EXPERIMENT 2

TIN(IV) HALIDES

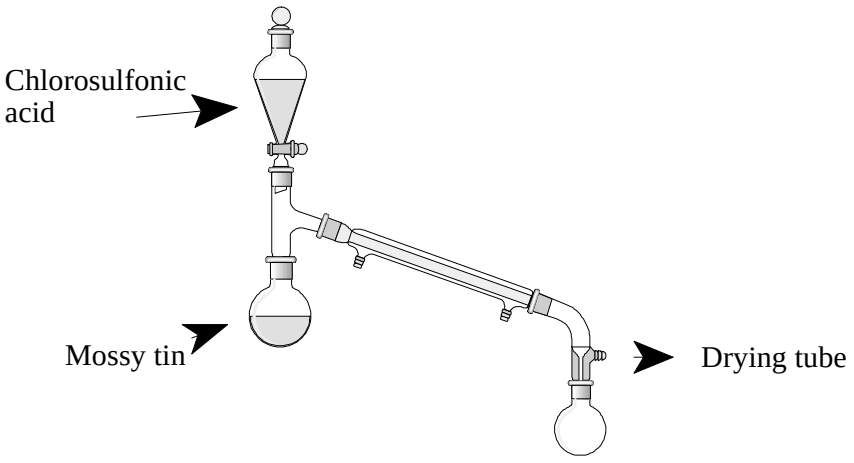
1. Introduction

Read the appropriate section of F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* 5th Edition in order to acquire some background for interpretation of the observations in Part 4 of this experiment.

2. Preparation of Tin(IV) Chloride

☞ **[*CAUTION:* $ClSO_3H$ REACTS VIOLENTLY WITH WATER.]**

Because the handling of reagents used in this experiment could be hazardous, *consult your instructor* before beginning. You MUST use a fumehood, and keep the window between you and the experiment. It is important that the apparatus you use is properly dried before you start.



Apparatus for the Synthesis of Tin(IV) Chloride

Put 5.5 g of mossy tin into a 25 ml semi-micro distillation flask and slowly add 13 ml of $ClSO_3H$ (chlorosulfonic acid) from a tap funnel. The addition should be just fast enough to maintain a steady reaction, and to provide enough heat to distil the stannic chloride into the receiving flask. When the reaction is complete, redistill the product, if necessary. It should be a colorless liquid, b. p. ~ 110° C.

$$Sn + 4ClSO_3H \rightarrow SnCl_4 + 2SO_2 + 2H_2SO_4$$

N. B. $SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl$

As soon as the product is obtained, stopper it in a flask.

3. Preparation of Tin(IV) Iodide

Weigh 1.0 g of granulated tin and 3.3 g of iodine into a 25 ml flask. Add 15 ml of carbon tetrachloride and one or two small boiling chips and fit a reflux condenser to the flask. Warm the flask gently, using a water bath on a hot plate, until the reaction starts and then remove the source of heat.

Re-apply heat as necessary to maintain a steady refluxing of the solvent until no free iodine remains. (Solution is orange-red instead of violet.)

Remove the condenser, heat the solution to boiling point and filter through a fluted filter paper to remove excess tin. The filtering equipment should be preheated with hot solvent in order to prevent the product from crystallizing prematurely. Wash the residue in the flask and on the filter with 3 ml of hot carbon tetrachloride, combining the washings with the main filtrate.

Cool the solution in an ice bath and filter off the solid. Evaporate the filtrate to about half-bulk to obtain a further crop of crystals. Weigh and record the yield. Calculate the theoretical yield (based on iodine).

The solid may be recrystallized from carbon tetrachloride.

4. Reactions of Tin(IV) Halides

Compare reactions of the two halides in the following tests explaining, as far as possible, the differences and similarities.

(a) Solubility in (i) ethanol, (ii) benzene, (iii) dilute hydrochloric acid, (iv) concentrated

hydrochloric acid, (v) 2M-sodium hydroxide solution. Note color of solutions, possible reactions, and write equations to explain all observations.

(b) Stability to oxidation, *e.g.* acidic permanganate solution.

(c) Stability to reduction, *e.g.* acidic stannous chloride, zinc metal and dilute hydrochloric acid.

(d) Complexation, or "adduct"-forming reactions. To a solution of 2.0 g triphenyl phosphine in 2 ml benzene, add a solution of 0.5 g of $SnCl_4$ in 2 ml benzene. Repeat this reaction with 0.5 g SnI_4. How does the reactivity of $SnCl_4$ change as a result of forming a complex with Ph_3P?

(e) Although $SnCl_4$ will react with triphenylphosphine, CCl_4 is unreactive in this regard. Explain why this is so.

Post-lab Questions

1. Based on the solubility properties of the tin(IV) halides, how do they differ from the more commonly encountered metal halides of metals such as sodium or magnesium?

2. What is an "adduct" ? Identify an example from the chemistry of $SnCl_4$, and also one from the chemistry of boron.

3. What structures would be predicted for $SnCl_2$, $SnCl_4$, and $Cl_4Sn \leftarrow PPh_3$ using VSEPR theory. (Assume $SnCl_2$ is monomeric)