I, $I^N = 14.49$ for pyridine). The core β terms were estimated by an empirical equation of the type $\beta_{xy} = A \exp[(B(Z^x{}_{eff} - Z^y{}_{eff})^2 - c)R_{xy}]$, where A, B, and C are empirical parameters and R_{xy} is the bond length.

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Preparation and Properties of Monocesium Xenate ($CsHXeO_4$)

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Abstract: Crystalline monocesium xenate has been prepared by the reaction of xenon trioxide with aqueous cesium hydroxide in the presence of fluoride ion. Good yields of cesium xenate are obtained from solutions which are approximately 0.1 M in xenon trioxide, 0.1 M in fluoride ion, and 2.5 M in cesium hydroxide. Cesium xenate, which has an apparent formula weight of 334, is stable in air and is considerably more stable than xenon trioxide. The existence of monocesium xenate has been confirmed by the determination of the oxidation equivalent by the "hi-lo" titration method, X-ray powder diffraction patterns, and infrared spectroscopy.

In a recent publication Spittler and Jaselskis[2] describe preparative methods for monosodium xenate and other alkali xenates by the reaction of equivalent amounts of alkali hydroxides and xenon trioxide followed by lyophilization of the mixtures. However, this method of preparation is not suitable for large-scale production. Thus further attempts to prepare alkali xenate salts from aqueous hydroxide solutions have been carried out.

Experimental Section

Chemicals and Apparatus. Xenon trioxide solutions were made by hydrolysis of xenon hexafluoride.[3] Xenon hexafluoride was made on heating xenon and fluorine for 16 hr at 300° with a total pressure of 40 atm, and a xenon-to-fluorine ratio of 1:20 in accord with Weinstock's equilibrium constants.[4] The reactants were heated in a welded container of Monel 400 fitted with an Autoclave Engineers 30 VM 6071 valve. Excess fluorine was removed from the container at Dry Ice temperature and after warming to room temperature the product was purified by distillation into a U-shaped Monel weighing can fitted with two Hoke A 431 valves, the can being cooled with Dry Ice.

To prevent a violent reaction when the xenon hexafluoride was hydrolyzed the reaction was carried out over a period of about 6 hr by sweeping the contents of the can through Kel-F tubing into water in a stream of nitrogen. To minimize possible metallic contamination the Hoke valve was removed from the exit of the can and the tubing connected directly to the can. The water was contained in a Teflon bottle in which the solution was afterwards stored. A bubbler had been constructed at the end of the Kel-F tubing by closing heated plastic into fine copper wires which were then removed with nitric acid. Quantitative character of the hydrolysis was shown by lack of a test for oxidizing power (starch iodide paper) in the nitrogen leaving the Teflon bottle.

The cesium and rubidium hydroxide solutions were prepared from the 99.9% purity hydroxide pellets supplied by K & K Laboratories. The insoluble residues in the 5 M cesium and rubidium hydroxide solutions were separated by centrifugation and the clear supernatant liquid used for the preparation of the crystalline cesium xenate.

Infrared spectra of the resulting precipitate were run in a silver chloride matrix using Perkin-Elmer 21, KBr Infracord, and Perkin-Elmer 521 recording spectrophotometers. The X-ray powder diffraction patterns were obtained on a Norelco instrument using a 114-mm camera and the copper Kα line with a nickel filter.

Preparation of Crystalline Monocesium Xenate. The monocesium xenate was prepared by mixing 1.0 ml of 0.25 M xenon trioxide hydrolysate with approximately 1.5 ml of 5.0 M cesium hydroxide. After mixing the solution was placed in a refrigerator and kept for about 6 hr. The supernatant liquid was decanted and the white crystals were washed with several portions of ice-cold water. Similar attempts to prepare rubidium xenate yielded a mixed salt of xenon (VI) and xenon (VIII).

The amounts of xenon(VI) and xenon(VIII) in the crystalline compound were determined by the "hi-lo" titration method as described by Appelman and Malm.[3] Cesium was determined gravimetrically as cesium perchlorate after the decomposition of the xenate with aqueous methanol solution. A test for fluoride ion was made, after the decomposition of xenate with aqueous methanol, using the zirconium–alizarin complex.

