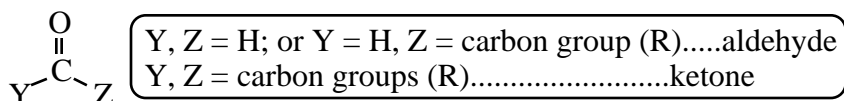


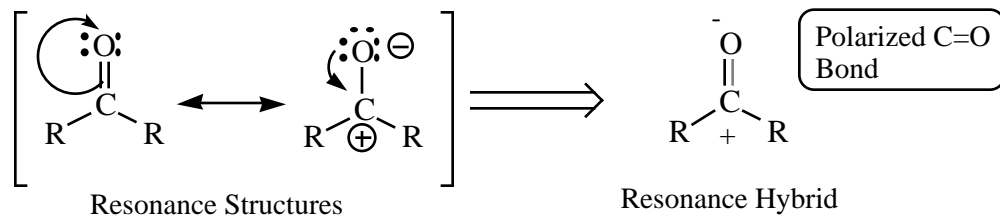
Chem 4563 Organic Qualitative Analysis Aldehydes and Ketones- Functional Group Tests

1. Introduction

Compounds containing the carbonyl functional group (C=O) where it has only hydrogen atoms or carbon groups as substituents are called aldehydes (RCHO) or ketones (RCOR). The chemistry of these compounds is primarily due to the chemistry of the carbonyl functional group. Reactions that occur because of the presence of this group include nucleophilic addition reactions and base catalyzed condensation. Aldehydes are also easily oxidized to carboxylic acids, which provides a convenient method to distinguish them from ketones.



The carbonyl group in aldehydes and ketones is highly polarized; the carbon bears a substantial partial positive charge and is susceptible to nucleophilic attack. Further, since it is sp² hybridized it is relatively open to attack. Because neither the aldehyde nor the ketone has a good leaving group, they react by a nucleophilic addition mechanism rather than a nucleophilic substitution.

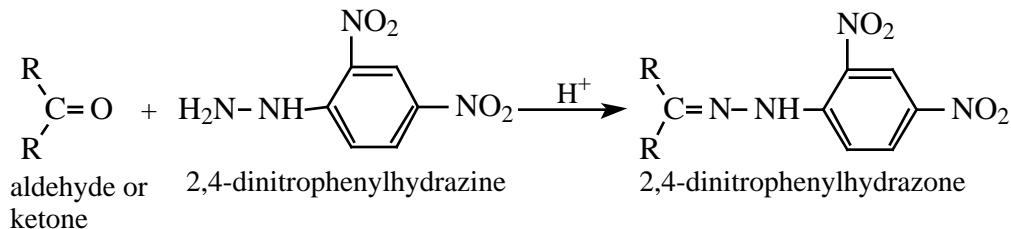


1. Reactions of Both Aldehydes and Ketones.

Both aldehydes and ketones will react with a number of nitrogen containing compounds through nucleophilic addition and subsequent loss of water to give reaction products that have a carbon-nitrogen double bond. These reactions are useful in distinguishing aldehydes and ketones from other functional groups, but cannot be used to distinguish between a ketone and aldehyde.

a. 2,4-Dinitrophenylhydrazine (2,4-DNP) Test

Most aldehydes and ketones will give a solid, orange to red precipitate when mixed with 2,4-dinitrophenylhydrazine; esters will generally not give this test. Thus an ester may generally be eliminated on the basis of this test.



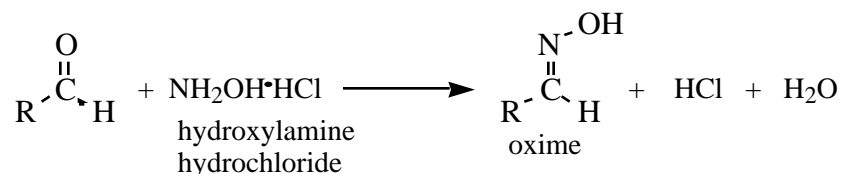
The color of the hydrazone precipitate formed is often a guide to the amount of conjugation in the original aldehyde or ketone. Unconjugated ketones such as cyclohexanone often give a yellow solid, while conjugated ketones such as acetophenone give orange to red solids. Compounds which are highly conjugated give red solids. However, the 2,4-dinitrophenylhydrazine is itself orange-red; thus the color must be judged with caution. In rare cases, compounds which are either strongly acidic or strongly basic will precipitate the unreacted reagent from solution.

Some allylic and benzylic alcohols have the capability to give a positive result for this test because the reagent is able to oxidize them to aldehydes or ketones. A precipitate formed

in small amounts from this oxidized impurity may be present. With some caution, a test that gives only a small amount of precipitate may be ignored.

