

43_{F-F} . The resonance integral β_{F-F} between two F atoms separated by 2.82 Å. was estimated (using Ballhausen's recipe¹) as 0.7 e.v. The 1850 Å. ($h\nu = 6.8$ e.v.) and the 1325 Å. ($h\nu = 9.4$ e.v.) bands are assigned to the allowed x, y polarized $b_{1g} \rightarrow e_u^+$ ($h\nu$ (estimated) = 7.0 e.v.) and $a_{1g} \rightarrow e_u^+$ ($h\nu$ (estimated) = 9.8 e.v.) transitions, respectively. The agreement between theory and experiment is gratifying and provides strong support for the bonding scheme prepared for these compounds.

The symmetry allowed $\pi \rightarrow \sigma$ type transitions $b_{2g} \rightarrow e_u^+$, $e_g \rightarrow e_u^+$ and $a_{2g} \rightarrow e_u^+$ should be located between the two strong $\sigma \rightarrow \sigma$ type transitions. These transitions may be hidden in the asymmetric onset of the $a_{1g} \rightarrow e_u^+$ absorption band.

Another potentially interesting feature of the absorption spectrum of XeF_4 should be noted. Since the excited M.O. is doubly degenerate (e_u type) a Jahn-Teller configurational distortion in the excited state is expected. This may lead to absorption bands exhibiting a doublet peak. The shape of the $a_{1g} \rightarrow e_u^+$ band may perhaps be caused by such an effect. However, further experimental and theoretical study is required to establish this point.

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XENON TRIOXIDE

Sir:

The slow hydrolysis of XeF_6 ¹ has been found to result in a white, transparent, non-volatile crystalline compound that has been identified as XeO_3 . This compound is so very explosive that preparations have been limited in amounts to less than 50 mg. An explosion involving 3 mg. has broken glassware, while an amount less than one milligram has fractured a KBr window. An intentional explosion involving 7.2 mg., in a 25 cc. evacuated infrared cell, seriously deformed and nearly ruptured a 2 mm. thick silver chloride window. Explosions have been produced by rubbing, pressing, or even gentle heating, and have been encountered when manipulating the powder, especially near aqueous solutions. There is some indication that XeO_3 is more unstable when the relative humidity exceeds 20% than in a drier atmosphere.

XeO_3 was first prepared when XeF_6 was inadvertently condensed in the short length of 6-mm. nickel tubing which served as a lead to a sample container. The day after the sample container had been closed and uncoupled from the sample transfer system, the reaction product was noted in the cone and throat of the female coupling of the 6 mm. nickel lead. Similar equipment was then used for subsequent preparations. The hydrolysis proceeds slowly as the XeF_6 , with a room temperature vapor pressure close to 20 mm., diffuses through the air toward the open end of the coupling, while atmospheric H_2O diffuses slowly through the air into the coupling. Crystals form on the wall of the coupling. Observations with a microscope indicated the presence of bubbles resembling soap bubbles, but

(1) J. G. Malm, I. Sheft and C. L. Chernick, *J. Am. Chem. Soc.*, **85**, 110 (1963), and E. E. Weaver, B. Weinstock and C. P. Knop, *ibid.*, **85**, 111 (1963).

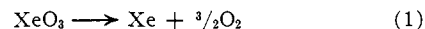
less than 30 μ in diameter, floating in the air near the throat of the coupling.

Most of the preparations have been carried out at a low uncontrolled humidity, but a few have been carried out in a chamber maintained at constant temperature and humidity. Needle-like crystals tend to form at the lower humidities, while at higher relative humidities, in the 20% range, dendritic forms predominate. The product at still higher humidities is a more characterless crystalline mass. The needle crystals are prisms, biaxially positive with $2v = 5$ to 10° . The index of refraction has been measured as $\alpha = 1.79$, while γ is much greater than 1.80.

Neutron activation analysis of this material indicates that it contains a substantial amount of xenon, but a negligible amount of fluorine. The infrared spectrum of the solid at wave lengths shorter than 25 μ indicates absorption only in the region 850-700 cm^{-1} where such ions as IO_3^- and BrO_3^- absorb. There is no appreciable absorption in the region where compounds containing Xe-F bonds have their strong stretching vibration bands: 557 cm^{-1} for XeF_2 , 585 cm^{-1} for XeF_4 and 612 cm^{-1} for XeF_6 .

In order to analyze this material, some of the product was placed in a Monel infrared gas cell with silver chloride windows. The cell was evacuated and pumped at least one hour, but sometimes overnight, without apparent loss of material. The cell was isolated and heated gently until the product exploded with a brilliant blue flash. There were no detectable infrared absorption bands of the decomposition product.

