dication could be present in very low concentration.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-69-1635, and is considered to be part XVII of a series.

Henry J. Shine, Yuzuru Murata
Department of Chemistry, Texas Technological College
Lubbock, Texas 79409
Received January 24, 1969

Preparation and Properties of Alkali Fluoroxenates, $M_x(FXeO_3)_x$

Sir:

The preparation of $CsF \cdot XeO_3$ by atmospheric hydrolysis of $CsF \cdot XeOF_4$ and $CsXeF_7$ was reported by Selig.[1] A similar salt containing cesium fluoride and xenon trioxide was prepared by precipitation from aqueous solutions and was reported by us.[2] In contrast to the explosive nature of xenon trioxide, this salt appeared to be as stable toward shock and heat as the most stable of the perxenates. In fact, the alkali fluoroxenates are the most stable solid oxygenated compounds of xenon(VI) reported to date. In this note we report the preparation and properties of cesium, rubidium, and potassium fluoroxenates.

Alkali fluoroxenate salts were prepared from aqueous solutions by either of two methods. (1) Aqueous xenon trioxide, 0.5 *M*, containing HF from the hydrolysis of xenon hexafluoride, was neutralized with 2 *M* rubidium or cesium hydroxide to pH 4. This solution was allowed to evaporate slowly until a good yield of crystalline salt was formed. Crystals were filtered, washed with ice-cold water, and stored in a desiccator. (The presence of atmospheric moisture apparently had no effect on the stability of these salts.) This procedure was successfully used with the cesium and rubidium salts.[2] Potassium fluoroxenate was prepared by taking approximately equal volumes of 0.5 *M* aqueous xenon trioxide and 1 *M* potassium fluoride. This solution was acidified with a few drops of 1 *M* HF and was slowly evaporated until the precipitate formed. High-purity cesium, rubidium, and potassium fluoroxenates were prepared by this procedure. However, all attempted preparations of sodium fluoroxenate contained impurities of sodium fluoride or xenon trioxide depending on the procedure used. This difficulty in preparing pure sodium fluoroxenate can be attributed to the relative solubilities of alkali fluoroxenates and alkali fluorides in water. Solubility of alkali fluoroxenates decreases with increasing atomic weight of alkali, and that of alkali fluorides increases. The potassium fluoroxenate is approximately three times more soluble than rubidium fluoroxenate, which yields saturated solutions of 0.22 *M* at 20°.

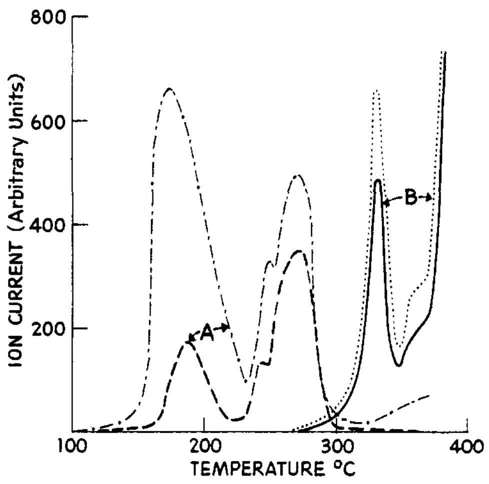


Figure 1. Thermal decomposition of Na_4XeO_6 (curve A) and $Rb_x(FXeO_3)_x$ (curve B): heating rates ~4°/min; mass spectrometer sensitivities for Xe and O_2 calibrated by decomposing $XeO_3 \rightarrow Xe + 1.5O_2$. (Evolution of O_2 is represented by dashed lighter lines and that of Xe by heavier lines.)

Formula weights were obtained from the oxidation equivalent and alkali and fluoride[3] analyses. Formula weights derived from these analyses for cesium, rubidium, and potassium fluoroxenates are 334 ± 3, 287 ± 3, and 236 ± 3, respectively. These values compare well with the calculated formula weights of $CsFXeO_3$ (283.8) and $KFXeO_3$ (237.4).

