

Polyiodides: Synthesis and Analysis of Me_4NI_3 and Me_4NI_5

(Adapted from: Andrew W.G. Platt in *Inorganic Experiments*, J. Derek Woollins, Editor; 2nd ed., Wiley, 2003.)

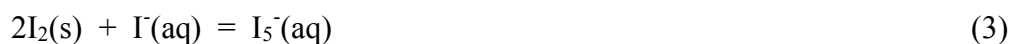
Polyhalide anions are classic examples of species that exceed the octet rule of Lewis Dot structures. Polyhalide ions can be considered as being derived from a simple ionic halide and one or more molecular halogens. By far the most important polyhalide ion is the triiodide ion, I_3^- . The formation of I_3^- is responsible for the increase in solubility of iodine in water in the presence of iodide ions (eq 1).



The intense blue color observed in iodine redox titrations is due to a complex formed between starch and the triiodide ion. Although I_2 forms the I_3^- ion in solution with any source of I^- , stable solid complexes can only be isolated in the presence of large cations. One of the reasons for this is that the lattice energies of solids which have a large anion (*i.e.* the polyhalide) and a small cation such as Na^+ or K^+ tend to be low compared with those of NaI or KI . Thus, attempted crystallization of NaI_3 from solutions of iodine and sodium iodide tends to lead to isolation of either very unstable salts, which decompose at room temperature with the release of iodine (eq 2), or of sodium iodide and iodine.



If greater amounts of iodine are used the pentaiodide ion, I_5^- is formed (eq 3). Again, a large cation is needed to isolate stable solids.



In this experiment, you will prepare two polyiodides using the tetramethyl ammonium ion, $(\text{CH}_3)_4\text{N}^+$, as the large cation. With this large cation, salts of both I_3^- and I_5^- can be isolated.

Experimental

a) Tetramethylammonium Triiodide

Finely powder 1 g of tetramethylammonium iodide and place in a beaker with 25 cm³ of ethanol. Add 1.3 g of iodine. Heat the mixture on a hot plate until all of the tetramethylammonium iodide has dissolved. Remove the mixture from the hot plate and allow it to slowly cool to room temperature, and then cool in ice. Isolate the resulting solid by vacuum filtration, wash with a little diethyl ether, and dry in air. Record the mass of the product and calculate the percentage yield.

b) Analysis

One of the accepted ways for chemists to prove that they have made the compounds they claim is by obtaining satisfactory elemental analyses. This usually means determining the percentage by weight of one or more of the elements present in the compound. In the case of the compound you have synthesized, iodine is the easiest element to determine.

Weigh **accurately** about 0.2 g of the product into a flask and add about 20 cm³ of ethanol. Stir the contents of the flask and add 50 cm³ of a 0.05 M silver nitrate solution in 10 cm³ portions. After the addition, the mixture consists of a fine yellow precipitate of silver iodide which must be coagulated before filtration. This is accomplished by heating the mixture on the hot plate until all the precipitate has settled and the supernatant is clear. Filter the silver iodide into a dry pre-weighed sintered glass crucible, ensuring that all the precipitate is collected. Make a note of the number etched onto the glass as identification. *Do not stick labels or write on the crucibles.* Wash the precipitate with a little water followed by a little ethanol and dry to constant weight.

From the weight of the dry silver iodide obtained, calculate the weight of iodine present (hence that amount of iodine in the original weight of compound) and calculate the percentage of iodine in your sample of Me₄NI₃. Compare your value with the theoretical percentage and comment on the result.

a) Tetramethylammonium Pentaiodide

Using a similar procedure to that above but with the appropriate amount of iodine, prepare and analyze a sample of tetramethylammonium pentaiodide.

Alternatively, half the class can prepare tetramethylammonium pentaiodide and the other half tetramethylammonium triiodide.

Questions

1. What are the shapes of the NMe₄⁺, I₃⁻ and I₅⁻ ions? The hybridization of the atoms?
2. What would be the products of the thermal decomposition of KICl₂ and KBrICl?
Explain your answer. (See page 92 in the class textbook.)