

# 1.Title

Comparison of Reactions of Aldehydes and Ketones

## 2.Aim

The purpose of this experiment is to compare the reaction behaviour of ethanal and propanone towards nucleophilic addition, condensation, alkali, oxidation and iodoform test.

## 3.Results & Calculations

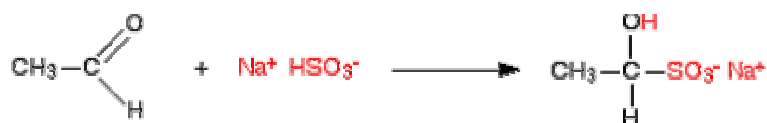
Rx	Test	Observations	
		Ethanal	Propanone
A	Addition reaction with sodium hydrogensulphate	White crystal	White crystal
B	Condensation reaction with 2,4-dinitrophenylhydrazine	Yellow precipitate	Orange precipitate
C	Reaction with alkali		
D	Oxidations : I) acidified dichromate(VI)	Orange solution turns green	No observable change
	II) Tollens' reagent	Silver mirror	No observable change
	III) Fehling's solution	Red precipitate	No observable change
E	Iodoform test	Yellow precipitate	No observable change

## 4.Discussion

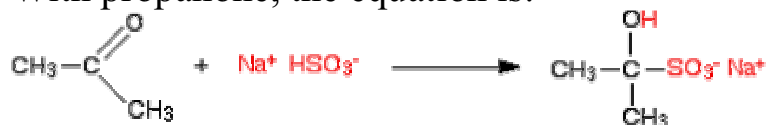
A: This reaction works well for aldehydes. In the case of ketones, one of the hydrocarbon groups attached to the carbonyl group needs to be a methyl group. Bulky groups attached to the carbonyl group get in the way of the reaction happening.

The aldehyde or ketone is shaken with a saturated solution of sodium hydrogensulphite in water. Where the product is formed, it separates as white crystals.

In the case of ethanal, the equation is:

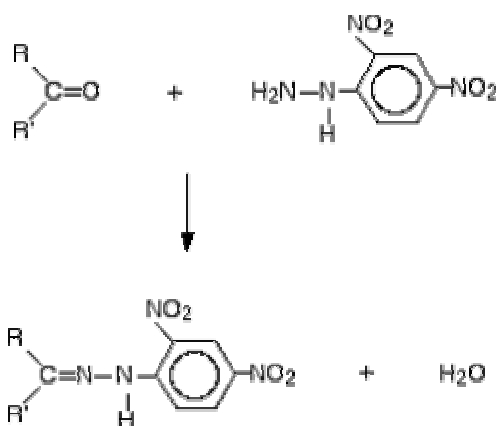


With propanone, the equation is:



B: Add either a few drops of the aldehyde or ketone, or possibly a solution of the aldehyde or ketone in methanol, to the a solution of the 2,4-dinitrophenylhydrazine in methanol and sulphuric acid. A bright orange or yellow precipitate shows the presence of the carbon-oxygen double bond in an aldehyde or ketone.

The overall reaction is given by the equation:



R and R' can be any combination of hydrogen or hydrocarbon groups (such as alkyl groups). If at least one of them is a hydrogen, then the original compound is an aldehyde. If both are hydrocarbon groups, then it is a ketone.

C:

D I: A small amount of dichromate(VI) solution is acidified with dilute sulphuric acid and a few drop of the aldehyde or ketone are added. If nothing happens in the cold, the mixture is warmed gently for a couple of minutes – for example, in a beaker of hot water.

The orange dichromate(VI) ions have been reduced to green chromium(III) ions by the aldehyde. In turn the aldehyde is oxidized to the corresponding carboxylic acid.

The electron-half-equation for the reduction of dichromate(VI) ions is :



Combining that with the half-equation for the oxidation of an aldehyde under acidic conditions:



The overall equation:



II: Tollens' reagent is usually ammoniacal silver nitrate, but can also be other compounds, as long as there is an aqueous diamminesilver(I) complex. The diamminesilver(I) complex is an oxidizing agent, which itself reduced to silver metal, which in a clean glass reaction vessel forms a "silver mirror" when silver nitrate solution is treated with sodium hydroxide (NaOH) till it forms precipitate and  $\text{NH}_4\text{OH}$  was added till the precipitate is dissolved so thus formed mixture is known as Tollens' reagent.