Infrared studies carried out in a silver chloride matrix showed four bands at 812 (s), 761 (m), 380 (w), and 333(w) cm^{-1}, the exact position of these bands depending on the alkali metal. No bands were observed in the usual Xe–F stretching region, 500–600 cm^{-1}.[4] Hydroxyl or water bands were completely absent.

Thermal stability of the alkali fluoroxenates was investigated by mass spectrometric, thermogravimetric, and differential thermal analysis methods. All showed that alkali fluoroxenates underwent no decomposition whatsoever up to 200°. Appreciable decomposition to oxygen and xenon began above 260° and became substantial around 300°. Some samples ultimately underwent explosive decomposition when heated above 300°, leaving alkali fluoride residues. Thermal decomposition characteristics of sodium perxenate and that of rubidium fluoroxenate are shown in Figure 1. Qualitative mass spectrometric examination of gases evolved during thermal decomposition of fluoroxenates confirmed the unhydrous nature of the compounds and showed only xenon and oxygen with a small amount of CO_2. We have shown that the fluoroxenates are thermally more stable than sodium perxenate, in the sense of being able to withstand higher temperatures without decomposition.

The high stability of fluoroxenates has allowed small samples to be ground and subjected to shock without explosion. Caution: in the presence of basic xenates or of xenon trioxide fluoroxenate samples so treated can explode. In addition, solid fluoroxenates do not react with normal alcohols, while basic xenate salts[5] or xenon trioxide react explosively. The unusual stability of alkali fluoroxenates may be due to the pseudo-octahedral coordination of the xenon atom in these compounds. A recent X-ray diffraction study of crystalline potassium

---

[1] H. Selig, *Inorg. Chem.*, **5**, 183 (1966).

[2] T. M. Spittler, B. Jaselskis, and J. L. Huston, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[3] M. S. Frant and J. W. Rosa, *Science*, **154**, 1533 (1966).

[4] H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, **49**, 255 (1968).

[5] B. Jaselskis, T. M. Spittler, and J. L. Huston, *J. Amer. Chem. Soc.*, **88**, 2149 (1966).

fluoroxenate, $K_x(FXeO_3)_x$, by Hodgson and Ibers[6] has definitely shown the presence of polymers held together by xenon–fluorine bridges, where the Xe–F distance is somewhat greater than in the simple xenon fluorides but less than the sum of the van der Waals radii of xenon and fluorine. We find that mass spectrometric examination of the gases evolved when fluoroxenates are decomposed in concentrated H_2SO_4 shows Xe, O_2, and HF but no xenon compounds, as would be expected from the absence of primary Xe–F bonds in the fluoroxenates.

The stability and ease of preparation of haloxenates increases with decreasing atomic weight of the halogen: $CsFXeO_3 > CsClXeO_3$[7] $> CsBrXeO_3$, the cesium bromoxenate being the most difficult to prepare and to handle. We prepared this unstable compound from saturated cesium bromide solutions, at pH 9 at 0°. The solutions are quite unstable and caution should be exercised when preparing this compound.

Acknowledgments. The authors wish to thank the National Science Foundation (Contract GP 5045) for partial support of this project.

(6) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 326 (1969).

(7) B. Jaselskis, T. M. Spittler, and J. L. Huston, *J. Amer. Chem. Soc.*, **89**, 2770 (1967).

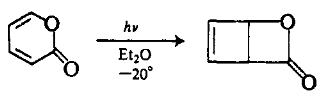
Bruno Jaselskis, John L. Huston
Department of Chemistry, Loyola University of Chicago
Chicago, Illinois 60626
T. M. Spittler, S.J.
Department of Chemistry, University of Detroit
Detroit, Michigan

Received December 12, 1968

Flash Vacuum Pyrolysis. V. Cyclobutadiene[1]

Sir:

The chemistry of cyclobutadiene[2] and the corresponding theoretical calculations[3] of its properties have been of intense interest.[4] Here we report the results of some of our experiments on the characterization of cyclobutadiene by flash vacuum pyrolysis (FVP)[1] of photo-α-pyrone (**1**).[5]



