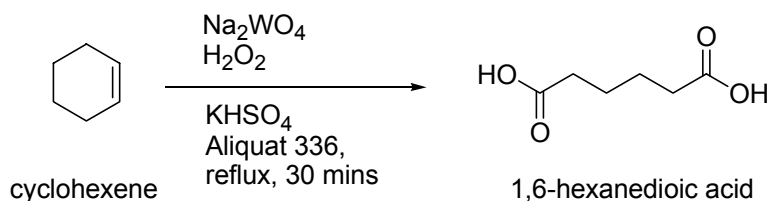


Experiment 12
Green Chemistry:
An Environmental-Friendly Preparation of 1,6-Hexanedioic Acid

Student Handout

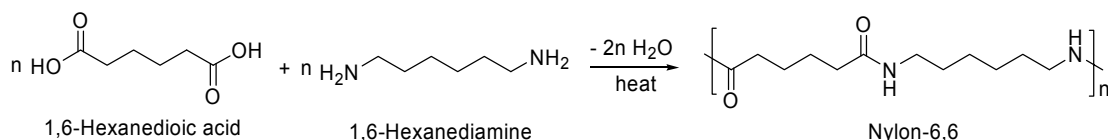
Purpose

To prepare 1,6-hexanedioic acid (adipic acid) by catalytic oxidation of cyclohexene in the presence of a phase-transfer catalyst (Aliquat 336).



Background

1,6-Hexanedioic acid is an industrially important compound. It is the monomer used in the manufacture of nylon-6,6 as shown below:



The worldwide industrial production of 1,6-hexanedioic acid is about 2.2 million metric tons per year. It involves the oxidation of cyclohexanol or cyclohexanone by nitric acid. On the other hand, small-scale preparation of 1,6-hexanedioic acid can be carried out in the laboratory by the oxidation of cyclohexanol by potassium permanganate or dichromate. The oxidants used in both cases cause certain environmental problems.

In the industrial production of 1,6-hexanedioic acid by nitric acid, N_2O is produced as a by-product. N_2O is known to be an environmental contaminant as it is commonly thought to cause global warming and ozone depletion as well as acid rain and smog. It is estimated that about 400,000 metric tons of nitrous oxide is emitted annually due to the 1,6-hexanedioic acid production, which corresponds up to 8% of the worldwide anthropogenic emission of N_2O . The laboratory preparation of 1,6-hexanedioic acid

is also problematic from the environmental point of view because the oxidants used are constituted of toxic metals and these reactions have problems in chemical waste disposal.

As the public awareness on environmental issues is increasing, the environmental consideration taken in the design of chemical synthesis is growing in importance. It includes careful selection of reactants and reaction conditions. Aqueous H_2O_2 solution is an ideal clean oxidant because it is converted into water, which is harmless. Recent research shows that 1,6-hexanedioic acid can be obtained by the oxidation of cyclohexene with 30% aqueous H_2O_2 solution in the presence of small amounts of sodium tungstate(VI) (Na_2WO_4) and Aliquat 336 acting as the catalysts. In the reaction, H_2O_2 is used as the principal oxidant to substitute the environmentally hazardous nitric acid. The other two reagents, sodium tungstate(VI) and Aliquat 336, are used only in very small amounts as catalysts and therefore chemical waste disposal and environmental problems are kept to a minimum. Furthermore, the two catalysts are not consumed in the reaction. These two reagents can be recycled for further use and therefore the reaction is both environmentally and economically 'friendly'.

Safety

The experiment should be performed in a well-ventilated laboratory or fumehood. Handle all chemicals with great care. Avoid direct contact of chemicals with skin. Dispose of chemical waste, broken glassware and excess materials according to your teacher's instruction.

Aliquat 336 is known to be toxic and irritating. Avoid contact it with skin.

KHSO_4 is acidic and is a mild irritant.

Aqueous 30% H_2O_2 solution is highly corrosive. It blisters skin and causes severe contact burns on skin and in eyes. Never contact it with bare skin. Protective gloves and goggles must be worn when handling this reagent.

Cyclohexene is a flammable organic liquid. Keep it away from all ignition sources.

