CHCH}_3\text{CHO}$, has a special place in perfume chemistry. When Marilyn Monroe was asked what she wore in bed, she replied ‘Chanel No. 5’. The perfume she referred to was created in 1921 by Ernest Beaux, for the designer ‘Coco’ Chanel. In addition to natural oils derived from flowers, Beaux included a synthetic substance, 2-methylundecanal, to provide the most volatile part of the perfume. This was the first time a synthetic substance had been included in a prestigious perfume. The components in Chanel No 5 are blended to vaporize at the same rate so that the scent does not change over the course of the day.

Propanone, CH_3COCH_3 , is a very versatile solvent for lacquers and perfumes, and is used to manufacture Perspex, poly methyl 2-methylpropanoate. Propanone can also be produced in the body. In people suffering diabetes, abnormal metabolic reactions lead to the production of propanone. It builds up in the tissues and appears in the breath and urine of diabetics, unless they are successfully treated.

The Nature of the Carbonyl Group

The carbonyl group consists of two pairs of electrons being shared between a carbon atom and an oxygen atom:



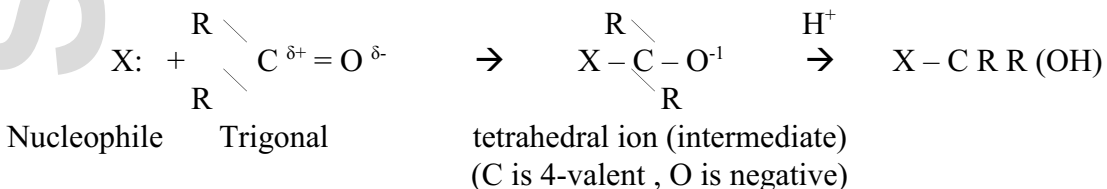
The experimental evidence indicates that the carbonyl carbon atom is sp^2 hybridized; three single σ -bonds, which are coplanar, thus the molecule is flat, lying in a plane, with angles of 120° between bonds. The double bond is made up of an σ -bond and a π -bond, the latter being positioned above and below the plane of the molecule.

Alkenes are also planar, sp^2 hybridized, containing an σ -bond and a π -bond with bond angles of 120° . However, the difference between the alkene double bond and the carbonyl double bond arises from the different electronegativities of the elements involved.

The oxygen has a stronger pull on the mobile π -electron cloud than the carbon atom, the electrons being unevenly distributed and being more concentrated around the oxygen atom. This means that the carbonyl bond will be strongly polar as indicated by the $\delta+$ and $\delta-$ signs. The electron deficient C atom will be liable to, i.e. a good target for **nucleophilic attack**, and since the molecules are flat, the C atom is relatively open; therefore comparatively little steric hindrance is expected by an approaching group.

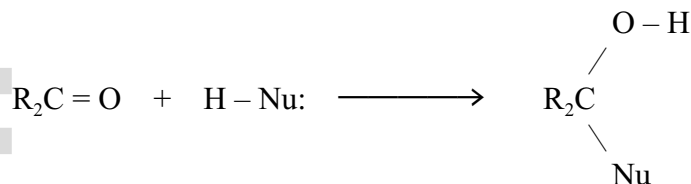
One further feature assists **nucleophilic addition**. Carbon is particularly stable when it has four covalent bonds tetrahedrally arranged (sp^3), nucleophilic addition to a carbonyl group brings about a change, from a trigonal planar molecule, to one which is tetrahedral.

The attacking nucleophile forms a bond to the C, which causes the π bond in the $\text{C}=\text{O}$ to break, since the π electrons are repelled away from the carbon atom towards the oxygen atom. The displaced electrons of the π -bond can go to the electronegative oxygen atom to make a relatively stable tetrahedral intermediate carrying a negative charge:



To complete the addition, this intermediate can be protonated on the O^{-1} atom, (acting as a base), i.e. the oxygen atom acquires an electrophile, usually a proton to become a hydroxyl, ($-OH$).

