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.

Year Level:	2nd year introductory inorganic
Student time required:	two 3-hour lab periods
Instructor time required:	~3 hours??
Technician notes?	Available upon request
Study question solutions?	Available upon request
Contact:	Craig MacKinnon (craig.mackinnon@lakeheadu.ca)

Lakehead
UNIVERSITY

Chemistry 2351: Inorganic Chemistry I
Laboratory Manual

Instructor: C. D. MacKinnon
Department of Chemistry
Faculty of Science and Environmental Studies

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,

$$I^- + 2\ I_2 \rightleftarrows I_5^-$$

$$I^- + 3\ I_2 \rightleftarrows I_7^-$$

$$2\ I_3^- + I_2 \rightleftarrows I_8^{2-}$$

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_4I_x

PREPARE ONE OF THE FOLLOWING

Version #1 Dissolve 2.5 g of I_2 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_4I and stir until dissolved. As the NMe_4I 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_4I. Stir and keep the solution hot (not boiling) until all the NMe_4I 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!):

$$I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^-$$

Because the colour fades gradually, a starch indicator is added which gives a bright blue colour when complexed with I_2. This is also titrated to a colourless endpoint, but the difference in colour is more dramatic. Finally, additional I^- is added to the solution to enhance solubility by the equilibrium

$$I_2 + I^- \rightleftarrows I_3^-$$

Preparation and Standardisation of sodium thiosulfate solution

Dissolve 5.0 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g of Na_2CO_3 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_3 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,

$$IO_3^- + I^- + H^+ \rightarrow I_3^- + H_2O$$

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.