This reaction may have some undesirable odours. It should be carried out in a well-ventilated laboratory, or ideally, in a fumehood.



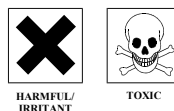
EYE PROTECTION
MUST BE WORN

Pay special attention when heating a mixture under reflux. Never heat a closed system or explosion may occur. Make sure the rubber tubings of the water condenser are connected properly.

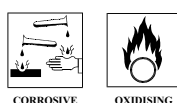
The reaction mixture contains toxic Aliquat 336. Properly and cautiously dispose of all the materials from the reaction as organic chemical waste.

Materials and Apparatus

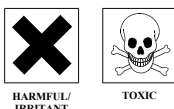
Aliquat 336 (Methyltrioctylammonium chloride)



30% Hydrogen peroxide solution



Sodium tungstate(VI) dihydrate



Anhydrous CaCl₂



KHSO₄



Cyclohexene



Oil bath

Ice-water bath

50-cm³ Conical flasks (2 pcs.)

Suction flask

Filter paper

Weighing balance

Büchner funnel

Droppers

Spatula

50-cm³ Round-bottomed flask

Water condenser

Drying tube

Electric stirring hotplate



Magnetic stirrer bar

Experimental Procedure




Photos of the experiment are available at <http://www.chem.cuhk.edu.hk/ssc.htm>.




Note: The reaction may have unpleasant odours. Perform the reaction in a well-ventilated fumehood. If fumehood is not available, fit a drying tube with calcium chloride to the top of the water condenser to minimise the odours.

1. Fill a drying tube with calcium chloride. 
2. Add sodium tungstate(VI) dihydrate (0.80 g), Aliquat 336 (0.80 g), 30% hydrogen peroxide solution (10.8 cm³) and KHSO₄ (0.60 g) in succession to a 50-cm³ round-bottomed flask. 

Note: 30% hydrogen peroxide solution is highly corrosive and can cause severe injuries to eyes and skin. The substance should be handled with great care.

3. Put a magnetic stirrer bar into the round-bottomed flask and stir the mixture on an electric stirring hotplate.
4. Add 2.5 cm³ of cyclohexene to the mixture in the round-bottomed flask.
5. Fit a water condenser to the round-bottomed flask and fit a drying tube with calcium chloride to the top of the water condenser to minimise the odours. 
6. Boil the mixture under reflux with a hot oil bath for 30 minutes with vigorous stirring.

Note: The reaction mixture should be stirred vigorously during heating. The efficiency of the reaction depends on the very efficient mixing of the organic and aqueous layers.