In general, if $Nu:$ is the nucleophile, then the complete reaction is the addition of HNu across the double bond:



Because the carbonyl group has a double bond, it might be expected that the nucleophilic reaction will be addition. In fact nucleophilic addition is one of the principle reactions of the carbonyl group. (Recall: However, Electrophilic addition occurs in alkenes)

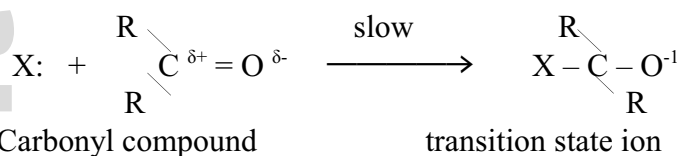
The $C=O$ double bond at 804 kJ mol^{-1} is more than twice as strong as the $C-O$ single bond at 327 kJ mol^{-1} . This contrasts sharply with the situation in alkenes. As a result the carbonyl group is less reactive than the alkenes.

Nucleophilic Addition to Carbonyl Compounds

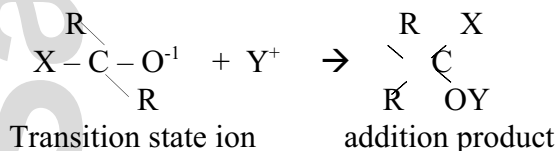
Nucleophilic addition to carbonyl compounds can be brought about by using the nucleophiles: CN^{-1} , H^{-1} , HSO_3^{-1} , $:NH_3$ (Only in the case of aldehydes)

Note: The cyanide, CN^{-1} , and hydrogen sulphite (aka: the bisulphite) ions, HSO_3^{-1} , are both conjugate bases of weak acids and are therefore strong bases themselves, (Recall: weak acids have strong conjugate bases), which add on to the carbon-oxygen double bond by donating an electron pair to the carbonyl atom.

The reactions proceed through to a transition state as follows:

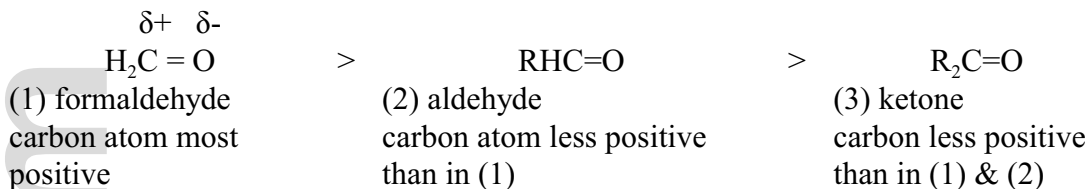


This then reacts with the positive ions in the reaction medium, forming the final product:



In general **aldehydes are more reactive than ketones**. The reasons for this are:

A) The extra alkyl group possessed by the ketones has a positive inductive effect. This will lessen the electron deficiency on the carbon atom of the carbonyl group; therefore it decreases its reactivity towards a nucleophile. Hence the order of reactivity is:



B) Steric factors also play an important role as the H atom of an aldehyde would be expected to offer little steric hindrance to the approach of a nucleophilic reagent; compared with the bulkier nature of the alkyl group of a ketone which will hinder the approach of the nucleophile.

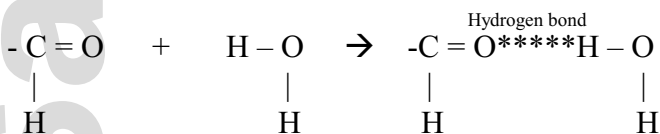
Examples of Reactivity:



Physical Properties

Lower members are colourless liquids, which are completely miscible with water. The boiling points of carbonyl compounds are high compared with the boiling points of non-polar hydrocarbons, due to the dipole moment associated with the polar carbonyl group, but lower than the boiling points of alcohols; since no hydrogen bonding is involved. Alkane molecules are held together by Van der Waals' forces, and alcohol molecules are held together by hydrogen bonding. The carbonyl compounds have dipole-dipole forces, they possess a dipole moment, which accounts for their difference in boiling point from alkanes.

Carbonyl compounds are unable to form hydrogen bonds with one another, but they can form them with water.



