

Reaction time 45 min

ture in the second flask to 15°C. Wipe the flask containing the dichromate solution, pour the solution into the cyclohexanol-acetic acid mixture, rinse the flask with a little solvent (acetic acid), note the time, and take the initially light orange solution from the ice bath, but keep the ice bath ready for use when required.<sup>2</sup> The exothermic reaction that is soon evident can get out of hand unless controlled. When the temperature rises to 60°C cool in ice just enough to prevent a further rise and then, by intermittent brief cooling, keep the temperature close to 60°C for 15 min. No further cooling is needed, but the flask should be swirled occasionally and the temperature watched. The usual maximal temperature is 65°C (25–30 min). When the temperature begins to drop and the solution becomes pure green, the reaction is over. Allow 5–10 min more reaction time and then pour the green solution into a 250-mL round-bottomed flask, rinse the Erlenmeyer flask with 100 mL of water, and add the solution to the flask for steam distillation (Chapter 6) of the product (Fig. 3 in Chapter 6). Distill as long as any oil passes over with the water and, because cyclohexanone is appreciably soluble in water, continue somewhat beyond this point (about 80 mL will be collected).

Alternatively, instead of setting up the apparatus for steam distillation, simply add a boiling chip to the 250-mL flask and distill 40 mL of liquid, cool the flask slightly, add 40 mL of water to it, and distill 40 mL more. Note the temperature during the distillation. This is a steam distillation in which steam is generated *in situ* rather than from an outside source.

## Isolation of Cyclohexanone from Steam Distillate

Cyclohexanone is fairly soluble in water. Dissolving inorganic salts such as potassium carbonate or sodium chloride in the aqueous layer will decrease the solubility of cyclohexanone such that it can be completely extracted with ether. This process is known as “salting out.”

To salt out the cyclohexanone, add to the distillate 0.2 g of sodium chloride per milliliter of water present and swirl to dissolve the salt. Then pour the mixture into a separatory funnel, rinse the flask with ether, add more ether to a total volume of 25–30 mL, shake, and draw off the water layer. Then wash the ether layer with 25 mL of 10% sodium hydroxide solution to remove acetic acid, test a drop of the wash liquor to make sure it contains excess alkali, and draw off the aqueous layer.

2. When the acetic acid solutions of cyclohexanol and dichromate were mixed at 25°C rather than at 15°C the yield of crude cyclohexanone was only 6.9 g. A clue to the evident importance of the initial temperature is suggested by an experiment in which the cyclohexanol was dissolved in 12.5 mL of benzene instead of 10 mL of acetic acid and the two solutions were mixed at 15°C. Within a few minutes orange-yellow crystals separated and soon filled the flask; the substance probably is the chromate ester,  $(C_6H_{11}O)_2CrO_2$ . When the crystal magma was let stand at room temperature the crystals soon dissolved, exothermic oxidation proceeded, and cyclohexanone was formed in high yield. Perhaps a low initial temperature ensures complete conversion of the alcohol into the chromate ester before side reactions set in.

To dry the ether, which contains dissolved water, shake the ether layer with an equal volume of saturated aqueous sodium chloride solution. Draw off the aqueous layer, pour the ether out of the neck of the separatory funnel into an Erlenmeyer flask, add about 5 g of anhydrous sodium sulfate, and complete final drying of the ether solution by occasional swirling of the solution over a 5-min period. Remove the drying agent by decantation or gravity filtration into a tared Erlenmeyer flask and rinse the flask that contained the drying agent, the sodium sulfate, and the funnel with ether. Add a boiling chip to the ether solution and evaporate the ether on the steam bath under an aspirator tube (Fig. 5 in Chapter 8). Cool the contents of the flask to room temperature, evacuate the crude cyclohexanone under aspirator vacuum to remove final traces of ether (Fig. 3 in Chapter 10), and weigh the product. Yield is 11–12.5 g.

The crude cyclohexanone can be purified by simple distillation or used directly in the following experiment.

