Experiment 17

Investigation of Some of the Properties of a Pair of Cis-Trans Isomers

Date: 10-5-2006

Objective

To study the physical and chemical properties of fumaric acid and maleic acid.

Introduction

Maleic acid and fumaric acid are geometrical isomers. They are isomers for which the spatial arrangement of atoms is different because of the restricted rotation about a covalent bond. The following are their structural formula:

The two isomers differ in their physical and chemical properties. Since maleic acid has the lager groups of atoms on the same side, maleic acid is also called cis-butenedioic acid. On the other hand, fumaric acid has the larger groups on opposite sides of the double bond, and is also called trans-butenedioic acid.

Maleic acid can be made into fumaric acid by heating the acid, with concentrated hydrochloric acid added beforehand. The hydrochloric acid acts as a catalyst in this reaction. In the process, the carbon atom is rotated. As a result, the - bond is broken.

Procedure

Conversion of maleic acid to fumaric acid

1. About 4g of maleic acid was weighed out. $10cm^3$ of deionized water was added to the acid. The acid was then warmed until it dissolves.
2. $10cm^3$ of concentrated hydrochloric acid was added into the acid. The beaker containing the acid mixture was covered with a watch glass.
3. Anti-bumping granules were added into a water bath. The beaker containing the acid mixture was put into the boiling water bath.
4. The beaker was removed from the water bath 5 minutes after solids were found to form in the mixture.
5. The beaker was cooled by putting the beaker into an ice bath.

6. The reaction mixture were filtered by suction using the following set-up:

7. After a few minutes, the suction was stopped by removing the Buchner funnel from the flask.
8. The residue was soaked with water, and the suction was resumed for a few more minutes.
9. The crystals were transferred onto a weighed watch glass and put into an oven to dry at about 60°C for 1 night.
10. The dried crystals were weighed.

Comparison of properties of the 2 isomers

1. About 1g of the acids was put into 2 separate test tubes and water was poured in. The test tube was shaken and the solubility of both acids was observed.
2. 0.1g of each isomer was dissolved in water. They are divided into 3 portions.
   (a) The pH of each acid was measured with pH paper.
   (b) A strip of magnesium ribbon was added to each acid to observe the rate of reaction.
   (c) Sodium carbonate was added to each acid to measure the rate of reaction.
3. 0.1g of each acid was suspended in water. 3 drops of bromine was added to each test tube and was shaken. The color change was observed.

Determination of the boiling points of the acids

1. One end of 2 capillary tubes was burned with a Bunsen flame.
2. The two acids were inserted into the capillary tubes.
3. With the following set-up, the melting points of the two acids were determined.

Data and Calculation

A. Conversion of maleic acid to fumaric acid

Mass of maleic acid + weighing bottle	8.7453g
Mass of weighing bottle	4.6659g

Mass of fumaric acid	(28.082 - 26.547)= 1.535g
Percentage yield	37.63%

B. *Comparison of the properties of the 2 isomers*

1. Water solubility: Maleic acid is more soluble.
2. Acid strength

Test	Maleic acid	Fumaric acid
pH of the solution	4	4~5
Reaction with Mg	Gas bubbles evolved at a faster rate	Gas bubbles evolved at a slower rate
Reaction of Na_2CO_3	Gas evolved faster	Gas evolved slower

3. Reaction with bromine water
   Maleic acid: the solution turns pale yellow.
   Fumaric acid: the solution turns pale yellow.
4. Melting points of the two acids
   Maleic acid: $150^oC \sim 156^oC$
   Fumaric acid: $287^oC \sim 300^oC$

Conclusion

Maleic acid displays acid properties to a higher extent.
Maleic acid is more soluble in water.
Both acids decolorize bromine water.
The melting point of maleic acid is lower than fumaric acid.