Once it has been identified that there is a carbonyl group on the organic molecule using

2,4-dinitrophenylhydrazine (also known as Brady's reagent or 2,4-DNPH), Tollens' reagent can be used to ascertain whether the compound is a ketone or aldehyde. Importantly, there is a special case in which Tollens' Reagent will give a positive for a ketone. If the ketone is an alpha-hydroxy ketone, then the Tollens' reagent will react.

When adding the aldehyde or ketone to Tollens' reagent, the test tube is put in a warm water bath. If the reactant under test is an aldehyde, Tollens' test results in a silver mirror. If the reactant is a ketone, it will not react because a ketone cannot be oxidized easily. A ketone has no available hydrogen atom on the carbonyl carbon

that can be oxidized – unlike an aldehyde, which has this hydrogen atom.

The reagent should be freshly prepared and stored refrigerated in a dark glass container. It has an approximate shelf-life of 24 hours when stored in this way. After the test has been performed, the resulting mixture should be acidified with dilute acid before disposal. These precautions are to prevent the formation of the highly explosive silver nitride.

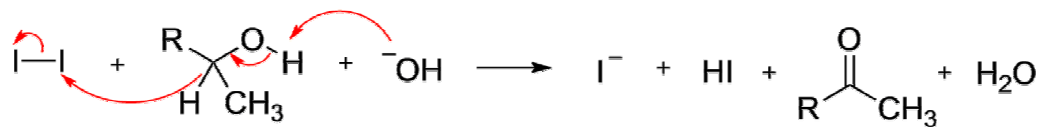
III: Fehling's solution is a solution used to differentiate between water soluble aldehyde and ketone functional groups. To carry out the test the substance to be tested is heated together with Fehling's solution; the aldehyde oxidizes to an acid and cupric ions, which were complexed with the tartrate ion, are reduced to cuprous ions, a red precipitate indicates the presence of an aldehyde. Ketones (except alpha hydroxyl ketones) do not react.



E: The iodoform reaction is a chemical reaction where is produced by the exhaustive halogenation of a methyl ketone (a molecule containing the R-CO-CH<sub>3</sub>) group in the presence of a base. R may be H, alkyl or aryl. The reaction can be used to produce CHI<sub>3</sub>.

When iodine and sodium hydroxide are used as the reagents, a positive reaction gives iodoform. Iodoform (CHI<sub>3</sub>) is a pale yellow substance. Due to its high molar mass due to the three iodine atoms, it is solid at room temperature. It is insoluble in water and has an antiseptic smell. A visible precipitate of this compound will form from a sample only when either a methyl ketone, ethanal, a methyl secondary alcohol or ethanol are present.

If a secondary alcohol is present, it is oxidized to a ketone by the hypohalite:



If a methyl ketone is present, it reacts with the hypohalite in a three step process:

- (1)  $\text{R}-\text{CO}-\text{CH}_3 + 3 \text{OX}^- \rightarrow \text{R}-\text{CO}-\text{CX}_3 + 3 \text{OH}^-$
- (2)  $\text{R}-\text{CO}-\text{CX}_3 + \text{OH}^- \rightarrow \text{RCOOH} + ^-\text{CX}_3$
- (3)  $\text{RCOOH} + ^-\text{CX}_3 \rightarrow \text{RCOO}^- + \text{CHX}_3$

## 5. Answers to Question

### 5.1 Describe how Tollens' reagent can be prepared. Write a balanced chemical equation for the reaction between Tollens' reagent and ethanal.

Tollens' reagent needs to be prepared fresh by adding a drop of dilute sodium hydroxide to aqueous silver nitrate to give a brown precipitate of silver oxide. The precipitate is dissolved by adding concentrated ammonia to give the reagent,  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$  (aq):

### 5.2 Consider the mechanism of nucleophilic addition reaction to unsaturated carbonyl group, predict and explain the relative reactivity of ethanal and propanone.

Reactivity of the ethanal is higher than that of propanone. Unlike the non-polar and electron rich carbon double bond,  $\text{C}=\text{O}$  double bond has a positive centre and undergoes nucleophilic addition. More positive on carbon, so it is more vulnerable to nucleophilic attack. Ethanal is more reactive than propanone since electron donating group of R makes the carbon in  $\text{C}=\text{O}$  in propanone less positive, less

attractive to the nucleophile. Moreover, steric hindrance of two bulky R groups in propanone prevents the attack of the nucleophile on  $C=O$

## **6. Conclusion**

Ethanal is more reactive than propanone in the following chemical reaction such as nucleophilic addition, condensation, alkali, oxidation and iodoform test.