EXP4 – Preparation of Propanone

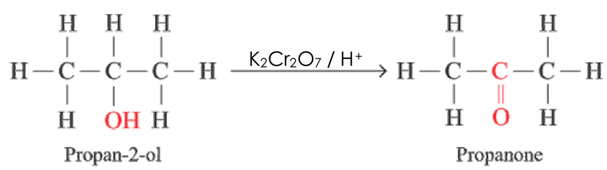
Aim:

The purpose of this experiment is to synthesis propanone (58 g/mol) from propan-2-ol (60 g/mol).

Principle:

This synthesis is an oxidation reaction of secondary alcohol. Secondary can be oxidized by either acidified potassium dichromate (VI) or acidified potassium permanganate (VII).

In our synthesis, we oxidize propan-2-ol which is the smallest secondary alcohol available; its oxidation will form a propanone (commonly called acetone) according to the below equation. The most common reagent used for oxidation of secondary alcohols to ketones is chromic acid, H_2CrO_4.



Chromic acid is produced in situ by reaction of potassium dichromate (VI), sulphuric acid and water.

$$K_2Cr_2O_7 + H_2O + 2H_2SO_4 \rightarrow 2\ H_2CrO_4 + 2\ NaHSO_4$$

The oxidation mechanism is outlined below, the propan-2-ol and chromic acid produce a chromate ester, which then reductively eliminates the Chromium species and produce the propanone product.

Method:

The experiment is a oxidation reaction where a secondary alcohol (propan-2-ol) is oxidized by acidified potassium dichromate. The reaction readily occurs in room conditions. The product is propanone and the reaction stops at that stage, no catalyst is needed for the reaction and the reaction completes within a few minutes.

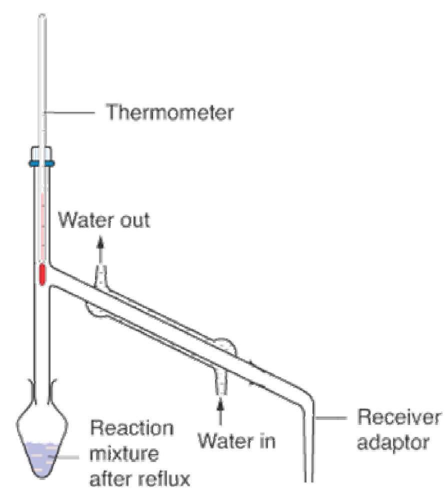
The reaction is started by adding acidified potassium dichromate to the alcohol. The colour of the oxidizer is initially orange and the colour changes to dirty green upon mixing. The oxidation reaction produce a large amount of heat which heats up the reaction mixture. The flask used for the reaction is situated in an ice bath to cool down the mixture to prevent reactants or products being boiled away. After addition of the oxidizer, the products are collected by simple distillation.

To increase the yields of reaction, the oxidizer is used in excess to make sure reaction is complete. Distillates of boiling point ranged from 54 °C to 58 °C should be collected as products. The resulting product is wet and may be treated with inert dehydrating agents (eg: anhydrous calcium chloride) and re-distillation for purification.

The ketone could be tested with a melting point pointing point test after I has reacted with a hydrazine to form a hydrazone. The hydrazone has a sharp and distinct melting point in which the ketone structure could be found when results are compared with data book values.

Apparatus and chemicals:

- Propan-2-ol
- Concentrated sulphuric acid
- Potassium dichromate (VI)
- 2,4-dinitrophenylhydrazine
- Ice bath
- Boiling tubes
- Droppers
- Measuring cylinder 10cm^3
- Quick fit apparatus for simple distillation.
- Thermometer



Experiment Procedure and Observations

1. Approximately 3 gram of potassium dichromate and $10cm^3$ of distilled water was added to a boiling tube and shook to dissolve the powder. The resulting solution is bright orange with a little un-dissolved powder.
2. Approximately 3 cm^3 (accurately 5.35gram) of concentrated sulphuric acid were slowly added to the aqueous potassium dichromate solution using a dropper. Heat was generated and warmed up the solution, the un-dissolved powder was observed to be completely dissolved.
3. A reflux setup was constructed and 3.17gram of propan-2-ol was added to the pear shaped flask which was sat in an ice bath.
4. The acidified potassium dichromate solution was added to the reflux with a dropper through the vertically placed Liebig condenser with water running through the condenser wall. The clear liquid alcohol turned to dirty green colour right after the addition of the orange acidified potassium dichromate solution.
5. The reflux setup was to prevent the heat generated by the reaction to boil away the propanone product.
6. After the addition of the two liquids, the ice bath was removed and the pear shaped flask was placed in a simple distillation setup.
7. Some anti-bumping granules were added to the flask.
8. The reaction mixture was distilled and distillate started to drip out at 40 °C. Distillate were collected as useful products when boiling temperature ranged from 54 °C to 58 °C. Distillate was collected in a boiling tube which stood in an water bath.
9. The distillation residue was dirty green colour and distillate was colourless clear liquid.
10. The distillate collected were 1.93 gram.
11. A clean boiling tube was filled with approximately 2 cm^3 of orange colour 2,4-dinitrophenylhydrazine (2,4-DNP).
12. 5 drops of the products were added to the solution and warmed in a 70 °C water bath for 1 minute, the boiling tube is then placed in a ice water bath for 3 minutes. Yellowish precipitate was formed and the solid was dried by a suction filtration setup. The solid obtained was believed to be propanone 2,4-dinitrophenylhydrazone.

Results Recorded

Stage of Reaction	Mass	Number of Mole	Remaining percentage
Starting propan-2-ol	3.17g	0.0528	100%
Theoretical Yield of propanone	**3.06g**	0.0528	100%
Final product of propanone (Not Dried)#	**1.93g**	0.0332	**63.0%**

#The mass of the final product may contain water and may not truly represent the product.

