

S.K.H. Lam Woo Memorial Secondary School

F.7 Chemistry Laboratory Report

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Experiment 3: Identification of carbonyl compounds by preparing their derivatives

Date of Experiment: 15-10-2010

Objective:

To identify an unknown carbonyl compound by determining the melting point of its derivative formed from the reaction with 2,4-dinitrophenylhydrazine solution.

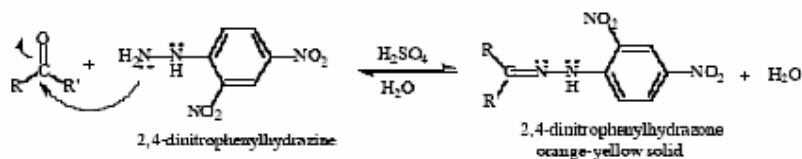
Introduction:

In the experiment, carbonyl compound underwent condensation reaction with 2,4-dinitrophenylhydrazine solution to form 2,4-dinitrophenylhydrazone. The solid formed was then purified by recrystallization in order to give an accurate, distinct melting point. As the 2,4-dinitrophenylhydrazone formed from different carbonyl compound would have different boiling points, by matching the measured boiling point with that stated officially, the type of carbonyl compound could be identified.

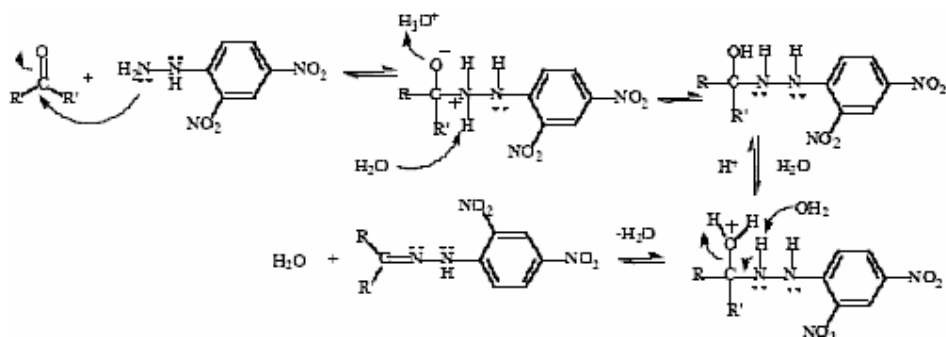
Carbonyl compound contained a C=O functional group which was polar. The electron cloud was displaced to the more electronegative oxygen atom and made the carbonyl carbon partial positive. The carbonyl carbon was hence electron deficient and susceptible to attack by electron rich nucleophile.

Carbonyl compound could undergo condensation with derivative of ammonia. In this case, carbonyl compound could serve as electrophiles and nucleophile at the same time. Water was eliminated as a by-product and 2,4-dinitrophenylhydrazone was produced.

Equation of reaction:



Mechanism of condensation



Results:

Melting point of crystal = 156°C

Melting point of propanal = 156°C

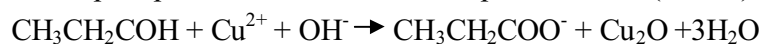
Melting point of pentan-3-one = 156°C

As the melting point of the crystal matched the 2,4-dinitrophenylhydrazone formed from propanal and pentan-3-one, thus the carbonyl compound was a propanal or pentan-3-one.

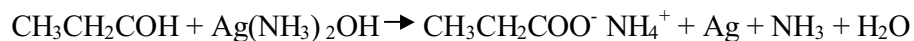
To determine whether the carbonyl compound was a propanal or pentan-3-one, the carbonyl compound

should be tested before the addition of 2,4-dinitrophenylhydrazine.

It could be tested by Fehling's solution and red precipitate would be formed for propanal (an aldehyde) but no precipitate would be formed for pentan-3-one (ketone).



It could also be tested by Tollen's reagent. Silver mirror would be formed for propanal but not for pentan-3-one.