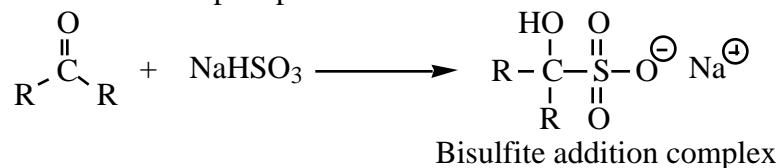
b. Hydroxylamine Hydrochloride Test

This test is quite similar to the 2,4-DNP test in that an oxime containing a C=N bond is formed. The formation of the oxime is accompanied by liberation of hydrogen chloride which can be indicated by an indicator such as a wetted pH paper.



c. Sodium Bisulfite Addition Complex

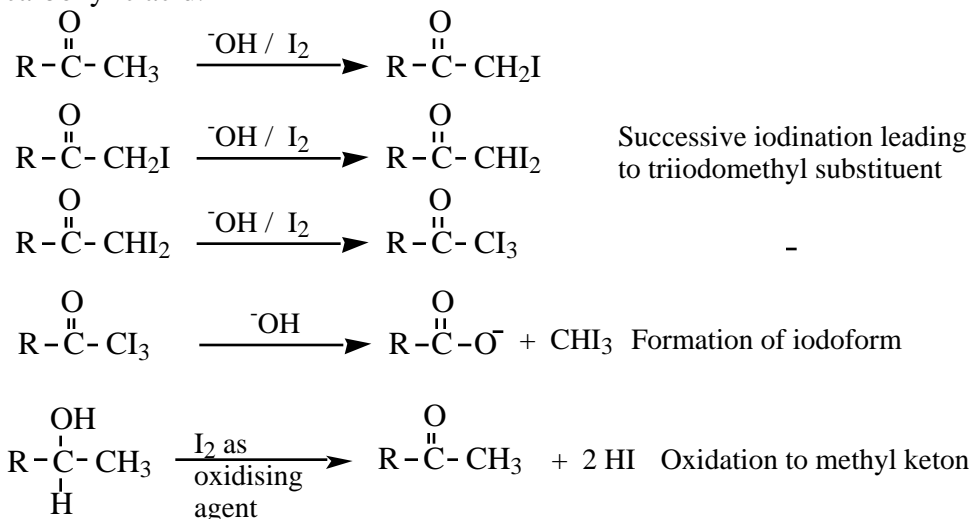
The formation of a bisulfite addition complex is indicative of a variety of carbonyl compounds. This reaction is greatly influenced by the steric environment of the carbonyl group, thus this reaction does not occur with certain sterically hindered ketones. The procedure works best with aldehydes. A positive test for aldehydes and ketones is indicated by the appearance of a white precipitate.



The above reaction is a general one for aldehydes, most methyl ketones, and low molecular weight cyclic ketones (up to eight carbons). Ketones form the complex very slowly.

d. The Iodoform Test

Methyl ketones can be distinguished from other ketones by their reaction with iodine in a basic solution to yield iodoform (CHI₃) as a yellow colored precipitate. However, acetaldehyde (CH₃CHO) and alcohols with their hydroxyl groups at the 2 position of the chain will also form iodoform under these same conditions. Alcohols of the type described are easily oxidized to methyl ketones under the conditions of the iodoform reaction (I₂ is an oxidizing agent). The other product of the iodoform reaction is the sodium or potassium salt of a carboxylic acid.

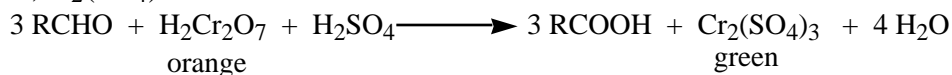


3. Tests for Aldehyde Functional Groups

Aldehydes are very easily oxidized to yield carboxylic acids or their salts if the oxidation is done in a basic solution. Since Ketones are not readily oxidized, this difference provides a convenient method to distinguish aldehydes from ketones. Strong oxidizing agents such as chromic acid has been used, however much less vigorous oxidizing agents such as Tollen's and Benedict's Reagents have been used.

a. Chromic Acid Test (Jones Test)

This test is the result of the fact that aldehydes are easily oxidized to the corresponding carboxylic acid by chromic acid. The chromic acid has an orange-red color due to the presence of Cr(+6) ions, upon oxidation of the aldehyde, the chromium is reduced to Cr(+3), which has a green color. A positive result is indicated by a green precipitate due to chromous sulfate, Cr₂(SO₄)₃.



Primary and secondary alcohols are also oxidized by this reagent. For this reason, this test is not useful for distinguishing aldehydes **unless** a positive identification of a carbonyl group has been obtained from the 2,4-DNP test.

b. Tollen's Test

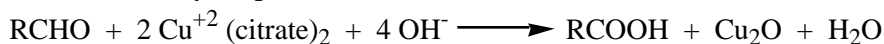
Most aldehydes will reduce ammoniacal silver nitrate solution to give a precipitate of silver metal, The aldehyde is oxidized to a carboxylic acid. A positive result is the formation of a silver mirror on the surface of the test tube, or a black precipitate of the metal. The reaction often involves an induction period of a few minutes.



Ordinary ketones do not give a positive result in this test. The test should be used only if it has already been shown that the unknown compound has a carbonyl group. It should be noted that certain aromatic amines, phenols and amino ketones are also able to reduce ammoniacal silver nitrate.

c. Benedict's Test

A cupric (Cu⁺²) citrate solution is able to oxidize an aliphatic aldehyde to a carboxylic acid while being itself reduced to a cuprate (Cu+1). Aromatic aldehydes do not undergo this reaction, thus it is useful to differentiate between the two aldehyde types. Benedict's Reagent is a basic citrate solution of cupric ion, when treated with an aliphatic aldehyde a yellow to red precipitate of Cu₂O may be produced.



Benedict's Reagent is also reduced by: hydroxy aldehydes, hydroxy ketones, keto aldehydes, sugars and hydrazines. The presence of a mercapto group (-SH) will interfere with this test.

