by including bending strain due to deviations from their equilibrium values of the five other bond angles in each methyl and each methylene group, but the results are not much different. If γ and δ are the deviations of the CCH and HCH angles, respectively, from their equilibrium values at the methylene carbon in *trans-n*-butane, then the total bending strain in each methylene group is $(k_\alpha\alpha^2 + 4k_\gamma\gamma^2 + k_\delta\delta^2)/2$. For small angles $\gamma = C\alpha$ and $\delta = D\alpha$, where $C = -k_\delta/(4k_\delta + k_\gamma)$ and $D = -k_\gamma/(4k_\delta + k_\gamma)$. Thus the bending strain is $k_\alpha'\alpha^2/2$, where $k_\alpha' = k_\alpha + 4k_\gamma C^2 + k_\delta D^2$. Taking k_γ and k_δ as 6.84×10^{-12} and 5.31×10^{-12} erg radian^{-2}, respectively,[32] leads to $k_\alpha' = 12.13 \times 10^{-12}$ erg radian^{-2}. An analogous treatment of bending at a methyl carbon leads to an effective force constant k_β' of 7.67×10^{-12} erg radian^{-2}. With these higher effective bending force constants the results of energy minimization become $\theta_1 = 0.038$, $\theta_2 = 0.116$, $\alpha = 0.016$, and $\beta = 0.014$ radian, $r = 2.32$ A, and E(total) = 0.77 kcal mole^{-1}. For the locked configuration the results are $\alpha = 0.027$ radian, $\beta = 0.024$ radian, $r = 2.19$ A, and E(total) = 1.07 kcal mole^{-1}.

The Preparation and Properties of the Yellow Potassium Salt Containing Xenon in Oxidation States VI and VIII

T. M. Spittler[1] and Bruno Jaselskis

Contribution from the Department of Chemistry, Loyola University, Chicago, Illinois. *Received February 3, 1966*

Abstract: The yellow salt of the potassium-containing xenon in mixed oxidation states VI and VIII is prepared by mixing equal volumes of approximately 0.2 *M* xenon trioxide with 5.0 *M* potassium hydroxide and subjecting the solution to ozonolysis for 20 min. The resulting yellow salt corresponds to an apparent formula $K_4XeO_6 \cdot 2XeO_3$ (mol wt 742). This salt is explosive and very sensitive to a mechanical shock. However, it is thermally stable up to 201°. Above this temperature it is converted to a white anhydrous potassium perxenate salt.

Appelman and Malm[2a] have reported the formation of a yellow salt which they obtained by mixing concentrated potassium hydroxide with xenon trioxide. This salt has neither the properties of potassium perxenate nor the properties of alkali xenates as reported by Zalkin, *et al.*,[2b] and Spittler and Jaselskis,[3] respectively. Koch and Williamson[4] conclude from analysis of the potassium hydroxide–xenon trioxide system that the ratio of Xe(VI)/Xe(VIII) can vary between 4 and 0.1 when compared by algebraic difference to the total amount of xenon remaining in solution. However, we observe that the composition of the yellow salt is slightly affected by the precipitation conditions. A closer investigation of the yellow potassium salt has been undertaken and is reported in a later section.

Experimental Section

Chemicals and Apparatus. Solutions of xenon trioxide were obtained from the Argonne National Laboratory. Approximately 0.25 *M* xenon trioxide solutions were employed for the preparation of potassium yellow salt. Reagent grade potassium hydroxide was used to prepare the 5.0 *M* hydroxide solution.

The infrared spectra were obtained of the yellow salt in a silver chloride pellet by the use of Perkin-Elmer 21, Perkin-Elmer 521, and KBr Infracord recording spectrophotometers. The X-ray powder diffraction patterns were obtained using a Norelco X-ray diffraction unit equipped with a 114-mm camera and Ni filter. The thermal stability was determined by use of differential thermal analysis apparatus. The collected gases, as a result of heating the yellow salt, were measured by the use of conventional vacuum-line techniques.

Preparation of the Yellow Salt and Analysis. In a typical preparation 1 ml. of 0.25 *M* xenon trioxide was mixed with 1 ml of 5.0 *M* potassium hydroxide. Ozone was bubbled through the solution for 20 min. The supernatant liquid was separated from the precipitate by decantation, and ozone again was bubbled through the solution until no further yellow precipitate resulted. The yellow salt was washed several times with water and dried gradually, bringing the temperature to 140°. The supernatant liquid was concentrated to about one-fourth of its original volume. On concentration a copious white potassium perxenate precipitate formed.

