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Improved Synthesis of Perxenates. Preparation of XeO_3 and Na_4XeO_6

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Sodium perxenate, first identified by Appelman and Malm, is one of the most stable xenon compounds known.[1] The compound is made by the disproportionation of XeO_3 in a strongly basic solution of NaOH.[2] However, the preparation requires the synthesis of XeO_3 in solution. Previous methods involved careful hydrolysis of XeF_6 and subsequent removal of HF in a time-consuming process.[3] Nevertheless the danger of forming some dry XeO_3 within the apparatus is always present. Our synthesis involves the preparation of XeO_3 via reaction of XeF_6 with $HOPOF_2$. In the same system, the XeO_3 is immediately quenched with a solution of NaOH. Formation of perxenate is achieved by letting the solution stand for 1–2 weeks at ambient temperature. This preparation of Na_4XeO_6 as well as the apparatus are described herein.

Experimental Section

General Data. Volatile materials were handled in a 304 ss vacuum system. Connection to the system were by means of compression fittings employing Teflon ferrules. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Temperatures were measured with a digital-indicating iron–constantan thermocouple. Amounts of materials were determined by PVT measurements or direct weighing. All traps for purification and transfer of XeF_6 were made of Kel-F tubing passivated with 1 atm of F_2 before exposure to XeF_6. [*Caution! Anyone contemplating the handling of XeF_6 and XeO_3 should be thoroughly informed of the hazards involved* (*see ref 3c*).]

Reagents. Xenon was 99.95+% pure from Cryogenic Rare Gas Laboratories and was used as is. Technical grade fluorine, from Air Products, Inc., was purified through an NaF scrubber before use. Difluorophosphoric acid was purchased from Ozark Mahoning, Inc., and was purified before use by the literature method.[4] The acid was stored for delivery in a 10-mL Pyrex graduated cylinder with a Teflon-glass valve and a 10/30 $\overline{\mathsf{T}}$ joint (Figure 1, A). Commercial sodium hydroxide was used as received. Xenon hexafluoride was prepared by an alternate method. Xenon (3.2 mmol) and fluorine (50.0 mmol) were condensed into a 6-mL Monel autoclave (AWP 11 000 psi) at −195 °C. After being warmed to 22 °C, a tube furnace was used to heat the mixture at 260 °C for 72 h. The reactor was then allowed to cool to 22 °C. It was then connected to the vacuum system through two successive Kel-F U-traps, a T-connection, and a Kel-F storage tube. Excess fluorine was removed at −195 °C, and pure XeF_6 was collected in the traps as the reactor warmed from −195 to 22 °C under dynamic vacuum. After all the XeF_6 was pumped from the reactor, it was transferred to the storage tube. The XeF_6 was kept under $N_2(g)$ at −195 °C to prevent inward leakage during storage. A Raman spectrum of the XeF_6 did not detect the presence of XeF_4. While small amounts of XeF_4 were undoubtedly present, the XeF_6 was suitable for reaction with $HOPOF_2$.

Preparation of XeO_3/Na_4XeO_6. For the synthesis of XeO_3, the apparatus is illustrated in Figure 1. An inverted 50-mL flask (C) was joined by a 3/8-in. Swagelok union (D) to the main reactor (B). A port in the top of the inverted flask (E) allowed NaOH solution to be introduced immediately before use. Via a Kel-F T-connection (F), XeF_6 was delivered from its storage tube (G). A readily accessible Kel-F U-trap (H) was fitted in a way to replace the XeF_6 storage tube.

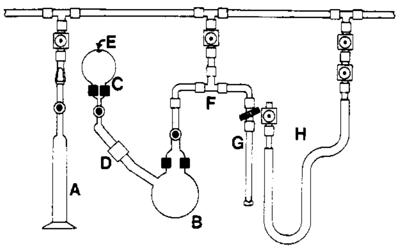

Figure 1. Apparatus for the synthesis of XeO_3/Na_4XeO_6.

