

## Synthesis and identification of a polyiodide salt

### ABSTRACT

Iodine can form anionic chains with the formula  $I_x^{n-}$ , ranging from  $I_3^-$  to  $I_{18}^{4-}$  and beyond. In this experiment, the student will synthesize a polyiodide salt and analyse/determine the value of “x” using iodometric titration.

### Equipment

No special equipment required.

### Safety Hazards

No particular hazards.  $I_2$  is toxic. Methanol is flammable and poisonous.

<b>Year Level:</b>	2nd year introductory inorganic
<b>Student time required:</b>	two 3-hour lab periods
<b>Instructor time required:</b>	~3 hours??
<b>Technician notes?</b>	Available upon request
<b>Study question solutions?</b>	Available upon request
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## Chemistry 2351: Inorganic Chemistry I Laboratory Manual

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## Experiment Three:

# Synthesis and Identification of a Polyiodide Salt

### Purpose of the Experiment

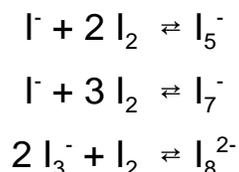
You will synthesise a polyiodide salt, and determine its stoichiometry by iodometric titration.

### Introduction

As you know from organic chemistry, carbon can catenate - form chains of C-C bonds. Likewise, other non-metals can form rings or chains, including Si and S. Iodine can form a series of *anions*, called the polyiodides, that consist of chains of iodines with one or more extra electrons. The most common is the linear species  $I_3^-$ . In some cases it exists with equal I-I bonds, in other cases it looks more like an I coordinating to an  $I_2$  molecule (distances are in Å):



A whole series of these polyiodides have been identified. Some are monoanionic ( $I_5^-$ ,  $I_9^-$ ), while others are more highly charged ( $I_8^{2-}$ ,  $I_{16}^{4-}$ ). Most of these higher-order polyiodides are considered to be combinations of  $I^-$ ,  $I_2$ , and  $I_3^-$ . For example,



In this experiment, you will isolate an  $I_x^-$  salt with a  $NMe_4^+$  cation. The salt will be monoanionic, while the number of iodines “x” will have to be determined by iodometry, a titration to determine the amount of iodine in the species.

### Experimental Procedure

Each student will prepare and analyse ONE OF THE FOLLOWING TWO SALTS. They both have the formula  $NMe_4I_x$ , but different experimental conditions give different values of x.

### *Special Notes and Safety Precautions*

Methanol is flammable. Make sure all flames are extinguished when using this solvent. You must standardise and use the  $Na_2CO_3$  solution in one afternoon - carbonate will slowly decompose (with release of  $CO_2$ ). Iodine is toxic in moderate doses, so take care when handling it.

### ***Preparation of NMe<sub>4</sub>I<sub>x</sub>***

#### PREPARE ONE OF THE FOLLOWING

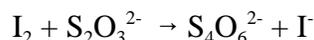
Version #1 Dissolve 2.5 g of I<sub>2</sub> in 30 mL of cold methanol. This will have to be stirred and crushed with a glass rod to get it into solution. Once it's dissolved, add 1.0 g of finely powdered (mortar and pestle) NMe<sub>4</sub>I and stir until dissolved. As the NMe<sub>4</sub>I is dissolving, the product (metallic green) should start crystallising from solution.

Allow to stand 1 hour to complete crystallisation. Suction filter, wash with 5 mL of cold methanol. Recrystallise by dissolving 1.0 g of product in boiling methanol. Cover (watch glass or filter paper) the beaker and let stand for a week to crystallise. The next week, filter, wash with 5 mL of cold methanol, and air dry while preparing your titration solutions.

Version #2 Dissolve 2.5 g of iodine in 30 mL of hot methanol (this should be done in the fumehood). Add 0.5 g of NMe<sub>4</sub>I. Stir and keep the solution hot (not boiling) until all the NMe<sub>4</sub>I is dissolved. Cover and allow the crystals to form over the course of at least 1.5 hours (but it can be left for a week if in the dark). Decant off the mother liquor, add 5 mL of cold methanol as a wash, and decant it off as well. Air dry. Do not recrystallise.

### ***Iodometry***

Once you have isolated one of the two salts, analyse using iodometry. First, all iodide is converted (oxidised) to iodine, which gives a brown solution that is decolourised by reaction with thiosulfate according to (this is a redox reaction you'll have to balance!):



Because the colour fades gradually, a starch indicator is added which gives a bright blue colour when complexed with I<sub>2</sub>. This is also titrated to a colourless endpoint, but the difference in colour is more dramatic. Finally, additional I<sup>-</sup> is added to the solution to enhance solubility by the equilibrium



### ***Preparation and Standardisation of sodium thiosulfate solution***

Dissolve 5.0 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O and 0.1 g of Na<sub>2</sub>CO<sub>3</sub> in 500.00 mL of distilled water. Mix well and store in a sealed (plastic, if possible) container.

Accurately weigh 0.05 g of pre-dried KIO<sub>3</sub> into each of three 250 mL Erlenmeyer flasks. Just before titrating, add 25 mL of deionised water and 1 g of KI. When all the KI is dissolved, add 10 mL of 0.5 M HCl and titrate to a light straw yellow. Add a couple drops of starch indicator (the solution will turn blue) and finish the titration to the colourless endpoint. Calculate the molarity of your thiosulfate based on the following (unbalanced) equation,



### ***Analysis of $NMe_4I_x$ Samples***

Weigh out accurately two 0.2 g samples of your product into an Erlenmeyer. Immediately before titrating, add 0.25 g of KI and stir in 20 mL of methanol (for 5 - 10 minutes). Add 20 mL of distilled water and titrate to a starch end point as above.

### **Final Report**

This experiment is to be written as a formal report, so be sure to review the material on pp. vi - vii for the correct format. You will need to report the percent yield of product, but first you will have to determine the identity of your product (*i.e.*, the value of  $x$ ). To do this, determine the number of moles of  $I_2$  consumed in your titration, bearing in mind that  $I_x^-$  can be represented by  $I^- + (x-1)/2 I_2$ . You can then convert this into a mass percentage of your material, which will give you  $x$  in your salt  $NMe_4I_x$ .

Answer the following questions in your report.

- (1) Give the identity of the polyiodide salt  $I_x^-$  (*i.e.*, the value of  $x$ ). Propose a structure for this species.
- (2) Iodine is the most electropositive halogen and can form interhalogen species where I is the central atom. Propose structures and give the point groups for the following interhalogen species:  $ICl_2^-$ ,  $IF_4^-$ , and  $IF_6^-$ .

### **References**

General references on iodometry:

1. A.I. Vogel, Vogel's Textbook of Quantitative Inorganic Analysis, New York : Wiley, 1987
2. D.C. Harris, Quantitative Chemical Analysis, New York: W.H. Freeman, 1987

Some references on polyiodides:

3. C.A.L. Filgueiras, *et al. Acta Cryst.* **2001**, E57, p. o338.
4. R.E. Buckles, *et al. J. Am. Chem. Soc.* **1952**, 74, p. 4379.