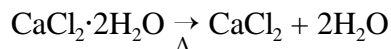


## Preparation of Anhydrous CrCl<sub>3</sub>

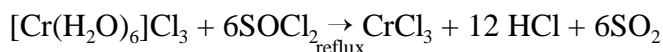
### Introduction

Many ionic halide salts are obtained from aqueous solution as hydrated salts. In some cases, where the waters of hydration merely occupy regular positions in the crystal lattice, the anhydrous form of the compound can be obtained by heating; e.g.,

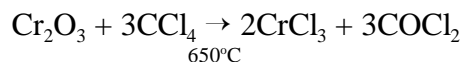


In cases where waters of hydration are coordinated directly to the metal ions, heating usually does not produce the anhydrous salt, but rather an oxohalide or an impure product. This is typically the case when the cation is small and/or highly charged or is a transition metal ion.

Since anhydrous halide salts are synthetically useful, it is desirable to have alternate techniques for obtaining them, particularly when simple heating will not suffice. One strategy that is commonly employed is to treat the hydrous salt with some dehydrating agent that effectively destroys the water and leaves the anhydrous halide salt. In the case of chlorides, refluxing with thionyl chloride, SOCl<sub>2</sub>, is generally useful to effect dehydration; e.g.,



An alternative approach is to use either the metal or metal oxide and a halogenating agent at high temperature; e.g.,



This latter approach is the one we will use to produce anhydrous chromium(III) chloride, CrCl<sub>3</sub>.

The reaction will be conducted by heating solid Cr<sub>2</sub>O<sub>3</sub> in a Vycor tube to 700°C and then passing CCl<sub>4</sub> vapor, entrained in a stream of nitrogen, over the sample. The CrCl<sub>3</sub> so formed will sublime and collect as a violet solid in the cooler end of the tube (<600°C). The product is a network solid consisting of interconnected octahedral CrCl<sub>6</sub> units. As such, the anhydrous CrCl<sub>3</sub> is quite unreactive toward water, unless it is contaminated with traces of Cr(II) compounds such as CrCl<sub>2</sub>. The presence of Cr(II) ions allows formation of Cr(II) aquo complexes when the sample is placed in water. These complexes catalyze substitution of Cl by H<sub>2</sub>O in the CrCl<sub>6</sub> octahedra of CrCl<sub>3</sub>, thereby facilitating dissolution.

## Procedure

If  $\text{Cr}_2\text{O}_3$  is not provided, it can be made by placing 2.5 g of ammonium dichromate,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , in a pile in the center of a large porcelain dish (at least 20 cm diameter) and igniting by touching it with a red-hot wire until the reaction continues from its own exothermicity:



The accompanying release of  $\text{N}_2$  throws hot solids into the air, so care should be taken that no flammable objects are in the vicinity of the reaction. If the reaction does not go to completion, it may be started again by reheating. Extract the green insoluble product with hot distilled water until the washings are colorless. Dry the  $\text{Cr}_2\text{O}_3$  at approximately  $110^\circ\text{C}$ .

The reaction to prepare  $\text{CrCl}_3$  must be run with the tube furnace placed in the fume hood with the door of the hood closed, since highly toxic phosgene gas,  $\text{COCl}_2$ , is produced (fatal concentration  $\sim 50$  ppm). Place 1.5 g of  $\text{Cr}_2\text{O}_3$  *in the center* of the Vycor reaction tube and place it in the cold tube furnace. The sample must be placed in the center of the tube, since the ends will not reach as high a temperature. Use a Scoopula attached to a long rod to facilitate placing the sample in the center of the tube. Attach a hose adapter fitting to one end of the tube. The Vycor tube should be wound with insulating tape or fitted with insulating shields at each end of the furnace, so that a tight fit results when the lid of the furnace is closed. This is necessary to reach a stable high temperature.

Fit a three-neck 250-mL round bottom flask with a bubbler frit in one side neck and a hose adapter in the other side neck. Add sufficient  $\text{CCl}_4$  to the flask to cover the frit, and then seal the center neck with a hollow ground glass stopper. Connect a hose from the regulator on a tank of nitrogen to the inlet of the bubbler frit in the flask. Connect another tube from the hose adapter on the flask to the hose adapter on the Vycor tube. Turn on the tube furnace and set the temperature for  $700^\circ\text{C}$ . Turn on the nitrogen and adjust the regulator to achieve a minimal flow, so that only gentle bubbling is observed in the  $\text{CCl}_4$ . There should be no frothing. Too fast a stream of  $\text{N}_2$  will blow either  $\text{Cr}_2\text{O}_3$  or the newly formed  $\text{CrCl}_3$  out of the end of the Vycor tube. Once the furnace is nearly at the set temperature, watch for telltale wisps of white or violet smoke exiting from the tube, which show that the nitrogen flow rate is too high. Depending on the behavior of your regulator, the flow rate may require frequent readjusting.

When the temperature rises above approximately 600°C, the  $\text{CrCl}_3$  that has been formed will begin to sublime and will collect as violet flakes near the cooler exit end of the tube. Complete reaction, indicated by disappearance of the pile of  $\text{Cr}_2\text{O}_3$ , should take about 1½ to 2 hours. If the reaction is not proceeding at a satisfactory rate, as evidenced by the steady disappearance of the pile of green powder in the center of the tube, try increasing the flow rate of the nitrogen and/or gently warming the carbon tetrachloride with a heating mantle under the flask. When no green  $\text{Cr}_2\text{O}_3$  remains, turn off the furnace, open its lid, and allow the tube and product to cool under a flow of nitrogen. Scrape the  $\text{CrCl}_3$  from the reaction tube onto a clean piece of paper, and then transfer the product to a tared vial. Determine the yield.

### Laboratory Report

1. Submit your sample, clearly labeled with the names of all group members participating in the preparation. [The sample will be returned for use in another preparation.]
2. Your written report should include statements of yield and percent yield, and brief explanations of any departures from the procedure.
3. Why is it necessary to maintain a nitrogen atmosphere in the reaction tube?
4. Add a small amount of your product to 10 - 15 mL of water in a test tube and stir. Look for evidence of solubility. Add a few drops of hydrochloric acid ( $\sim 6M$ ) to the mixture. Repeat the experiment with added NaOH solution ( $\sim 4M$ ). Is there any change in the apparent solubility of  $\text{CrCl}_3$ ? Try the same series of tests with  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . Report and explain your observations, giving balanced equations where appropriate.
5. Give two examples (other than  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) of hydrated chloride salts that could be dehydrated by heating alone and four examples (other than  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) that would require chemical means to produce the anhydrous form. Of the four that would require chemical means, cite two with main group cations and two with transition metal cations. Give reasons for the differences in dehydration behavior among all your examples. Give literature references for the sources of information by which you chose your examples. [cf. A. R. Pray, *Inorganic Syntheses*, vol. 5, McGraw-Hill, New York, 1957, p. 153.]