Testing with acidified potassium dichromate solution was also possible. Propanal would reduce the solution to change from orange to green but pentan-3-one would not.

Although, the above test was not carried out in this experiment, the type of carbonyl compound could also be guessed from the amount of 2,4-dinitrophenylhydrazine. Groups using carbonyl compound A obtained similar melting point with that of this carbonyl compound. However, this carbonyl compound required much more 2,4-dinitrophenylhydrazine to react and give crystal than carbonyl compound A. Aldehyde was more reactive than ketone. Because of positive inductive effect, the alkyl groups in pentan-3-one donate electrons to carbonyl carbon and made it less positive. Hence, it was less susceptible to nucleophilic attack. Besides, as the alkyl groups were more bulky than hydrogen atom. The higher steric effect hindered the close approach of nucleophile to the carbonyl compound. As pentan-3-one was less reactive, more 2,4-dinitrophenylhydrazine would be needed to react with it in order to give similar amount of crystal. Therefore, it was believed that there was a larger chance of the carbonyl compound to be pentan-3-one.

It should also be noted that the carbonyl compound could not be identified by matching with the melting point of different carbonyl compound. It was because the melting point of carbonyl compounds usually close to each other. The identification would be inaccurate as error may be presented to change the melting point slightly and this slight difference may show another compound. As the melting point of 2,4-dinitrophenylhydrazone of carbonyl compounds were larger, it could be easier to identify particular compound.

By reacting carbonyl compound with hydroxylamine, oxime could be produced. The melting point of oxime could also be matched with melting point of oxime of different carbonyl compound. However, as oxime usually had lower melting and more soluble in the solvents. Reaction with

2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazine was preferred.

Discussion:

Removal of impurities

The solid formed after reaction of carbonyl compound with 2,4-dinitrophenylhydrazine was not pure.

The impurities presented in the rough product would be mainly 2,4-dinitrophenylhydrazine. Excess 2,4-dinitrophenylhydrazine was added in order to consume all the carbonyl compound present for a larger yield. The remaining 2,4-dinitrophenylhydrazine would also be precipitated out after warming and cooling in hot and cold water bath respectively. This solid appeared to be the same as 2,4-dinitrophenylhydrazine. Some of the carbonyl compound or other impurities that originally present in the solution would also precipitate out. These precipitates mixed with the 2,4-dinitrophenylhydrazine and needed further process to remove them.

Then, the solid was dissolved in ethanol. If any insoluble impurities like pieces of filter paper were presented, they could be filtered out by funnel. Recrystallization then took place to purify the product. Only the compound which was soluble in hot ethanol and less soluble in cold ethanol (mainly 2,4-dinitrophenylhydrazine) would be precipitated out as crystal. The compounds that were soluble in cold ethanol remained dissolved in it. Then, the solution was filtered to obtain the crystal. The crystal was washed by cold ethanol to remove the soluble compound in recrystallization that stick on the surface of the crystal. Finally, pure 2,4-dinitrophenylhydrazine was obtained and its melting point was determined. If the determination of melting point was carried out immediately without purification, an indistinct and inaccurate melting point would be obtained by this mixture of product.

Solvent used in recrystallization

The solvent used in recrystallization must not react with the 2,4-dinitrophenylhydrazine. Moreover, the solubility of 2,4-dinitrophenylhydrazine in this solvent must be high at **high temperature** and **low at room temperature**. Therefore, an appropriate choice would be ethanol. However, only small amount of ethanol should be used to dissolve and washed the solid. If too much ethanol was added to dissolve the solid, the time for recrystallization would be very long. It was because the solubility of a larger volume of solution would be larger than that of a smaller volume. If too much ethanol was added, longer time was needed for enough solvent to evaporate in order to give a concentrated solution. Only for a concentrated solution with saturated amount of solute could the solute start to precipitate. Added to the above, if too much ethanol was added, the solubility of the solution increased and very fine crystal would be formed.

