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DIDACTIC

Properties of antimony triiodide photodecomposition and Lewis acidity

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Abstract Antimony triiodide is a versatile compound that is not studied in detail in the current Inorganic Chemistry literature at the undergraduate level. In this work we propose a simple microscale synthesis describing two other interesting properties which are not reported in the common chemical literature: photo-oxidation and acid–base reaction in non-aqueous media. The experiment can be successfully and safely achieved in a two-hour lab class at the sophomore level.

PALABRAS CLAVE
Triioduro de antimonio;
Síntesis en microescala;
Fotooxidación;
Ácidos y bases de Lewis

Propiedades del triioduro de antimonio fotodescomposición y acidez de Lewis

Resumen El triioduro de antimonio es un compuesto versátil que no se describe detalladamente en la bibliografía de Química inorgánica que se emplea habitualmente en las carreras de grado. En este trabajo proponemos su síntesis en microescala y describimos 2 propiedades interesantes que no se reportan en la bibliografía química más accesible: la fotooxidación y su reactividad ácido-base en solventes no acuosos. La experiencia puede realizarse de manera exitosa y segura en una clase de laboratorio de 2 h en un curso básico de Química inorgánica.

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Introduction

Antimony trihalides are interesting compounds used as flame retardant for plastics (Kirk & Othmer, 1992). Antimony triidodide is also related to SbXI (X: O, S or Se); this compound as well as SbXBr exhibits important ferroelectricity, pyroelectricity, photoconduction and dielectric polarization properties (Kirk & Othmer, 1992; Mady, Eid, & Soliman, 1987). In the last years, many new physical and chemical properties of SbI_3 have been reported (Bharathi Mohan, Anu Philip, & Sunandana, 2008; Kepinska, Nowak, Duka, Kotyczka-Morańska, & Szperlich, 2011; Kepinska et al., 2014; Nobrega, Espínola, Fonseca, Arakaki, & de Oliveira, 2007; Pereira dos Santos, Fonseca, Espínola, de Oliveira, & Arakaki, 2005), including its application as dopant in thermoelectric materials (Chung et al., 2000). However, SbI_3 is rarely mentioned in modern inorganic chemistry textbooks; on the other hand, the only physical or chemical properties of SbI_3 which are frequently reported in reference or ''classic'' inorganic chemistry literature are: crystal color (yellow or red depending on temperature), tendency to sublimate (above 100 °C), pyramidal molecular structure, physical and chemical (by complex formation) solubility as well as melting (168 °C) and boiling points (420 °C) (Remy, 1956; Wells, 1962).

The preparation of SbI_3 is described in an interesting book on chemical curiosities (Roesky & Mockel, 1996). On the other hand, many years ago we report the acid–base properties of SbI_3 (Guerrero & Fasoli, 1987) and noticed about its photo-oxidation as an inconvenience for the UV/VIS spectrometrical analysis of Sb(III) in presence of iodide and Rhodamine B (Guerrero & Fasoli, 1988).

We propose here a simple microscale synthesis of SbI_3 with ca. ideal yield describing two other interesting properties which are not reported in the common chemical literature: photo-decomposition (Mellor, 1947) and acid–base reaction in non-aqueous media.

The experiment can be successfully and safely achieved in a two-hour lab class at the sophomore level.

Experimental

Microscale synthesis of antimony triiodide. Preparation of a stable dilute solution

Place 100 mg (0.8 mmol) of antimony powder into a 25 mL round-bottom flask. Wrap the flask with aluminum foil to prevent the action of light. Dissolve 10 mg (0.4 mmol) of iodine in 15 mL of dry toluene (use anhydrous Na_2SO_4). Add the iodine solution to the flask containing the antimony. Attach a reflux condenser and heat to boil. Keep boiling until the color of the refluxing solution is amber (violet tinge of I_2 should not be observed). Filter through a fritted glass funnel to remove the excess of antimony, and collect the solution into a 25-mL Erlenmeyer flask (wrapped with aluminum foil). Beautiful crystals of antimony triiodide are formed cooling down the solution to room temperature. Filtrate to separate the crystals of antimony triiodide (a Hirsch funnel is recommended); then, the saturated solution should be diluted by adding 15 mL of fresh toluene. Keep the yellow solution protected from the action of light.