In a typical preparation of XeO_3, the 150-mL bulb was evacuated and dried with a heat gun. A 3.39-mmol sample of XeF_6 was condensed in by vacuum transfer to form a ~3-cm diameter spot on the bottom of the vessel at −195 °C. After transfer, the system was closed to the vacuum line, and the storage tube was replaced with the U-trap. After reevacuation, the liquid-N_2 level was raised higher around the bulb and 20.0 mmol (1.2 mL) of $HOPOF_2$ was condensed in a ring above the XeF_6. At this time, the $HOPOF_2$ cylinder was removed to minimize the damage from a possible detonation and the bulb allowed to warm directly to 22 °C. As the XeF_6 dissolved in the $HOPOF_2$, a yellow green solution was formed. Around 0 °C, vigorous bubbling began followed by a nearly instantaneous precipitation of white XeO_3 crystals. At this point, the U-trap was cooled to −195 °C and a 0 °C bath was placed around the bulb. Slowly, excess $HOPOF_2$, HF, and OPF_3 were pumped away until evolution of gas was barely evident. The bulb was isolated once more, and the 0 °C bath was carefully replaced by one of liquid N_2. Then ~40 mL of 4 M NaOH at 0 °C was funneled into the inverted bulb, and the stopcock was opened slowly to minimize thermal shock as the solution flowed onto the XeO_3. Upon warming to 22 °C, the solution turned yellow, indicative of alkaline XeO_3 solutions.[5] The solution was allowed to stand for 2 weeks, during which the solution decolorized and crystals of Na_4XeO_6 were formed. After being cooled and filtered, the solution (when acidified) was oxidizing toward KI. The white solid was washed with cold H_2O and then dried in a vacuum dessicator over P_4O_{10} for 12 h at 22 °C. The yield was 0.523 g.

Results and Discussion

With use of an excess of $HOPOF_2$, the reaction of XeF_6 with the acid is controlled and the byproducts are easily removed by pumping at 0 °C. The presence of small amounts of $HOPOF_2$ in the XeO_3 apparently lessens the probability of detonation, corresponding to similar results observed previously with H_2SO_4.[7] No explosions have been encountered in at least 20 preparations by this method.

The purity of XeO_3 prepared in this way is quite high. The oxidizing equivalents determined on several samples were always very nearly 6.0 as expected. Similarly, the expected weight changes ($XeF_6 \rightarrow XeO_3$) were very close to, but somewhat greater than, the calculated values.

The reaction of XeO_3 with NaOH(aq) can be conviently and safely carried out according to the procedure given in the Experimental Section. The isolated perxenate corresponds to a yield of 64% based on the following stoichiometry:

$$4XeF_6 \xrightarrow{HOPOF_2} 4XeO_3 \xrightarrow{NaOH} 3Na_4XeO_6 + Xe$$

Previous yields of perxenate by hydrolysis of XeF_6 with 2 M NaOH gave a maximum yield of 54% when carried out on a somewhat larger scale.[8]

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The purity of the perxenate was very high when the hydrolysis was carried out with pure NaOH in a closed system and the product dried under vacuum at 22 °C. A typical iodimetric analysis indicated a purity of 99.0% with the assumption of anhydrous Na_4XeO_6. Since samples dried under vacuum will contain some water, the actual purity may be somewhat greater than 99.0% and is very near 100% if one assumes 0.6 waters of hydration. The latter is believed to be the degree of hydration for Na_4XeO_6 dried under vacuum at 22 °C.[3c] Both the yields and purity of Na_4XeO_6 were lower if less pure NaOH was used for hydrolysis, if the solution was not adequately protected from the atmosphere, or if the perxenate was dried at elevated temperatures.

In conclusion, the reaction of XeF_6 with $HOPOF_2$ presents a more safe and convenient method for synthesis of small amounts of XeO_3.[9] In turn, excellent yields of sodium perxenate are possible with minimal handling of the trioxide.

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Registry No. XeO_3, 13776-58-4; Na_4XeO_6, 13721-44-3; XeF_6, 13693-09-9; $HOPOF_2$, 13779-41-4.

[9] The scale described here is only 3 mmol. However, the same procedure has been successfully carried out on both larger (6–7 mmol) and smaller (1 mmol) scales.