This accounts for the fact that lower members of carbonyl compounds are very soluble in water. Mixing propanone with water causes heat to be evolved, because of hydrogen bonds being made. *Aldehydes and ketones will be isomers of one another:*

Example: $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3

Preparation of Aldehydes and Ketones

Laboratory Preparation

1. Oxidation of alcohols

Primary Alcohols are oxidized to aldehydes, secondary alcohols to ketones. The oxidizing agent is acidified potassium dichromate (VI), or acidified potassium permanganate.

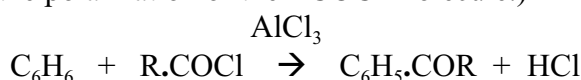
2. Oxidation of alkyl benzenes

Methyl benzene \rightarrow benzaldehyde

Oxidation also occurs when a vapour of a 1° or 2° alcohol is passed over Cu catalyst.

3. Friedel-Crafts Reaction

Aromatic ketones of the form R–CO–Ar, can be made with good yields by the action of acyl chlorides on the aromatic compounds, in the presence of a Lewis acid such as iron (III) chloride or aluminium chloride. (Recall: Electrophilic substitution, the role of the Lewis acid in the polarization of the RCOCl molecule.)



Industrial Preparation

Generally by vapour phase dehydrogenation of alcohol

(1° or 2° \rightarrow aldehyde / ketone) with catalyst at high temperature.

The most important aldehydes and ketones for industrial use are methanal, ethanal, acetone and butanone. The last two are important solvents, methanal is used to make the polymer Bakelite, ethanal is used to make ethanoic acid. (Formalin is a 37% solution of methanal, formaldehyde)

Chemical Properties: Nucleophilic Addition to Carbonyl Compounds

1. Addition of HCN

When hydrogen cyanide is passed through a carbonyl compound, a hydroxy-nitrile (cyanohydrin) is formed. (HCN is produced by addition of cold H_2SO_4 to KCN. HCN is a weak acid, it produces a very low concentration of CN^- ions, so the reaction would be slow. Excess KCN is needed to increase the reaction rate by increasing the CN^- concentration.)

This is an important reaction because this is a very useful way of introducing an extra carbon atom into the carbon chain during organic synthesis, i.e. **to ascend the homologous series.**

Mechanism:

Hydrogen cyanide dissociates and the cyanide ion acting as a nucleophilic reagent attacks the electron deficient carbon atom of the carbonyl group in the first step:

The intermediate negatively charged ion then reacts with a proton in the second step to give an addition known as a cyanohydrin (hydroxynitrile):

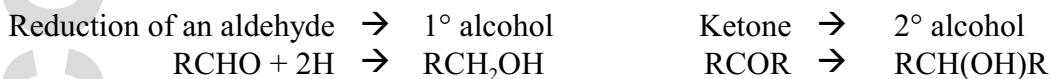
General Equation: $R R C = O \rightarrow R R C (OH) CN$

The hydrolysis of cyanhydrin, (hydroxynitriles), is a useful way of making hydroxycarboxylic acids:



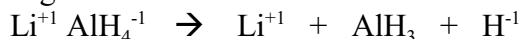
2. Addition of H^{-1} : Reduction

Aldehydes can be reduced to the corresponding primary alcohols, and ketones to secondary alcohols, by either $LiAlH_4$ or $NaBH_4$ (sodium borohydride, sodium tetrahydridoborate).



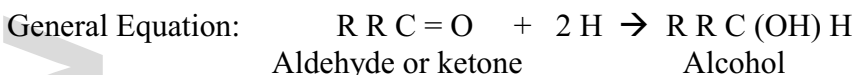
Lithium (I) tetrahydridoalumininate (III), (lithium aluminium hydride, $LiAlH_4$) dissolved in dry ether, (ethoxyethane) is used because the hydride reacts with water:

The complex hydride ion, AlH_4^{-1} , may be regarded as a hydride ion carrier ($:H^{-1}$) and hence as a nucleophilic reagent:



The addition is completed by protonation. $LiAlH_4$ reacts violently with water and alcohols so protonation is carried out after the reaction is complete.

Mechanism:



3. Addition of HSO_3^{-1} (bisulphite ion, hydrogensulphite ion)

Aldehydes and ketones react with a saturated solution of sodium hydrogen sulphate (IV), (sodium bisulphite, $Na^{+1} HSO_3^{-1}$). These compounds are sparingly soluble and frequently separate out as crystalline salts from which the carbonyl compound can be regenerated by treatment with acid or alkali, hence these derivatives are used to purify carbonyl compounds.