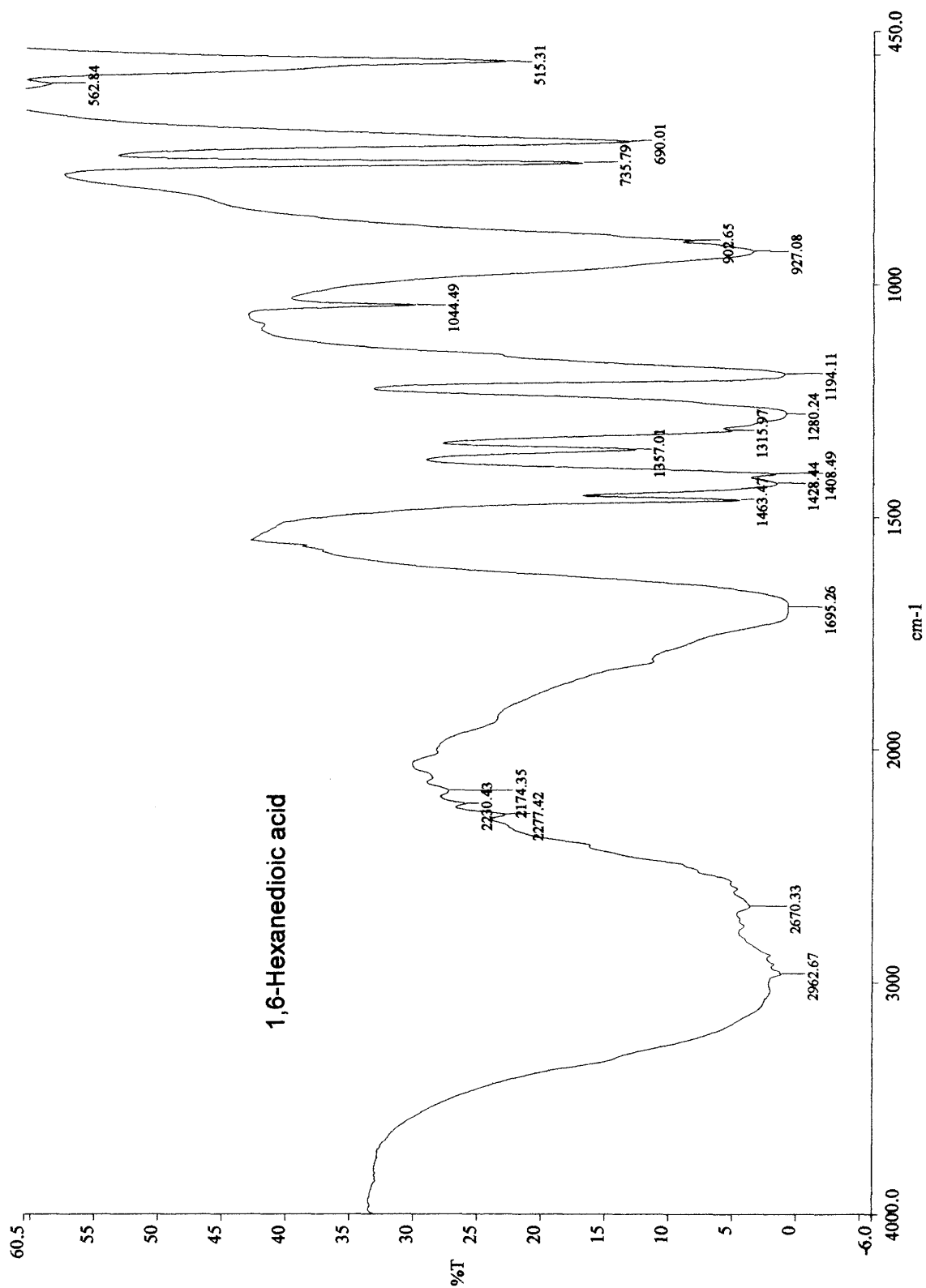
7. The completeness of the reaction can be determined by occasionally stopping the stirrer and checking whether the reaction mixture still consists of two separate layers. If the reaction is complete, i.e., all cyclohexene is transformed into the water-soluble 1,6-hexanedioic acid, there remains only one layer (the aqueous layer). 
8. Cool the round-bottomed flask to room temperature for a few minutes in water-bath to allow the product (1,6-hexanedioic acid) to crystallise. Cool the flask to 0 °C in an ice-water bath for another 3-5 minutes to ensure complete crystallisation. 
9. Filter the mixture by suction filtration. Wash the solid product on the Büchner funnel with a small amount of cold water. Dry the product on the Büchner funnel with the suction turned on for a few minutes. 
10. Weigh the 1,6-hexanedioic acid obtained and determine the percentage yield for the reaction.