2 **1**

1 was pyrolyzed at low pressures ($\sim$0.1 μ) and short contact times ($\sim$1 msec) in a quartz oven which was coupled directly into the ionization chamber of a mass spectrometer.[6] We found that (Figure 1) at temperatures up to 400° isomerization to α-pyrone occurred as shown by the increase of the parent mass (*m/e* 96) with increasing temperature and the decrease of the *m/e* 52 fragment, which is the base peak from **1** and a minor electronic fragment from α-pyrone.[7] Above 400°, the intensity of the *m/e* 52 fragment sharply increased and maximized at about 800°. Correspondingly, a less abundant signal due to a C_8H_8 (*m/e* 104) increased and maximized at about 800°. Thermal products having *m/e* 44, 78, 26, and 68 were also observed, but are not shown. These correspond to carbon dioxide, benzene, acetylene, and furan, respectively.

The appearance potential for *m/e* 52 (AP(52)) with the oven at 800° was at least 1.6 eV lower than AP(52) obtained at 20° (10.2 eV). The magnitude of the decrease in AP(52) with increasing temperature rules out vinylacetylene (IP 9.9 eV) and butatriene[8] (IP 9.4 eV)

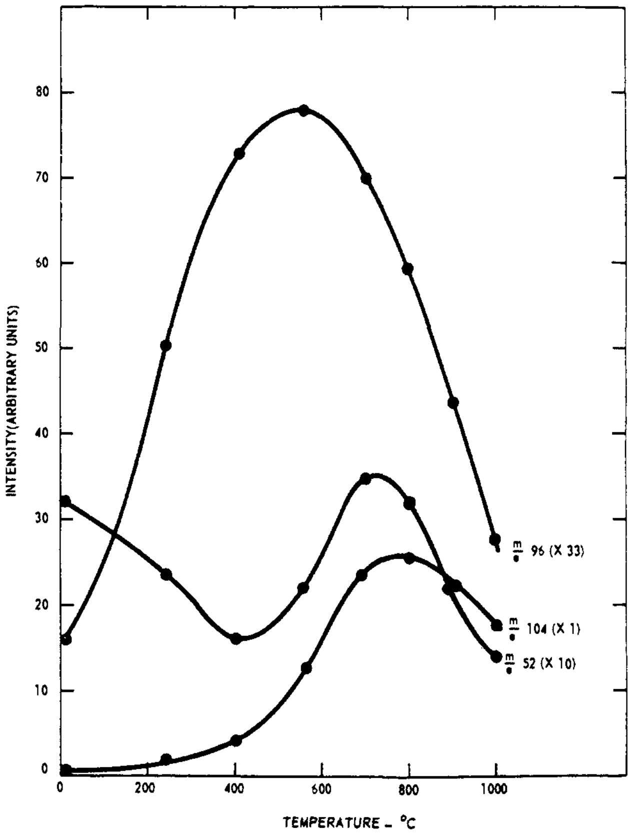


Figure 1. Photo α-pyrone (**1**) pyrolysis: intensity attenuations are indicated in parentheses. Electron bombardment spectrum obtained using 10.5 eV electrons.

---

(1) Part IV: E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(2) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); (b) M. A. Avram, I. G. Dinulescu, E. Marica, G. Matescu, E. Diam, and C. D. Nenitzescu, *Ber.*, **97**, 382 (1964), and references cited therein.

(3) (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); (b) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965); (c) J. R. Hoyland, D. A. Berta, D. G. Brannon, W. B. Glenn, P. J. Green, and R. B. Simmons, *Proc. West Va. Acad. Sci.*, **37**, 238 (1965); (d) N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, **24**, 2401 (1968); (e) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(4) For review articles see: (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967; (b) R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **1**, 519 (1962); (c) G. Subrahonanyam, *J. Sci. Ind. Res.* (India), **26**, 158 (1967); (d) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 43.

(5) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964). These authors discussed the use of **1** and analogous structures as potential cyclobutadiene sources.

(6) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 5061 (1968).

(7) The partial mass spectrum for **1** at 20° using 50-eV electrons, *m/e* (relative intensity): 96 (0.9), 95 (3.3), 68 (31.4), 52 (100), 39 (90); for **2**: 96 (44.2), 95 (8.5), 68 (84.0), 52 (0.4), 39 (100). The mass spectral intensities reported for **1** in ref 5 are considerably different.