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Heteroatomic Polyanions of Post Transition Elements. Synthesis and Structure of a Salt Containing the Diarsenichexaselenate(2–) Anion, $As_2Se_6^{2-}$

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Ternary systems of the type A^I–B^V–X^{VI}, where A^I represents an alkali metal, B^V = As, Sb, or Bi, and X^{VI} = S, Se, or Te, have been extensively studied and their physicochemical properties described by Lazarev et al.[1] In these phases, as well as in the mercury compounds $Hg_2P_2S_7$,[2] $Hg_2P_2S_6$, or $Hg_2P_2Se_6$,[3] there is no evidence for isolated heteroatomic polyanions of the electronegative elements; however, the anion $As_4S_6^{2-}$ was isolated by action of piperidine on a solution of As_4S_4 in $MeNH(CH_2)_2OH$[4] and its structure described by Porter.[5] In fact, such anions generally can exist only in compounds with relatively large and nonpolarizing cations. Recently, a general route to stabilize homopolyatomic anions of post transition elements from their alloys with alkali metals was found by Corbett and co-workers[6] in using the bicyclic 2,2,2-crypt[7] to complex the alkali cation and to prevent the electron transfer back from the anion to the cation in the solid state. This procedure has now allowed the isolation and characterization of the stable homopolyatomic anions such as Sn_9^{4-},[8,9] Pb_5^{2-} and Sn_5^{2-},[10] Sb_7^{3-},[11] Te_3^{2-},[12] Ge_9^{4-} and Ge_9^{2-},[13] Bi_4^{2-},[14] and As_{11}^{3-}.[15] More recently, the heteroatomic polyanion $Tl_2Te_2^{2-}$ was so synthesized and its structure described by Burns and Corbett.[16]

The purpose of our work was to isolate large heteroatomic polyanions from Na–As–Se ternary alloys, and the procedure described above still seemed to us the easiest and most appropriate way.

Experimental Section

Synthesis. Arsenic, selenium, the 2,2,2-crypt ligand, and sodium were obtained from Merck Laboratories. Although selenium and crypt were used without further purification, arsenic was purified through sublimation and sodium through several fractional crystallizations. Ethylenediamine (en) was first dried with CaH_2 and then distilled onto and stored over molecular sieve and again distilled from there for utilization.

An alloy of composition $NaAs_2Se_3$ was prepared in two steps: As_4Se_4 was first prepared by allowing arsenic and selenium to react in stoichiometric proportion in an evacuated Vycor ampule at 550 °C and then annealed for 1 day at 225 °C. Then, As_4Se_4, Se, and Na in the above composition were allowed to react at 700 °C in a tantalum tube previously weld-sealed in argon atmosphere and in turn enclosed in an evacuated Vycor jacket; after 2 days, the reactor was allowed to cool slowly to room temperature in the hope of obtaining single crystals, but the resulting black product crystallizes poorly, leaving a dark brown smear when ground to a very fine powder in the mortar. The product dissolved easily in ethylenediamine, particularly when crypt was added, giving a dark brown solution which, within 1 day, turned orange while a large amount of amorphous and green material deposited on the bottom of the Pyrex reactor. The solution was left to stand for at least 2 weeks and then evaporated very slowly, leaving a few parallelepipedic and, in larger quantity, needle-shaped, orange crystals. Preliminary oscillation and Weissenberg photographs showed that the parallelepipedic crystals possessed triclinic symmetry, while the others were demonstrated to be hexagonal; in this case, the rapidly falling intensities of diffraction spots when $(\sin\theta)/\lambda$ was greater than 0.30 seemed characteristic of highly disordered systems such as found in plastic crystals. Only the triclinic form was investigated. The crystals were selected under argon atmosphere with use of a microscope and wedged in Lindemann glass capillaries. A truncated block-shaped crystal of dimensions 0.23 × 0.30 × 0.30 mm which gave the best diffraction spots was mounted on a Nonius CAD4 automated diffractometer.

Since the compound was obtained in small yield, the arsenic and selenium ratio was verified by microanalysis[17] of a few single crystals. Anal. Calcd for $(2,2,2\text{-crypt-}Na^+)_2As_2Se_6^{2-}$: As, 10.53; Se, 33.30. Found: As, 8.87; Se, 28.46.

Data Collection and Reduction. Integrated diffraction intensities were collected at ambient temperature (25 °C). The profile analysis of a few low-angle reflections indicated that an ω–$^5/_3\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula $Sr = A + B \tan\theta$, where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to the $K\alpha_1$ and $K\alpha_2$ splitting; A and B were chosen as 1.2 and

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