The yellow salt also can be prepared from ozone-free solutions by letting the solution stand for 12 to 24 hr. However, the oxygen-to-xenon ratio in the resulting salt is somewhat lower than in the ozonized product.

The ratio of oxygen to xenon as a result of heating the yellow potassium salt was obtained using the vacuum-line technique. A freshly precipitated sample of the yellow potassium salt was dried at 140° in all Pyrex system and pumped to 1×10^{-3} mm. The sample chamber was slowly heated by means of a sand bath, and the pressure which remained between 10^{-5} and 10^{-4} mm up to 200° was monitored with a Miller gauge. At about 210° the pressure rose to 3 mm. The xenon gas was condensed and the oxygen transferred into a measuring volume by passage through a small U-tube trap held at nitrogen-slush temperature (−210°). After about 30 min of slow gas evolution and collection, the system pressure dropped to 1×10^{-5} mm. The evolved oxygen was measured and discarded. The nitrogen-slush bath was removed from the trap and the evolved xenon was measured in the predetermined volume.

The amounts of xenon(VI) and xenon(VIII) in the yellow potassium salt were determined by the "hi-lo" titration as described by Appelman and Malm.[2a] Potassium was determined gravimetrically as potassium perchlorate after the decomposition of the yellow salt with aqueous methanol.

Results

Stability and Properties. The yellow potassium salt once dried maintains constant weight and shows no tendency to absorb moisture, even at relatively high

---

[1] On leave of absence from the Department of Chemistry, University of Detroit, Detroit, Mich.

[2] (a) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964); (b) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *ibid.*, **86**, 3569 (1964).

[3] T. M. Spittler and B. Jaselskis, *ibid.*, **87**, 3357 (1965).

[4] C. W. Koch and S. M. Williamson, *ibid.*, **86**, 5439 (1964).

humidity. Even though the samples are stable on gradual heating up to 201°, they decompose violently upon mechanical shock, and thus they should be handled with care. The yellow salt is stable for weeks whether left in contact with the mother liquor or allowed to stand in distilled water. The conversion of the yellow salt to perxenate under our preparative conditions is very slow. The yellow salt, whether precipitated by slow reaction or rapidly in the presence of ozone, yields identical X-ray diffraction powder patterns and infrared spectra. However, the yellow salt precipitated by slow reaction yields lower O_2-to-Xe ratio than for the precipitates prepared by ozonolysis. The yellow salt when heated slowly and carefully to 201° yields xenon and oxygen and a white anhydrous potassium perxenate. The yellow salt in cold acid solution oxidizes manganese(II) to permanganate instantaneously.

Infrared Data. The infrared spectrum of the yellow potassium salt in silver chloride matrix has some similarity with xenon trioxide and perxenate as shown in Figure 1. The yellow potassium salt has no bands in the region 5000–1250 cm^{-1} which are found in all perxenates; however, it has strong bands at 788 (sometimes with a sharp shoulder at 795 cm^{-1}), 700, and 612 cm^{-1} and at 405, 373, 346, and 327 cm^{-1}, whereas xenon trioxide has sharp bands at 346 and 333 cm^{-1}. Potassium perxenate shows bands in the regions 5000–1250 (in part attributed to waters of hydration and hydroxyl groups), 750–650, and 500–450 cm^{-1}.

X-Ray Powder Diffraction. The X-ray powder diffraction patterns of the yellow salt prepared under a wide range of concentrations and precipitation conditions yield one unique pattern. The principal *d* spacings of these samples are listed: 9.84 (F), 5.03, 4.62 (B), 4.08 (C), 3.53 (E), 3.23, 3.12 (D), 3.00 (A), 2.73, 2.27, 2.16 (G), 2.02 (where the letters correspond to the relative intensities).

