ChemFactsheet

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Organic Chemistry 4: Carbonyl Compounds

To succeed in this topic you need to:-

- **Have a good knowledge and understanding of the organic chemistry covered so far (Factsheets 15, 16, 17, 27 31 and 32);**
- **Be confident in using organic nomenclature and structural formulae.**

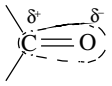
After working through this Factsheet you will:-

- **Know the functional groups of aldehydes and ketones;**
- **Know how to test for the carbonyl group, and how to distinguish between aldeydes and ketones;**
- **Have been given the required reaction types conditions and equations of the carbonyl compounds for the A2 exams.**

Carbonyl Compounds - Aldehydes and Ketones

The functional group is the carbonyl group:

Because oxygen is more electronegative than carbon, the electrons in the double bond of the functional group tend towards the oxygen atom making it δ-. The carbon atom becomes δ+, making it susceptible to **nucleophilic attack**.



In this Factsheet we shall look at several reactions of the carbonyl compounds, starting with common laboratory tests for these compounds.

There are two types of carbonyl compounds - the aldehydes and ketones.

Aldehydes

Functional group of the aldehydes:

The aldehydes are named using the suffix -al.
For example:

CH_2O	methanal
CH_3CHO	ethanal
CH_3CH_2CHO	propanal

Ketones

Functional group of the ketones:

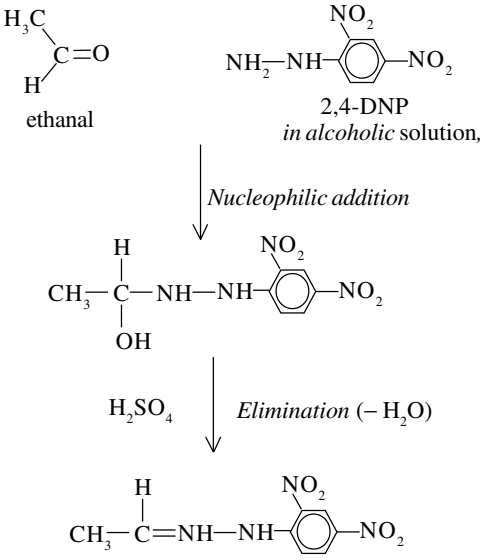
The ketones are named using the suffix -one.
For example:

CH_3COCH_3	propanone
$CH_3CH_2COCH_3$	butanone
$CH_3CH_2CH_2COCH_3$	pentan-2-one

Chemical Tests

Exam Hint *- Because these first four chemical tests are relatively easy to carry out, they are commonly asked about in both theory and practical exam papers. It is important to be able to describe the observations and recall the equations.*

1. Reaction with 2,4-dinitrophenylhydrazine (2,4-DNP) to give a red/orange precipitate.



ethanal 2,4-dinitrophenylhydrazine
(red/orange crystalline solid)

The formation of a red/orange precipitate with 2,4-DNP is a **test for carbonyl compounds - both aldehydes and ketones give a positive test.**

The reactions with 2,4-DNP are also used for the characterization and identification of the aldehydes and ketones because the products are mostly crystalline solids. These are easy to handle, and the melting points of the derivatives are different enough for it to be possible to distinguish between the various carbonyl compounds - whereas several of the pure carbonyl compounds have very similar melting points.

2. The Silver Mirror Test.

The reaction with alkaline ammoniacal silver nitrate solution (Tollen's reagent). This is a test for **aldehydes.**

Silver nitrate is dissolved in aqueous ammonia to form Tollen's reagent, incorperating the complex ion: $[Ag(NH_3)_2]^+$, diaminesilver (I) ion

When Tollen's reagent is warmed gently with an aldehyde, the aldehyde is oxidised to a carboxylic acid, and the silver (I) ions are reduced to silver metal. This appears on the the inside of a test tube like a silver mirror.

$$2Ag^+ + RCHO + H_2O \rightarrow 2Ag + RCOOH + H^+$$

Tollen's reagent has **no effect** on ketones.

3. Reaction with Fehling's Solution.
A test for **aldehydes**.

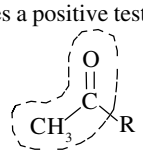
Fehling's solution turns **blue** → **red** if warmed with an aldehyde. Aldehydes are oxidised to carboxylic acids by Fehling's solution, which itself contains a blue copper (II) solution which is reduced to a red precipitate of copper (I) oxide.

Again: $CH_3CHO + [O] \rightarrow CH_3COOH$

Note that Fehling's solution has no effect on ketones, as **ketones cannot be oxidised.**

4. The Iodoform (or triiodomethane) Reaction.
The reaction of carbonyls with iodine in the presence of alkali.

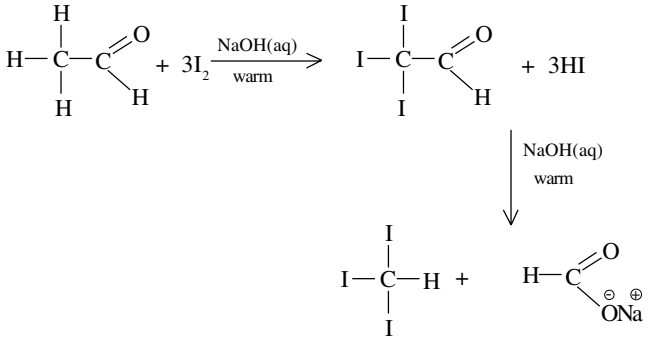
This reaction gives a positive test (a yellow precipitate) if the following group is present:



where R is alkyl group or H atom

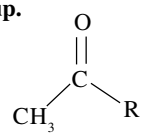
This is not, therefore, a test for aldehydes or ketones, but rather for this specific group.