The number of moles of gaseous decomposition products can be computed from the weight of the material exploded using the equation



The number of moles of gaseous decomposition products can also be determined by PVT measurements. These are compared in columns 1 and 2 of Table I. Mass spectrometer scans of the decomposition product showed that while most of this material is Xe and O_2 , there are small and variable amounts of CO_2 . The presence of CO_2 can be interpreted as resulting from the reaction of oxygen from the XeO_3 with carbon-containing material in the cell. The lowest concentration, 2 mole per cent, occurred when the thin Teflon gaskets were omitted in cell assembly. If the XeO_3 reacts to form some CO_2 in addition to O_2 , this does not change the number of moles of gaseous reaction product. The mass spectrometer has been used to measure the Xe, O_2 , and CO_2 concentrations. In Table I, column 3, twice the ratio of the O_2 molar concentration to the Xe molar concentration is listed. This is the atom ratio O:Xe without correction for the occurrence of CO_2 . Column 5 gives this O:Xe ratio corrected for the CO_2 concentration which is in turn given in column 4. These results are the evidence for the identification of this compound as XeO_3 .

TABLE I

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Millimoles of gas calcd. from wt. XeO_3	Millimoles of gas meas. by PVT	$\frac{2(O_2)}{Xe}$ mole ratio	CO_2 mole fraction	$\frac{O}{Xe} = \frac{2(O_2) + 2(CO_2)}{(Xe)}$ atom ratio
Not weighed	...	2.76	0.068	3.04
0.100	0.100	2.83	.045	3.01
.118	.125	2.88	.050	3.08
.154	.146	2.93	.020	3.01

Only a few observations of the chemical behavior have been made to date. At humidities greater than about 25%, XeO_3 begins to deliquesce. Bubbles form

in the liquid produced, and the XeO_3 decomposes. When the deliquescent XeO_3 is in contact with copper, the liquid acquires a pink color, and on drying a small amount of dark residue remains. With nickel, a green residue is left. When XeO_3 was added to dilute NH_4OH a very little at a time, there was a reaction which resulted in a residue when the solution was dried. This residue was water soluble. The infrared spectrum of the residue showed that NH_4^+ was present, and in addition an ion absorbing at 790 cm^{-1} . This observation was repeated once, but usually the XeO_3 exploded when brought near the NH_4OH solution.

Thanks are due to J. C. Horton for the mass spectrometry, and to H. Insley, Oak Ridge National Laboratory, for the optical crystallographic examination and to J. F. Emery, also of ORNL, for the neutron activation analysis.

(2) This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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CRYSTAL AND MOLECULAR STRUCTURE OF XENON TRIOXIDE¹

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.^{1a} 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 $\text{Mo K}\alpha$ radiation, $\lambda(\text{K}\alpha_1) = 0.70926\text{ \AA}$. 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 $a = 6.163 \pm 0.008$, $b = 8.115 \pm 0.010$, $c = 5.234 \pm 0.008\text{ \AA}$. 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 $\text{P}2_12_12_1$. 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 $a = 5.89$, $b = 7.73$, $c = 5.54\text{ \AA}$. (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 $R = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}$ was reduced to 0.098 with the parameters

	x	y	z	$B, \text{\AA}^2$
Xe	0.9438	0.1496	0.2192	1.3
O(1)	.537	.267	.066	2.3
O(2)	.171	.096	.406	2.2
O(3)	.142	.454	.389	1.8

Standard deviations of coordinates correspond to 0.002 \AA . for xenon and 0.03 \AA . for oxygen. The Xe-O bond distances are 1.74, 1.76 and 1.77 \AA ., each $\pm 0.03\text{ \AA}$. Bond angles O-Xe-O are 108° , 100° and 101° , each $\pm 2^\circ$. We estimate that thermal motion affects the bond distance less than 0.01 \AA . The deviations from threefold symmetry are of doubtful significance. The average bond distance, corrected for thermal motion, and the average bond angle are 1.76 \AA . and 103° , respectively. In iodate ion⁵ the angle is 97° , and the bond distance, 1.82 \AA ., is slightly longer as expected.

The shortest O-O distance between molecules is 2.91 \AA . As discussed by Wells,⁶ the corresponding contact in HIO_3 is unsuitable for hydrogen bonding. All other intermolecular O-O contacts in XeO_3 exceed 3.02 \AA . 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 \AA . 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 to our attention and Dr. C. W. Koch for assistance in the chemical analysis.

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(1a) NOTE ADDED IN PROOF.—This substance should be handled with great caution. Samples have detonated when undisturbed at room temperature (cf. N. Bartlett and P. R. Rao, *Science*, **139** (1963); S. M. Williamson and C. W. Koch, *ibid.*, in press).

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(3) B. S. Garrett, *Structure Reports*, **18**, 393 (1954).
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(5) J. A. Ibers, *Acta Cryst.*, **9**, 225 (1956).
(6) A. F. Wells, *ibid.*, **2**, 128 (1949).