Calculations

The predicted amount of products formed = 0.0528 mol X 58 g mol^{-1}

= 3.064 g

However, product loss due to incomplete reaction, side reactions, evaporation, spillage or residue on glassware could significantly reduce the percentage of yield.

Number of mole of actual product formed

= 1.93 g / 58 g mol^{-1} = 0.0332 mol

The actual product formed has 0.0332 mol. Thus the percentage yield was about 63.0% of the theoretical value.

Discussions

Characteristics of this experiment

This experiment is a oxidation reaction of secondary alcohol which its mechanism is mentioned in the principle section. The oxidation of secondary alcohol always produces a ketone while that of a primary alcohol, a aldehyde is formed. This experiment choose a secondary alcohol to demonstrate the production of ketone is a wise choice as the oxidation process is stopped at the ketone stage, where if a primary alcohol is used, the reaction will first produce an aldehyde. However, the aldehyde will continue to be oxidized to a carboxylic acid.

This oxidation requires a strong oxidizing agent such as potassium permanganate, potassium dichromate or other agents containing Cr(VI). Heating is applied to quicken the reaction. This method is the most common known method for preparing ketones in the laboratory, however there are numbers of other methods which ketones could be produced:

- Ketones are also prepared by Gem halide hydrolysis.
- Aromatic ketones can be prepared in the Friedel-Crafts reaction and the Fries rearrangement.
- In the Kornblum–DeLaMare rearrangement ketones are prepared from peroxides and base
- In the Ruzicka cyclization, cyclic ketones are prepared from dicarboxylic acids.

- In the Nef reaction, ketones are formed by hydrolysis of salts of secondary nitro compounds

Side reactions

The oxidation of secondary alcohol into ketone is a pretty reliable reaction with few side reactions. The further oxidation of ketone does not occurs readily, because such reaction requires the breakage of the strong Carbon-Carbon bonding. More severe conditions are required to further oxidize the ketone, for example by application of hot acidified potassium permanganate, the Carbon-Carbon bond may break up and forms a mixture of carboxylic acids.

Reaction yield

The synthesis in our experiment has a 63.0% product yield, which is a satisfactory figure in laboratory synthesis, when compared to the previous synthesis. The higher product yield may be contributed by less side reaction and the completion of reaction.

The batch size of the reaction is concerned to be very small scale with only a few grams, but this is suitable enough to demonstrate the oxidation reaction of alcohol to ketone. A higher yield is believed to be obtained when this reaction is done in a higher batch size.

The Importance of Ketone

The carbonyl function group of ketone plays a very important part in organic synthesis. Ketones and aldehydes can be synthesised into many other chemicals through different pathways. It is a very common and relatively cheap starting material for many synthesis reactions. Basic reactions involving ketones include a large number of nucleophilic addition reactions to the carbon-oxygen double bond. When nucleophile attacks the carbonyl carbon atom, it uses its lone pair electron to form a bond with the carbonyl carbon atom. An electron pair of the carbon-oxygen double bond can shift out to the carbonyl oxygen atom.

Another famous reaction for ketones and aldehyde is the condensation reaction with hydrazine or its derivatives. The reaction product hydrazone leads to the widely accepted method of carbonyl identification which detects carbon-oxygen double and performs melting point test. At the end of our experiment, the product propanone is treated with 2,4-dinitrophenylhydrazine to produce propanone 2,4-dinitrophenylhydrazone which has a distinct 128°C melting point. However due to time limitations, the melting point test is unable to be carried out.

Some other ketones and aldehydes reaction are listed below:

- Nucleophilic addition.
    - The reaction of a ketone with a nucleophile gives a tetrahedral carbonyl addition compound.
    - the reaction with the anion of a terminal alkyne gives a hydroxyalkyne
    - the reaction with ammonia or a primary amine gives an imine + water
    - the reaction with secondary amine gives an enamine + water
    - the reaction with a Grignard reagent gives a magnesium alkoxide and after aqueous workup a tertiary alcohol
    - the reaction with an organolithium reagent also gives a tertiary alcohol
    - the reaction with an alcohol, an acid or base gives a hemiketal + water and further reaction with an alcohol gives the ketal + water. This is a carbonyl-protecting reaction.
    - reaction of RCOR' with sodium amide results in cleavage with formation of the amide RCONH2 and the alkane R'H, a reaction called the Haller-Bauer reaction
- Electrophilic addition, reaction with an electrophile gives a resonance stabilized cation.
- the reaction with phosphonium ylides in the Wittig reaction gives alkenes
- reaction with water gives geminal diols
- reaction with thiols gives a thioacetal
- reaction with a metal hydride gives a metal alkoxide salt and then with water an alco hol
- reaction of an enol with halogens to a-haloketone
- reaction at an a-carbon is the reaction of a ketone with heavy water to give a deuterated ketone-d.
- fragmentation in photochemical Norrish reaction
- reaction with halogens and base of methyl ketones in the Haloform reaction
- reaction of 1,4-aminodiketones to oxazoles by dehydration in the Robinson-Gabriel synthesis
- reaction of aryl alkyl ketones with sulfur and an amine to amides in the Willgerodt reaction

Ketones are often used in perfumes and paints to stabilize the other ingredients so that they don't degrade as quickly over time. Other uses are as solvents and intermediates in chemical industry. Examples of ketones are acetone, acetophenone, and methyl ethyl ketone.

Notes on experiment techniques

When handling corrosive concentrated acids such as the concentrated sulphuric acid, a dropper is recommended for its transferral. Addition of concentrated sulphuric acid to aqueous potassium dichromate in this experiment should be done slowly to avoid spillage due to the generation and local acumination of heat.

THE END