From the weights of the initial and the unreacted antimony calculate the weight of metal that reacted with the initial iodine; the empirical formula of the compound is easy to calculate from this data.

Photodecomposition of antimony triiodide

Prepare three clean and dry 5-mL test tubes (use aluminum foil as before). Place 3 mL of antimony triiodide dilute solution in each tube and seal the tubes by mean of PVC cooking foil (or any plastic wrap). Proceed as follows:

Tube #1: Make a small hole in the plastic foil and eliminate the aluminum foil. Leave the test tube exposed to daylight in presence of air (same but fastest results can be obtained by bubbling oxygen or air into the solution).
Tube #2: Leave the solution in the tube exposed to daylight but not to air (nitrogen can be bubbled for best results).
Tube # 3: Make a small hole in the plastic foil but the tube is maintained in darkness, while the air enters.

After a few minutes, turbidity appears in tube #1 at the time that a violet tinge is easily perceived (iodine can be detected by shaking the toluene solution with a water-based starch dispersion). Tubes 2 and 3 show no changes for a long time (actually, protected antimony triiodide solutions are stable indefinitely). The light induced reaction can be written in a simplified way as (Mellor, 1947):

$$SbI_3 + h\nu \rightarrow SbIO + I_2$$

Note: Same results are obtained if the saturated solution is prepared from the filtered off crystals of antimony triiodide. However, the crystals dissolve very slowly and tend to form a colloidal dispersion.

Solvent effect on photodecomposition

Place 0.5 mL of the stock dilute solution of SbI_3 in two small test tubes. Add 4.5 mL of toluene to one of the tubes, and 4.5 mL of dry carbon tetrachloride to the other one. Expose both test tubes to sunlight. Decomposition in toluene solution is clearly observable after a few minutes; on the other hand, decomposition takes about half an hour to be observable in carbon tetrachloride solution.

Acid–base properties of SbI_3 in toluene solution

Add 2 or 3 drops of colorless toluene solution of Rhodamine B to 1 mL of diluted SbI_3 toluene solution. A purple color appears due to reaction of acid SbI_3 with the basic form of the dye. A few drops of ethylamine in toluene restore the system to the original situation (colorless). The indicator solution is prepared by extraction of 5 mL of 10^{-3} M aqueous solution of Rhodamine B with 5 mL of fresh toluene (Remy, 1956). The acid–base reaction can be written as:

$$SbI_3 + R^o = [SbI_3{\cdot}R]^{+-}$$

where R^o and R^{+-} accounts for the colorless and purple form of Rhodamine B.

Discussion

A close to 1:3 antimony (Sb) to iodine (I) ratio is obtained with normal skills.

The photodecomposition of antimony triiodide constitutes an interesting example of oxidation by O_2 catalyzed by light; there are no other simple experiment involving oxygen in a photo-induced reaction.

Although to the best of our knowledge there are no references about the mechanism of this reaction, it can be inferred that singlet-O_2 ($^1\Delta_g$) could be involved: according to recent papers, electron-donor solvents stabilized the singlet excited form of molecular oxygen (Abdel-Shafi & Wilkinson, 2000; Darmanyan, Lee, & Jenks, 1999).

On the other hand, SbI_3 provides an easy-to-perform experiment of Lewis acid–base reaction in organic solvent: group 15 trihalides are well-known electron acceptors by utilizing the available *d* orbitals (Sethy & Raghavan, 1998); Rhodamine B acts as an acid–base indicator of the neutralization between SbI_3 (Lewis acid, A) and amines (Lewis base, B) with formation of an acid–base adduct (A–B):

$$A + B \rightarrow A\text{–}B$$

However, it must be remembered that antimony (III) compounds can also act as poor soft Lewis bases (Shriver, Atkins, & Langford, 1996).

Conclusions

In a two-hour session interesting experiments involving inorganic synthesis, photochemical oxidation and acid–base properties in non-aqueous solvents can be easily performed. In brief, synthesis and properties of antimony triiodide constitute an excellent experimental basis for a course of Inorganic Chemistry at the sophomore level.

Conflict of interest

The authors declare no conflict of interest.

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