On the other hand, if too much ethanol was used to washed the crystal, the 2,4-dinitrophenylhydrazine may be dissolved back in ethanol again and less 2,4-dinitrophenylhydrazine could be obtained.

Errors and improvements

As errors occurred in this experiment, leading to a very small yield of 2,4-dinitrophenylhydrazine.

Firstly, excess 2,4-dinitrophenylhydrazine should be added to the carbonyl compound to ensure all of the carbonyl compound was reacted. Otherwise, only a small amount of 2,4-dinitrophenylhydrazine would

be produced. Secondly, the 2,4-dinitrophenylhydrazine should be mixed thoroughly with the carbonyl compound to increase contact between these two molecules and to allow reaction between them to take place. Thus, shaking was required until the solutions completely mixed together without seeing a clear boundary between two layers. Otherwise, the yield of 2,4-dinitrophenylhydrazone produced would be small again.

Errors also incurred in the recrystallization. If the solution was not warmed long enough, it may be too dilute for precipitation. Also, if the solution was not cooled enough, it was difficult to be saturated. The 2,4-dinitrophenylhydrazone still had a high solubility in this dilute, warm solution and little of them would precipitate out as crystal. To speed up the reaction and speed up the formation of precipitate in the condensation reaction, dilute sulphuric acid could be added as a catalyst.

Last but not least, as the yield of 2,4-dinitrophenylhydrazone was very small, the percentage loss of crystal during transfer was large. With this small amount of 2,4-dinitrophenylhydrazone, there was a higher possibility that this crystal would be impure or contaminated. Thus, the determination of melting point of 2,4-dinitrophenylhydrazone maybe less accurate.

Conclusion

As the melting point of the 2,4-dinitrophenylhydrazone matched with the melting point of 2,4-dinitrophenylhydrazones of pentan-3-one and propanal, the carbonyl compound may be a pentan-3-one or propanal. However, the possibility of being a propanal may be higher.

Procedure

A. Identification of the carbonyl compound as an aldehyde or ketone.

Carry out Tollens' and Fehling's tests on samples of the unknown compound. Try to remember the procedures before checking (Experiment 89). Classify the compound as an aldehyde or a ketone.

B. Preparation of a crystalline derivative.

1. Into a 100 cm³ beaker (or boiling-tube) put 0.5 cm³ (10 drops) of the unknown compound. [If the substance is solid dissolve 0.5 g in a minimum amount of methanol.] Add 5 cm³ of the 2,4-dinitrophenylhydrazine solution and stir.
2. If precipitation does not occur, carefully add 1 cm³ of dilute sulphuric acid.
3. Using the suction filtration apparatus in Fig. 49, filter the precipitate.
4. Stop suction, either by lifting the funnel or by disconnecting the tubing, and soak the precipitate in about 1 cm³ of methanol. (If you turn off the tap, you may get a 'suck-back' of water.)
5. Resume suction and dry the crystals by drawing air through them for a few minutes.
6. Recrystallize the solid using the following procedure.
 - (a) Transfer the crystals to a 150 cm³ beaker standing on a steam bath (or in a 250 cm³ beaker of hot water).
 - (b) Dissolve the crystals in the minimum amount of hot ethanol.
 - (c) When the crystals have dissolved, cool the solution in an ice-water mixture until crystals reappear.
 - (d) Filter the crystals as before. If necessary, rinse the beaker with the filtrate (not extra solvent) to complete the transfer. Finally, wash the crystals with a few drops of cold ethanol.
 - (e) Press the crystals thoroughly between two wads of filter paper to remove excess solvent. Then put the crystals on another dry piece of filter paper placed alongside a Bunsen burner and gauze, turning the crystals over occasionally until they appear dry.