If ethanal is warmed with iodine in alkaline solution, a two stage reaction occurs. Ethanal reacts with the iodine to form triiodoethanal; this then reacts with the alkali to form triiodomethane (or **iodoform**) - an insoluble yellow solid with a characteristic 'antiseptic' smell.



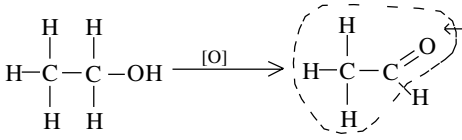
This reaction is specific to the following:

(a) Organic compounds containing a methyl group next to a carbonyl group.



where R is alkyl group or H atom

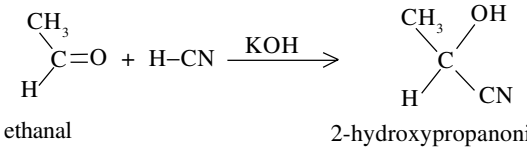
(b) Secondary alcohols that will oxidise under these conditions to <u>form</u> a methyl group next to a carbonyl group.



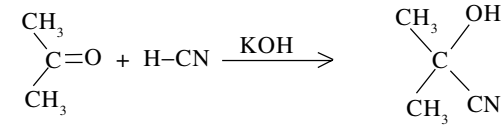
ethanol ethanal

The remaining three reactions of the carbonyls are not chemical tests, but are important and need to be learnt.

5. Carbonyl compounds and hydrogen cyanide.



ethanal 2-hydroxypropanonitrile



ethanal 2-hydroxy-2-methylpropanonitrile

Reaction type:	Addition
Reaction conditions:	HCN and a trace of KOH (HCN and CN^- must be present)
Reaction mechanism:	Nucleophilic

Note that this is a useful way of introducing one extra carbon atom into an organic molecule.

Reduction of the carbonyl compounds

6. Reduction using sodium tetrahydridoborate (III) - sodium borohydride, $NaBH_4$.

$NaBH_4$ is a useful laboratory reagent. Dissolved in ethanol it reduces:

Aldehydes → Primary alcohols
Ketones → Secondary alcohols

e.g. $CH_3CHO + 2[H] \xrightarrow{NaBH_4 \text{ in ethanol}} CH_3CH_2OH$
Ethanal Ethanol

Reaction type:	Reduction
Reaction conditions:	$NaBH_4$ dissolved in ethanol
Reaction mechanism:	Nucleophilic

7. Reduction using lithium aluminium hydride, $LiAlH_4$.

$LiAlH_4$ is an even more powerful reducing agent, which must be used in dry conditions (e.g dissolved in ether).
Again:

Aldehydes → Primary alcohols
Ketones → Secondary alcohols

e.g. $CH_3COCH_3 + 2[H] \xrightarrow{LiAlH_4 \text{ in ether}} CH_3CHOHCH_3$
Propanone Propan-2-ol

Reaction type:	Reduction
Reaction conditions:	$LiAlH_4$ dissolved in ether, dry
Reaction mechanism:	Nucleophilic

Questions

1. (a) Ethanal gives a positive iodoform test result. Give the reagents, conditions and equation for the reaction.

   (b) Describe what is observed in a positive iodoform test result.

   (c) Draw the structures of the following chemicals, and state whether or not they would give a positive iodoform test result.
   (i) Propanal.
   (ii) Propan-2-ol.
   (iii) Hexan-3-ol.
   (iv) Butanone.

2. (a) Chemical X is a carbonyl compound.
   Describe the product formed when X is reacted with 2,4-dinitrophenylhydrazine (2,4-DNP) followed by concentrated sulphuric acid.

   (b) Describe a chemical test (and the possible results) which could define X as either an aldehyde or a ketone.

3. Give the reaction equations and conditions for the reactions of propanal with:
   (a) HCN.
   (b) $LiAlH_4$.

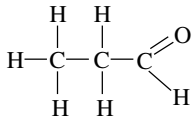
Answers

1. (a) $CH_3CHO + 3I_2 + NaOH \rightarrow CHI_3 + HCOONa + 3HI$

   Conditions: Alkaline, warm.

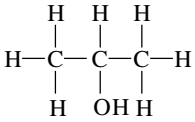
   (b) Insoluble yellow solid / precipitate witgh characteristic (antiseptic) smell.

   (c) (i)



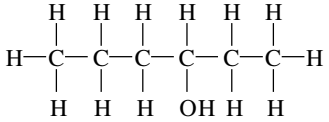
   No

   (ii)



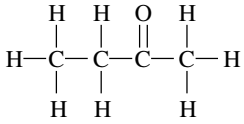
   Yes

   (iii)



   No

   (iv)



   Yes

2. (a) Red / orange (crystalline) solid / precipitate.

   (b) Either:

Silver mirror test:	or	Fehlings:
Tollens reagent / ammoniacal $AgNO_3$		Add Fehlings solution
Warmed		Warmed
Aldehyde gives silver mirror		Aldehyde causes blue to red
Ketone has no effect		Ketone has no effect

3. (a) $CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CHOHCN$

   Conditions: HCN and a trace of KOH.

   (b) $CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$

   Conditions: $LiAlH_4$ in dry ether

Acknowledgements: *This Factsheet was researched and written by Sam Goodman and Kieron Heath.* ***Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***