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OF XENON TROXIDE

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CRYSTAL AND MOLECULAR STRUCTURE OF XENON TROXIDE[1]

(1) This work was done in part under the auspices of the U. S. Atomic Energy Commission.

Sir:

Hydrolysis of xenon tetrafluoride yields a solution from which colorless crystals can be obtained by evaporation. By determination of the crystal structure and by chemical analysis we have identified this substance as xenon trioxide. The molecule XeO_3 is in the shape of a trigonal pyramid with dimensions similar to those of the isoelectronic iodate ion.

The crystals are stable for days in dry air, but readily absorb water from humid air to form a concentrated solution. The vapor pressure at room temperature is too low to permit distillation to be observed under high vacuum. Dry crystals react explosively with cellulose.

Violent detonation upon heating makes chemical analysis by the direct measurement of the oxygen and xenon difficult. By other experiments, the chemical formula of XeO_3 has been confirmed. Iodine and xenon were liberated when solid potassium iodide was added to an acidified aqueous solution of the xenon compound. The oxidation state of the xenon was determined by means of the iodine to xenon ratio. Also by means of this reaction, 5.12 mg. of the dry crystals yielded 28.75 micromoles of xenon gas. Anal. Calcd. for XeO_3: I/Xe, 6.00; Xe, 73.23. Found: I/Xe, 6.06; Xe, 73.73.

Crystals were transferred in air to thin-walled glass capillary tubes, where they were held to the walls by whatever solution was on their surfaces. Preliminary crystal data were obtained from oscillation and Weissenberg x-ray diffraction photographs. The structure reported here is based on angles and intensities measured with a goniostat and scintillation counter with Mo Kα radiation, $\lambda(K\alpha_1) = 0.70926$ Å. Ten crystals, in the form of rods elongated in the direction of the b axis, were examined. Because of decomposition, each crystal survived only a few hours of exposure to x-rays. Frequent adjustment of alignment was necessary.

Combination of measurements from three crystals gave intensities for the 482 independent reflections permitted by the space group with θ less than 30°, of which 16 were recorded as zero. Because the diffracting power dropped with time, it was necessary to make frequent adjustments of scale by comparison with measurements of the (200) reflection. In the subsequent refinement, it was found that the agreement was improved by adjustment of scale factors for 15 portions of the data, grouped according to the sequence of measurement.

The orthorhombic unit cell has dimensions $a = 6.163 \pm 0.008$, $b = 8.115 \pm 0.010$, $c = 5.234 \pm 0.008$ Å. With 4 molecules per unit cell the density is 4.55 g./ml. Systematic absence of odd orders of h00, 0k0, and 00ℓ correspond to space group $P2_12_12_1$. Atoms are in the general sets 4(a): x, y, z; $\frac{1}{2} - x, -y, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, -z$; $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

These crystal data resemble those of iodic acid,[2-4] for which

(2) M. T. Rogers and L. Helmholz, J. Am. Chem. Soc., 63, 278 (1941).

(3) B. S. Garrett, Structure Reports, 18, 393 (1954).

(4) H. E. Swanson, N. T. Gilfrich and G. M. Ugrinic, Nat. Bur. Standards Circular 539, 5, 28 (1955).

a = 5.89, b = 7.73, c = 5.54 Å (axes permuted) and which has the same space group. The atomic arrangement is very similar in the two crystals, a fact which was helpful but not essential in the determination of the structure.

Simple calculations yielded approximate coordinates for Xe, which tends to dominate the structure factors. A projection down the c axis revealed the three oxygen atoms near the positions found in HIO_3. Least-squares refinement (starting with the z coordinates reported for HIO_3) yielded the final structure. With adjustment of 12 coordinates, 4 isotropic temperature factors, and 15 scale factors, the conventional $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0.098 with the parameters

	x	y	z	B, Å.^{2}
Xe	0.9438	0.1496	0.2192	1.3
O(1)	0.537	0.267	0.066	2.3
O(2)	0.171	0.096	0.406	2.2
O(3)	0.142	0.454	0.389	1.8

Standard deviations of coordinates correspond to 0.002 Å for xenon and 0.03 Å for oxygen. The Xe-O bond distances are 1.74, 1.76, and 1.77 Å, each ± 0.03 Å. Bond angles O-Xe-O are 108°, 100°, and

101°, each ± 2°. We estimate that thermal motion affects the bond distance less than 0.01 Å. The deviations from three-fold symmetry are of doubtful significance. The average bond distance, corrected for thermal motion, and the average bond angle are 1.76 Å and 103°, respectively. In iodate ion[5] the angle is 97°, and the bond distance,

(5) J. A. Ibers, Acta Cryst., 9, 225 (1956).

1.82 Å, is slightly longer as expected.

The shortest O-O distance between molecules is 2.91 Å. As discussed by Wells,[6] the corresponding contact in HIO_3 is unsuitable

(6) A. F. Wells, Acta Cryst., 2, 128 (1949).

for hydrogen bonding. All other intermolecular O-O contacts in XeO_3 exceed 3.02 Å. The absence of hydrogen bonding makes the formulation $HXeO_3$ implausible in spite of the similarity of the structure to that of HIO_3. Another aspect of this lack of bonding is that the unit cell volume is greater in XeO_3 than in HIO_3 although the molecular dimensions are smaller.

Each xenon atom has oxygen neighbors at 2.80, 2.89, and 2.90 Å in three adjacent molecules.

Crystals of xenon trioxide were first prepared at Berkeley by Mr. K. A. Maxwell. We thank Prof. R. E. Connick for bringing them

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