Discussion

1. The reaction to convert maleic acid to fumaric acid is assumed to have gone to completion after boiling in a water bath for 5 minutes. However, some maleic or hydrochloric acid still remains in the reaction mixture after the reaction. As a result, maleic acid would be found on the surface of the residue of the mixture even after the filtration. If the contaminated residue is allowed to dry up in the oven, the weight of fumaric acid weighed in the balance would not reflect its actual value.
2. After having filtration for a period of time, the fumaric crystals could be washed with distilled water. In this way, the amount of impurities in the fumaric acid crystals can be reduced.
3. In this experiment, concentrated hydrochloric acid was used as a catalyst. Concentrated hydrochloric acid is extremely hazardous. It gives off a white fume

when its lid is opened. It gives a bad and toxic smell of hydrogen chloride.

4. To reduce the harms brought by the concentrated hydrochloric acid, a watch glass is used to cover the lid of the beaker after the hydrochloric acid is added to it. The watch glass remains on the lid throughout the whole heating process. This reduces the amount of hydrogen chloride given off to the surroundings. The watch glass is only allowed to be taken off when the beaker is cooled down.

5. Maleic acid cannot directly change into fumaric acid, due to the limited rotation of the carbon-carbon double bond. The fumaric acid is formed by adding hydrochloric acid and maleic acid together and being heated. The hydrogen chloride adds to the maleic acid, forming an intermediate in which there is unrestricted rotation about the C-C bond.

   As the fumaric acid is less soluble than water, the acid precipitates during the heating process.

6. The following are the structural formulas of fumaric acid and maleic acid:

   In the cis-butenedioic acid, the 2 bulky functional groups are on the same side of the double bond. The trans-butenedioic acid, on the other hand, has the 2 bulky functional groups on the opposite sides of the double bond. So, the packing efficiency of the trans- butenedioic acid is better than that of the cis- butenedioic acid. The distance between the trans- butenedioic acid molecules are closer, and the intermolecular interaction is higher. So, the trans- butenedioic acid should have a higher melting point.

7. In the cis-butenedioic acid, intramolecular hydrogen bonds are formed.

As a result, the intermolecular hydrogen bonds in the cis-butenedioic acid are less extensive. The neighboring molecules hold less strongly against each other. On the other hand, the trans-butenedioic acid has a more extensive hydrogen bond formation, and the forces holding each other are stronger. Thus, it can be predicted that the boiling point of the trans-butenedioic acid is higher.

8. On the other hand, the solubility of cis-butenedioic acid is higher than that of trans-butenedioic acid, although its hydrogen bond formation is not extensive as that of trans-butenedioic acid. This is because the cis-butenedioic acid has a greater dipole moment than trans-butenedioic acid.

9. To improve heating effect during the determination of the melting points, the extensive arm of the tube was heated. This creates a conventional current.

So, the oil was heated more efficiently.

10. The trans-butenedioic acid has a higher stability than cis-butenedioic acid. This is because in the trans-butenedioic acid, the bulkier groups are further apart. So, this acid has a lower intrinsic energy and thus a higher stability.

11. Maleic acid exhibits a higher acidic property than fumaric acid. This is because maleic acid contains intramolecular hydrogen bonds. This draw electron density away from the other O-H bond. This weakens the bond and makes the release of the first hydroxide ion much more ready. Fumaric acid does not have intramolecular hydrogen bonds. So, the first hydroxide ion is not easily released as maleic acid does.

12. However, the second acid dissociation constant of maleic acid is lower than that of fumaric acid. That is, the second hydroxide molecule does not leave the maleic acid easily. This is because the maleic acid has extra stability after the first hydroxide ion is lost.

13. As the two carboxyl groups of maleic acid are put at the same side, it can form anhydride when heated to 150°C.

    Fumaric acid does not form anhydride. But when it is heated to 250 °C, its -bond breaks and maleic acid is formed, which turns to anhydride at this temperature.
14. Due to this reason, the melting point of the two acids can only be determined once. If the test tube was heated to a temperature higher than the melting point, another substance is formed and we would fail in determining the correct melting point.