Preparation of adipic acid from cyclohexene

In this laboratory period the cyclohexene (supposedly) prepared in the previous experiment is oxidized to adipic acid. You will be provided with cyclohexene. As shown in the Procedure, we will use 2 mL. Read this document completely, and then answer the prelab questions below. Show these answers and your notebook set up for this experiment to your instructor before starting the experiment.

Theory:

The cleavage of double bonds by oxidation is useful in the synthesis of acids and ketones and determining structures. Several methods are available including ozonolysis and hot concentrated permanganate. The products obtained depend on the original structure of the olefin. The equations below illustrate the products from cleavage of alkenes:

\[ \text{CH}_2 = 
\text{CH} \quad \xrightarrow{\text{K MnO}_4} \quad \text{CH}_3 \quad \text{C} \quad \text{OH} + \text{CO}_2 \quad \text{acetic acid} \]

\[ \text{CH}_2 = \text{CH} - \text{CH} \quad \xrightarrow{\text{K MnO}_4} \quad \text{CH}_3 \quad \text{C} \quad \text{OH} + \text{O} \quad \text{C} \quad \text{CH}_3 + \text{CO}_2 \quad \text{acetic acid, acetone} \]

\[ \text{CH}_2 = \text{CH} \quad \xrightarrow{\text{K MnO}_4} \quad \text{CO}_2 \quad \text{only} \]

The balanced equation for the oxidation of cyclohexene with permanganate is shown:

\[ 3 \text{ cyclohexene} + 8 \text{ K MnO}_4 + 4 \text{ H}_2 \text{O} \rightarrow 3 \text{ adipic acid} + 8 \text{ KOH} + 8 \text{ MnO}_2 \]

Safety Considerations:

1. Add concentrated hydrochloric acid to the strongly basic solution very cautiously or erupting and spattering may occur. If acid is spilled on the skin, wash the affected area thoroughly with cold water.

2. Handle potassium permanganate carefully. It is a strong oxidizing agent. Avoid contact with skin and eyes. You may wish to wear gloves to avoid staining your fingers.

3. Avoid breathing vapors of cyclohexene and methanol.

**NOTE:** Stains of potassium permanganate and manganese dioxide can be removed from equipment, sinks and hands by washing with a solution of sodium bisulfite (NaHSO₃).
Disposal:

The brown/black filter cake of manganese dioxide should be disposed of in the container provided in the hood. Solutions can be flushed down the drain after dilution with tap water.

Procedure:

To a 250 mL Erlenmeyer flask, add water (50 mL), cyclohexene (2 mL, density = 0.81 g cm\(^{-3}\)), and potassium permanganate (8.4 g). Stopper the flask *loosely*, wrap with a towel and swirl vigorously for 5 minutes. The flask should feel warm. If no rise in temperature is detected, remove the stopper, warm the mixture *gently* on a hot plate and *loosely* replace the stopper. Swirl the flask at frequent intervals for 20 minutes (your yield depends on how well you mix the reactants at this stage).

The temperature of the mixture should be between 35° and 40°. If the temperature rises above 45°, briefly cool in an ice-water bath or a stream of water. After 20 minutes, remove the stopper and place the flask on a hot plate for 15 minutes. Continue to swirl the flask at frequent intervals.

Make a spot test by withdrawing some of the reaction mixture on the tip of a stirring rod and touching it to a filter paper; permanganate, if present will appear as a purple ring around the dark brown spot of manganese dioxide. If permanganate is still present, add 1 mL of methanol and heat. Repeat this procedure until the permanganate color has disappeared.

While the reaction is going on, prepare 25 mL of a 1% sodium hydroxide solution by diluting a portion of the 6 M stock reagent in the fume hood. Warm the resulting solution gently on the hot plate.

Filter the mixture through a large Buchner funnel (vacuum) into a clean filter flask. Rinse the reaction flask with 10 mL of hot 1% sodium hydroxide solution and pour through the filter. Repeat with a second portion of 10 mL of 1% sodium hydroxide solution.

Place the combined filtrate and washings in a 250 mL beaker (premarked at 10 mL), add a boiling chip and boil on the hot plate until the volume of the solution is about 10 mL. Working in the hood, cool the solution in an ice-water bath and acidify to about pH 1 by *cautiously* adding concentrated hydrochloric acid dropwise while stirring the solution. Check the pH of the solution with pHydron paper. Add an additional 3 mL of acid, stir and allow the beaker to stand in the ice bath for 5 - 10 min to complete the crystallization.
Collect the acid by vacuum filtration. Recrystallize it from not more than 5 - 10 mL of boiling water. Cool to room temperature, then place in an ice-water bath for 10 minutes. N.B.: The most common reason for “losing” your product in a recrystallization is using too much solvent.

Filter the product by vacuum (Hirsch funnel) and rinse the beaker of any residue with a small amount of ice-cold water. Dry by pulling air through the filter cake. Drying will go a little faster if you loosen the product cake with a spatula, taking care not to tear the filter paper. If you run out of time, set aside your product to dry in a safe place.

*Each* student must measure the melting point. Report your melting point and a literature (“official”) value. Calculate the yield of product and the percentage yield. Show your product to your instructor, who will collect or dispose of the material.

**Write-up:**

Remember that this experiment is the subject of a formal lab write-up. Review the information and sample files on the Blackboard, and discuss with your instructor anything that is not clear.

- Your results section should show all calculations you did, including the theoretical and per cent yield, and the calculation for dilution of the sodium hydroxide solution.
- Chemical equations should be prepared as graphics showing structures from the ChemSketch program!
- Be sure to cite appropriately the source for your literature value of the melting point.