Mechanism:

The sulphur atom of the HSO_3^{-1} ion becomes attached to the C atom of the carbonyl group:

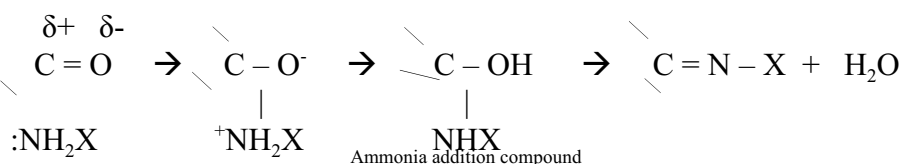
4. Addition of :NH₃

Introduction to nucleophilic addition – elimination, condensation reactions

These reactions involve a group of nucleophiles that carry **two hydrogen atoms on a nucleophilic nitrogen atom** (X – NH₂, where X- is OH, -NH₂, -C₆H₅, NH-, NH₂CONH-).

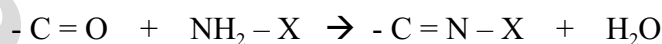
This means that the usual carbonyl addition product can then eliminate water to give an unsaturated product. These are called **addition-elimination or condensation** reactions.

Ammonia contains a N atom with an unshared pair of electrons and would, therefore, be expected to act as a nucleophilic reagent towards a carbonyl compound:

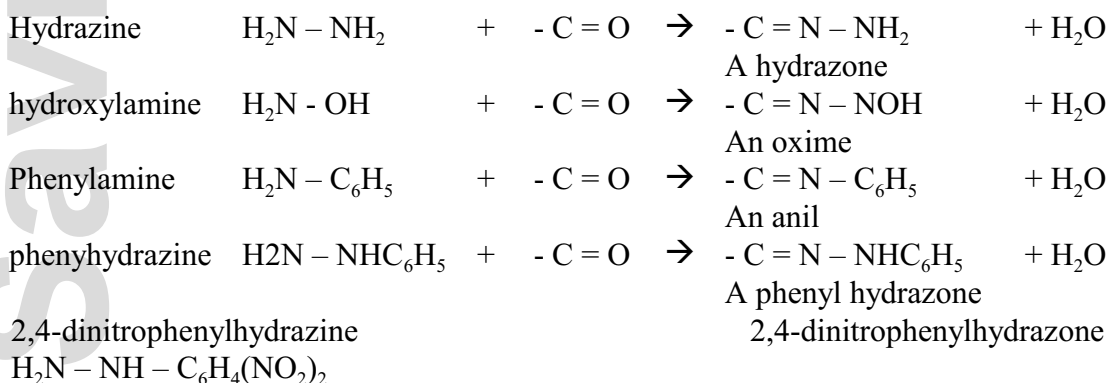


The addition compound is, however, too unstable to be isolated in general and the final product is a complex polymer. However the reactions of an aldehyde or ketone with derivatives of ammonia such as hydroxylamine, NH₂OH, and with hydrazine, NH₂.NH₂, and its derivatives are important in the isolation and characterization of carbonyl compounds, being crystalline solids, with characteristic colours the melting points can be used to identify the carbonyl compound. The compound chosen to make the derivative for identification is usually the 2,4-dinitrophenylhydrazine.

The development of spectroscopy, mainly IR and NMR, has rendered these, and many other test reactions relatively unimportant from the characterization point of view.



Examples of the reactions of carbonyl compounds with bases of the type H₂N – X are:



All of the compounds are nucleophilic reagents, as they contain a nitrogen atom with an unshared pair of electrons, and the reaction with the carbonyl compound consists of two steps – an addition followed by the elimination of water – the overall effect being substitution:

Mechanism:

Hydrazine (:NH₂ H₂N:), this is a good nucleophile. It is better than ammonia, NH₃, probably because of the repulsion between the nonbonded pairs of electrons on the adjacent N atoms. One of the nucleophilic nitrogen atoms uses its nonbonded pair to add to the carbonyl group (in the same way as H⁻ and CN⁻ did).