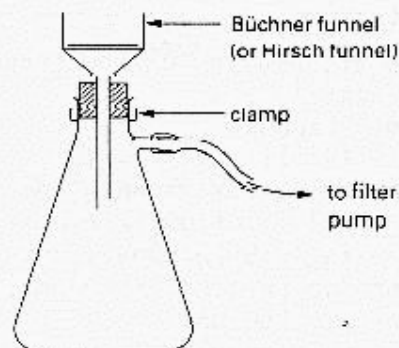


Fig. 49. Suction filtration

C. Determination of the melting-point of the derivative.

1. Take a melting-point tube and push the open end through a pile of the derivative on a watch-glass, until a few crystals have entered the tube.
2. Tap the closed end of the tube vertically against a hard surface, or rub with the milled edge of a coin, to make the solid fall to the bottom.
3. Repeat the filling and tapping procedure until a total length of between 0.5 - 1 cm is compacted at the bottom of the tube. Prepare another tube in this way.
4. Attach one of the prepared melting-point tubes to the thermometer, as shown in Fig. 50.

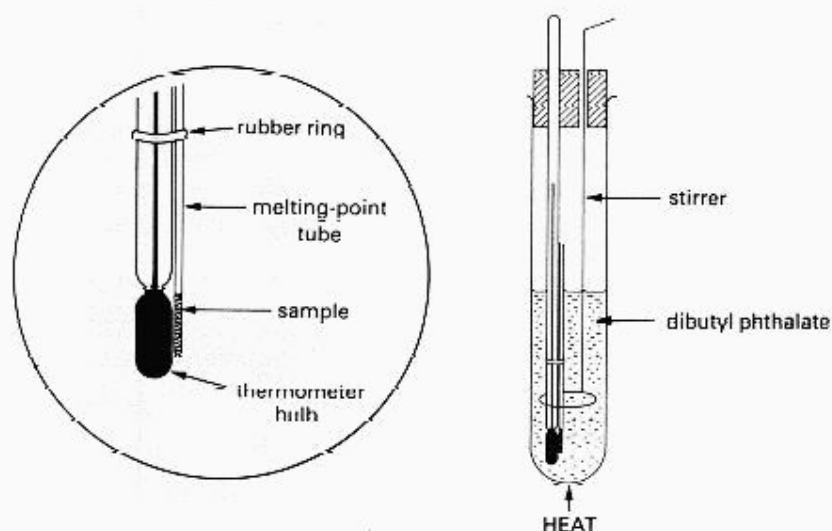


Fig. 50. Melting-point determination

5. Half-fill the boiling-tube with dibutyl phthalate and position the thermometer with attached tube and the stirrer through the bung, as shown in Fig. 50.
6. Position the apparatus over a micro-burner (or low Bunsen flame) and gauze and gently heat the apparatus, stirring the dibutyl phthalate all the time by moving the stirrer up and down.
7. Keep an eye on the crystals and note the temperature as soon as signs of melting are seen (usually seen as a contraction of the solid followed by a damp appearance). This first reading gives only a rough melting-point but is a guide for the second determination.
8. Remove the burner and the old tube containing derivative. Allow the temperature to drop about 10 °C before positioning a fresh melting-point tube containing another portion of the derivative.
9. Repeat the above procedure in order to obtain a more accurate value of the melting-point. Raise the temperature very slowly (about 2 °C rise per minute) until the crystals melt (take the formation of a visible meniscus as a sign of melting).
10. Compare the melting-point of your crystals with the values given in the table which follows and identify the unknown compound.
11. Check with your teacher or the technician whether you have identified X correctly.

(A) Prepare 2,4-dinitrophenylhydrazone

1. pour 2 cm³ carbonyl compound
2. + 5 cm³ 2,4-dinitrophenylhydrazone, shake test tube
3. place in hot water bath for 3 min
4. cool in water bath for 3 min
5. suction filtration to obtain crystal
6. Rinse with cold water

(B) Recrystallization

1. Transfer crystal to beaker
2. in hot water bath, dissolve with < 4 cm³ hot ethanol, add drop by drop
3. filter with short stem funnel, connect by boiling tube
4. place in hot water bath
5. cool in ice-water bath
6. suction filtration
7. wash with ethanol
8. transfer to water glass
9. dry in oven
10. determine mp