Spectroscopic Analysis

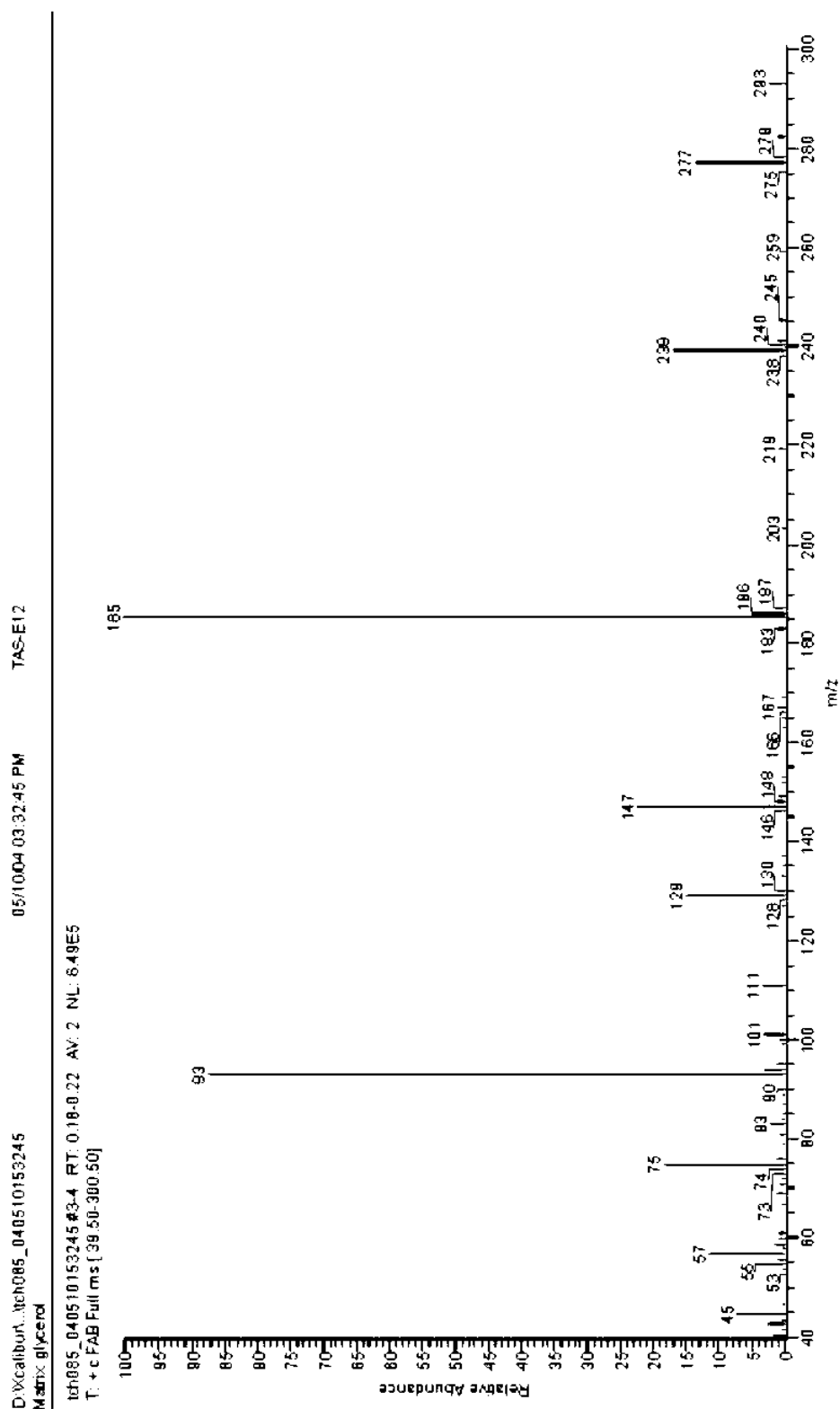
The infra-red and the mass spectra for 1,6-hexanedioic acid are given below. Make use of them to:

- (i) identify which functional groups will give rise to the following infra-red absorption bands.
 - (a) 1695 cm⁻¹
 - (b) 2500 - 3300 cm⁻¹ (very broad band)
- (ii) identify the molecular ion peak from the given mass spectrum.

Spectrum 1: IR spectrum of 1,6-hexanedioic acid



Spectrum 2: Mass spectrum of 1,6-hexanedioic acid



Questions for Further Thought

1. What are the functions of a catalyst in a chemical reaction?
 2. (a) Calculate the number of moles for the following reagents used in the reaction:
 - Cyclohexene
 - Hydrogen peroxide solution
(30% by weight, density = 1.1100 g cm^{-3})
 - Aliquat 336
 - Sodium tungstate(VI) dihydrate(b) Explain very briefly why some of the above reagents are only added to the reaction in very small amounts.
 3. Explain briefly why the reaction mixture should be stirred vigorously during heating.
 4. How do you determine the completeness of the reaction by observation?
 5. List the advantage(s) of this reaction when compared with the traditional industrial production of 1,6-hexanedioic acid by the oxidation of cyclohexanol/cyclohexanone with nitric acid.
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References

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