A tetrahedral intermediate is formed as usual, this then gains a proton on the O⁻ ion and loses a proton from the NH₂⁺ group to give an unchanged addition product (i.e. a gain-and-loss of protons):

The unchanged intermediate then eliminates water to give the final product, a hydrazone, which has a – C = N double bond.

Individual members of the alkanal and alkanone series may be identified by preparing a crystalline derivative and then determining its melting point. The best derivative to make is with 2,4-dinitrophenylhydrazine. The compound chosen to make a derivative for identification must be...

- a) easily prepared to give a high yield
- a) it must be a stable compound at temperatures of its melting point
- a) one must be able to obtain a purified form of it by recrystallisation easily
- a) it should have a sufficiently high melting point in the range of 50°C – 250°C so that it may be easily determined.

Effect of Carbonyl Groups on Alkyl and Aryl Groups

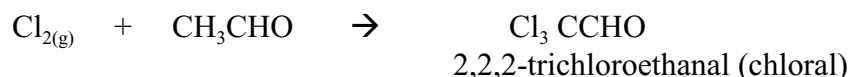
1. Effect on the aromatic ring

The positive carbon atom of a carbonyl group has the effect of pulling electrons away from the π – orbital of the benzene ring, and this has the effect of deactivating the ring.

The carbonyl group in aryl compounds behaves in much the same way as it does in alkyl compounds (i.e. benzaldehyde reduces MnO₄⁻, Cr₂O₇⁻² itself oxidized to the acid, it adds on CN⁻, HSO₃⁻, condenses with NH₂OH, and NH₂.NH₂ to form an oxime and a hydrazone. Benzophenone, C₆H₅.CO.C₆H₅, and acetophenone, CH₃.CO.C₆H₄ behave in the same way as alkyl ketones).

2. Effect of the carbonyl groups on C – H bonds in alkyl groups

A carbonyl group makes the C – H bonds on adjacent C atoms more reactive than in alkanes. This is due to its effect on the electron distribution in the C – H bonds, making them more polar. Therefore, substitution can be brought about more easily, without the use of UV light or high temperatures. Example:



Assignment

1. The alkene group reacts with compounds of formula HX. What can X be?
The carbonyl group reacts with compounds of formula HY. What can Y be?
Compare the reactivity of the alkene group and the carbonyl group in reactions of this type.
2. The formation of butanone hydroxynitrile is speeded up by the addition of cyanide ions and retarded by the addition of hydrogen ion. Explain these observations.
3. Why does HBr attack $C = C$ but not $C = O$?
4. Pentan-2-ol yields a ketone when heated with potassium dichromate solution under acid conditions.
 - a) Give the structural formula and name of the ketone.
 - b) What is the change in the oxidation number of chromium during the reaction?
 - c) What other reagents will oxidise the alcohol?
 - d) How can the product be identified as a ketone?
5. An aliphatic aldehyde **A** has the formula $RCHO$
 - a) **A** reacts with 2,4-dinitrophenylhydrazine. Explain what happens and name the type of reaction. Say how the product of the reaction could be used to identify **A**.
 - b) When **A** is treated with warm, acidified $K_2Cr_2O_{7(aq)}$, **B** is formed. Give the structural formula of **B**.
 - c) When **A** reacts with lithium tetrahydridoaluminate(III) in ethoxyethane solution, **C** is formed. Give the structural formula of **C**.
 - d) **B** and **C** react to form **D**. Write the structural formula of **D**.
 - e) Of the compounds A, B, C and D, which would you expect to have (i) the highest boiling point, (ii) the lowest boiling point. Explain your answers.
6. A carbonyl compound **X** undergoes the following reactions:
 - X** gives an orange precipitate with 2,4,-dinitrophenylhydrazine
 - X** does not react with warm, acidified potassium dichromate(VI), $K_2Cr_2O_{7(aq)}$
 - X** does not react with aqueous bromine
 - X** is reduced by hydrogen in the presence of a catalyst to a mixture of isomers **Y** and **Z** of formula $C_4H_{10}O$.Identify **X**, and give the structural formula of **X**, **Y** and **Z**.