**Cleaning Up** To the residue from the steam distillation add sodium bisulfite to destroy any excess dichromate ion, neutralize the solution, dilute it with a large quantity of water, and pour it down the drain if local laws allow. If not, collect the precipitate of chromium hydroxide that forms when the solution is just slightly basic and dispose of the filter paper and precipitate in the hazardous waste container designated for heavy metals. The filtrate can be flushed down the drain. Combine water layers from the extraction process, neutralize with dilute hydrochloric acid, and dispose of the solution down the drain. Any ether should be placed in the organic solvents container, and the drying agent, if completely dry, can be placed in the nonhazardous waste container. If it still has organic solvent on it, then it must be placed in the hazardous waste container. It is *much* more expensive to dispose of hazardous waste.

*The use of Celite will speed up the filtration*

## 2. Hypochlorite Oxidation of Cyclohexanol

Into a 250-mL Erlenmeyer flask in the hood place 8 mL (0.075 mole) of cyclohexanol and 4 mL of acetic acid. Introduce a thermometer and slowly add to the flask with swirling 115 mL of a commercial household bleach such as Clorox (usually 5.25% by weight NaOCl, which is 0.75 molar). This can be added from a separatory funnel clamped to a ring stand or from another Erlenmeyer flask. Take care not to come in contact with the reagent. During the addition, keep the temperature in the range of 40–50°C. Have an ice bath available in case the temperature goes above 50°C, but do not allow the temperature to go below 40°C because oxidation will be incomplete. The addition should take about 15–20 min. Swirl the reaction mixture periodically for the next 20 min to complete the reaction.

Since the exact concentration of the hypochlorite in the bleach depends on its age, it is necessary to analyze the reaction mixture for unreacted hypochlorite and to reduce excess to chloride ion with bisulfite.

Add a drop of the reaction mixture to a piece of starch-iodide paper. Any unreacted hypochlorite will cause the appearance of the blue starch-iodide complex. Add 1-mL portions of saturated sodium bisulfite solution to the reaction mixture until the starch-iodide test is negative.

Add a few drops of thymol blue indicator solution to the mixture, and then slowly add with swirling 15–20 mL of 6 M sodium hydroxide solution until the mixture is neutral as indicated by the blue color.

Transfer the reaction mixture to a 250-mL round-bottomed flask, add a boiling chip, and set up the apparatus for simple distillation. Distillation under these conditions is a steam distillation (see Chapter 6) in which the steam is generated *in situ*. Continue the distillation until no more cyclohexanone comes over with the water (40 mL of distillate should be collected).

See the section entitled “Isolation of Cyclohexanone from Steam Distillate” in the previous experiment to complete the reaction sequence.

**Cleaning Up** The residue from the steam distillation contains only chloride, sodium, and acetate ions and can therefore be flushed down the drain.

### 3. Adipic Acid

The reaction to prepare adipic acid is conducted with 10.0 g of cyclohexanone, 30.5 g of potassium permanganate, and amounts of water and alkali that can be adjusted to provide an attended reaction period of one-half hour, procedure (a), or an unattended overnight reaction, procedure (b).

- (a) For the short-term reaction, mix the cyclohexanone and permanganate with 250 mL of water in a 500-mL Erlenmeyer flask, adjust the temperature to 30°C, note that there is no spontaneous temperature rise, and then add 2 mL of 10% sodium hydroxide solution. A temperature rise is soon registered by the thermometer. It may be of interest to determine the temperature at which you can just detect warmth, by holding the flask in the palm of the hand and by touching the flask to your cheek. When the temperature reaches 45°C (15 min) slow the oxidation process by brief ice-cooling and keep the temperature at 45°C for 20 min. Wait for a slight further rise (47°C) and an eventual drop in temperature (25 min), and then heat the mixture by swirling it over a flame to complete the oxidation and to coagulate the precipitated manganese dioxide. Make a spot test by withdrawing reaction mixture on the tip of a stirring rod and touching it to a filter paper; permanganate, if present, will appear in a ring around the spot of manganese dioxide. If permanganate is still present, add small amounts of sodium bisulfite until the spot test is negative. Then filter the mixture by suction on an 11-cm Büchner funnel, wash the brown precipitate well with water, add a boiling chip, and evaporate the filtrate over a flame from a large beaker to a volume of 70 mL. If the solution is not clear and

*Note the temperature of the vapor during this distillation*

*Choice of controlling the temperature for 30 min or running an unattended overnight reaction*