In addition, gases evolved by the cesium xenate on heating and on decomposition in concentrated sulfuric acid were analyzed in a time-of-flight mass spectrometer. On heating, carbon dioxide, water, and larger quantities of oxygen and xenon were observed. The same gases were observed from the sulfuric acid decomposition and in addition a small amount of HF was produced which could be detected after removal of xenon and oxygen and fractionation of the HF from a much larger quantity of carbon dioxide. The cesium xenate does not incorporate fluoride in any significantly stoichiometric amount even though the presence of fluoride ion in the xenic acid solution is essential for its formation.

No xenon compounds were observed in the gases in either case.

Results

Infrared Data. The infrared spectrum of monocesium xenate in silver chloride matrix shows, besides very weak bands at 3120 and 1430 cm^{-1}, two sets of four bands at 783, 740, 721, and 699 cm^{-1} and a 451,

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(1) On leave from Detroit University, Detroit, Mich.

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386, 347, and 316 cm^{-1}. The 783- and 438-cm^{-1} bands have shoulders at 775 and 438 cm^{-1}.

X-Ray Powder Diffraction. The X-ray diffraction patterns of crystalline monocesium xenate have been contrasted with cesium periodate and cesium carbonate, likely impurities in crystalline cesium xenate. The principal *d* spacings are different from sodium and potassium perxenates. The principal *d* spacings in angstrom units for the crystalline cesium xenate are: 4.03 (s), 3.66 (s), 3.40 (m), 3.33 (w), 3.05 (s), 2.56 (w), 2.30 (m), 2.27 (w), and 1.97 (s), where s denotes strong, m medium, and w weak relative intensities of the lines.

Stability and Properties. Crystalline monocesium xenate can be stored in dry air without decomposition. The crystalline monocesium xenate shows instability to mechanical shock, grinding, and thermal shock. On slow heating, it goes through a small endothermic transition at 115° and a strong exothermic transition at 151°. At 151° the white crystals change color to deep yellow (likely cesium superoxide).

Cesium xenate is sparingly soluble in ice-cold water. It is insoluble in anhydrous alcohol, chloroform, and carbon tetrachloride. It reacts vigorously with moist methanol.

Formula Determination. Several determinations by the "hi-lo" method on various preparations yield average oxidation equivalents of 55.78 and 56.00 for hi and lo titrations, respectively. The determination of cesium as the perchlorate salt yields an average formula weight of 333 ± 3. This value compares well with the apparent formula weight of 336 ± 5 obtained by the use of the oxidation equivalents. The calculated molecular weight for monocesium xenate, $CsHXeO_4$, is 329.2.

A small amount of impurities such as cesium perxenate, cesium carbonate, and water are always present. These amount to less than 1% and vary from one preparation to another. No appreciable amount of fluoride was observed using the zirconium–alizarin complex and mass spectrograph. In our worst preparation the maximum contamination by fluoride did not exceed 1% as calculated on the basis of cesium fluoride. Mass spectrographic observations confirmed the presence of CO_2 and, on heating, liberation of small amounts of water.

Discussion

The crystalline monocesium xenate is more stable than the lyophilized powder and shows somewhat different characteristics. In the infrared spectra the two sets of four strong sharp absorption bands at 783, 741, 721, and 699 cm^{-1} and at 451, 386, 347, and 316 cm^{-1} are characteristic of the crystalline cesium xenate; the lyophilized compound shows a strong band at 790 cm^{-1}, broad medium band at 499 cm^{-1}, and a strong band at approximately 360 cm^{-1}. The crystalline compound has two very weak bands at 3120 and 1430 cm^{-1}, while in the lyophilized powder these bands are stronger and are shifted to 3500 and 1600 cm^{-1}, suggesting a higher hydration than in the crystalline salt. All the available analytical data support the apparent empirical formula of $CsHXeO_4$ which corresponds to a molecular weight of 329.2. Since the calculated apparent formula weights from the cesium and the "hi-lo" titration data are 333 and 336, respectively, the difference probably can be attributed to the impurities which include a small amount of water, carbonate, and cesium fluoride. The structure of the crystalline cesium xenate does not seem readily accessible from a simple comparison of the infrared and X-ray diffraction patterns of the crystalline compound to those of analogous cesium periodates and tellurates.

The role of fluoride in the formation of monocesium xenate is not understood; seemingly it prevents to some extent the formation of perxenate, since in the absence of the fluoride, ion xenon trioxide and cesium hydroxide form a mixed perxenate–xenate salt.

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