Formula Determination. The thermal decomposition of 6.38 mg of the yellow potassium salt at 205–215° in a vacuum line of a predetermined volume (4.99 cm^3) at 25° yields 9.32 cm^3 of oxygen and 6.31 cm^3 of xenon. This corresponds to the ratio of O_2/Xe of 1.48 while the theoretical value is 1.50. After converting the volumes of evolved xenon and oxygen gas to mass units, it was found that a total of 2.99 mg of gas were lost by the sample. The ratio of the weight of the residue to the weight of the gases lost is then 3.29/2.99 or 1.10. This compared favorably to the theoretical value of the ratio 1.07 for $K_4XeO_6/2XeO_3$, as expected for the reaction $2XeO_3 \cdot K_4XeO_6 \rightarrow K_4XeO_6 + 2Xe^0 + 3O_2$.

The "hi-lo" titrations of the yellow potassium salt (prepared by the ozonolysis procedure) yield the oxidation equivalents of 37.50 for high and 41.51 for low titrations. The calculated apparent formula weight corresponds to 750 and 747.2 calculated on the basis of a 20 electron- and 18 electron-transfer, respectively, for high and low titrations. The potassium analysis yields an equivalent weight of 186.68 or a formula weight of 746.7 calculated on the basis of four potassiums per molecule.

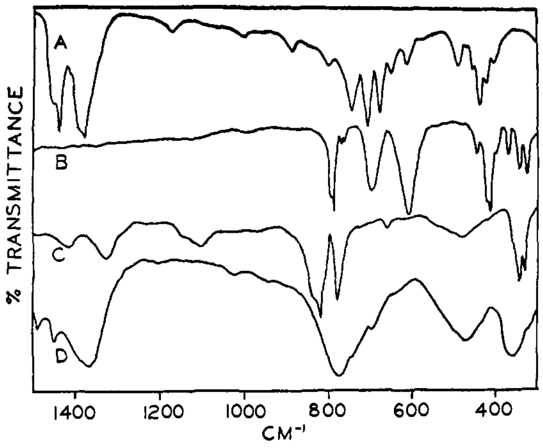

Figure 1. Infrared spectra of (A) white thermal decomposition product of the yellow salt, (B) yellow potassium salt containing xenon in oxidation states VI and VIII, (C) xenon trioxide, and (D) potassium xenate. All spectra were run in AgCl pellets.

Discussion

Appelman and Malm[2a] have suggested that the yellow potassium salt has an apparent formula of $K_4XeO_6 \cdot 2XeO_3$ (mol wt 742). This formula is supported by our analytical data for the precipitates which have been obtained by a rapid ozonolysis method. On the other hand, the stoichiometry for the precipitates which have been prepared by slow precipitation varies as reported by Koch and Williamson.[4] In addition, our infrared, thermal stability, and X-ray powder diffraction studies suggest that the xenon trioxide in the yellow potassium salt is likely coordinated to the central perxenate moiety through an oxo bridge to yield a salt, $K_4Xe_3O_{12}$. Typical xenon trioxide bands at 780 and 820 cm^{-1} and 346 and 333 cm^{-1} are shifted in the yellow potassium salt (see Figure 1). The bands in the region 600–705 cm^{-1} are somewhat shifted from those of potassium perxenates. The presence of the bands in the region 650–700 cm^{-1} in the perxenate compounds has been suggested in a review by Hyman[5] to be characteristic of the octahedral configuration of perxenates. The yellow potassium salt is thermally stable (on slow heating) up to 201°; at this temperature it loses oxygen and xenon equivalent to 2 moles of xenon trioxide per mole of the yellow potassium salt, and it is converted to anhydrous potassium perxenate, while xenon trioxide decomposes at approximately 110°. Furthermore, the spacings of the yellow potassium salt are different from those of xenon trioxide and potassium perxenate; this excludes the possibility of a mixture of xenon trioxide and perxenate. All these observations suggest that the stability of the yellow potassium salt is primarily due to the stabilization of xenon trioxide by coordination with perxenate moiety, and that the probable structure contains a central octahedral perxenate unit coordinated through two oxo bridges with tetrahedral xenon trioxide.

Acknowledgment. The authors thank John Malm and E. H. Appelman of Argonne National Laboratory for supplying materials and valuable assistance in this study, and the analytical section of the International Minerals and Chemical Company, Skokie, for the use of their Perkin-Elmer 521 instrument. This work in part has been supported by the National Science Foundation Grant GP 5045.

---

(5) H. H. Hyman, *Science*, **145**, 773 (1964).