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Authors

Templeton, David H.

Zalkin, Allan

Forrester, J.D.

et al.

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University of California
Ernest O. Lawrence
Radiation Laboratory

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
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DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TRIOXIDE*

David H. Templeton, Allan Zalkin, J. D. Forrester
and Stanley M. Williamson

April 1963

Determination of the Crystal Structure of Xenon Trioxide*

David H. Templeton, Allan Zalkin, J. D. Forrester and Stanley M. Williamson

Department of Chemistry and Lawrence Radiation Laboratory

University of California, Berkeley, California

April, 1963

Xenon trioxide was characterized by determination of its crystal and molecular structure by x-ray diffraction by single crystals. Four molecules of XeO_3 occupy an orthorhombic cell in space group $P2_12_12_1$ with dimensions $a = 6.163 \pm 0.008 \text{ \AA}$, $b = 8.115 \pm 0.010 \text{ \AA}$, $c = 5.234 \pm 0.008 \text{ \AA}$. The crystal structure is closely related to that of the isoelectronic HIO_3 . The XeO_3 molecule has trigonal pyramidal shape with average Xe-O bond length 1.76 \AA (corrected for thermal motion) and average O-Xe-O bond angle 103° .

INTRODUCTION

This paper is a more detailed version of an earlier report¹ of the identification of XeO_3 by determination of its crystal and molecular structure. The preparation of this material by hydrolysis of XeF_4 and its chemical analysis have been described by Williamson and Koch.² It was independently prepared from XeF_6 and identified by Smith.³

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

(1) D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, J. Am. Chem. Soc. 85, 817 (1963).

(2) S. M. Williamson and C. W. Koch, Science 139, 1046 (1963).

(3) D. F. Smith, J. Am. Chem. Soc. 85, 816 (1963).

EXPERIMENTAL

The material used in this work resulted from the hydrolysis of XeF_4 , after which the solution was evaporated to dryness. A very small amount of the white powder was placed on a glass slide in air and was allowed to pick up water from the atmosphere until it completely dissolved. Crystals were then grown by focusing a microscope lamp on the saturated drops on the slide to provide gentle heating. With a microscope of about 40 power, crystals were observed to develop as very fine needles which grew in a few minutes to elongated rods. The b axis coincides with the long dimension of the crystal and is an extinction direction of light with crossed polarizers.

Crystals 0.1 to 0.5 mm in size were separated from the solution and stored on a glass slide (warm to the touch) in air, where they were stable for short periods. After a selection of crystals had been made, they were individually transferred into thin-walled capillaries of 0.5 mm diameter and stored with one end open in a desiccator charged with CaSO_4 (Drierite). When a crystal was needed for x-ray examination, a capillary was removed from the desiccator and the end sealed off. Each crystal stuck to the side of the capillary with its long direction, the b axis, parallel to the direction of the capillary.

Several crystals were required for the work because of decomposition during the irradiation. The first five or six crystals were used in learning how to handle the substance and to take Weissenberg patterns to establish the crystal symmetry. An additional four or five crystals were required to get accurate cell dimensions and to take intensity data. These measurements were made with a General Electric XRD-5 apparatus equipped with a goniostat and scintillation counter and with Mo K α

x-rays. The tube was operated at 40 Kv and from 1 to 20 ma, the milliamperage being boosted as the crystal decayed. The cell dimensions were measured with the resolved $K\alpha_1$ ($\lambda = 0.70926 \text{ \AA}$) x-ray using a take-off angle of 2° . The intensity data were obtained using 10 second counts with take-off angle of 4° . Ultimately 482 independent reflections were observed, 16 of which were below the detection limit and recorded as zero. The intensities were measured only for 2θ below 60° .

The crystals contained a film of moisture on their surfaces, probably acquired during their exposure to the room before sealing. During irradiation the crystal would decompose and the resulting gas would form bubbles in this film. Where the crystal contacted the capillary these bubbles caused the crystal to move out of alignment, necessitating frequent realignment of the crystal. The crystal could be observed to break up during the measurements. The decomposition rate decreased markedly when the irradiation was stopped; therefore to diminish this damage a beam stop was used which exposed the crystal to x-rays only during the actual 10 seconds of counting. Even with these precautions, a crystal would only last for about four to six hours of measurements.

The (200) reflection was used as the standard reflection with which to normalize all of the data. The data were taken in an order dictated primarily by the convenience of setting the angles on the goniostat. The actual order has been retained in reporting the observed and calculated values in Table 3. The intensities fell off with time principally because the fragments were rotated to each other and therefore not all in diffraction position, rather than because of destruction of the lattice. This rotation was not isotropic, and therefore the method of normalization is not correct. It was patched up by introduction of additional scaling factors as described below.

The Fourier and least-squares calculations were done on an IBM-7090 computer. We used a Fourier program of our own design and a least-squares program written by Gantzel, Sparks and Trueblood.⁴ The least-squares program minimizes the function $\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2$, and utilizes a full matrix. For lack of any better estimate, we used unity for all of the weighting factors, w. Lorentz-polarization corrections were applied to the data. Absorption corrections were not made. Atomic scattering factors for neutral xenon and oxygen were taken from Tables 3.3.1B and 3.3.1A in the International Tables.⁵ Anomalous dispersion corrections were omitted.

DETERMINATION OF THE STRUCTURE

A set of Weissenberg films was sufficient to determine a set of cell dimensions. A comparison of the a/b and c/b ratios with those in Crystal Data⁶ showed a resemblance to HIO_3 . A thorough check showed the extinctions to correspond to space group $P2_12_12_1$. As xenon is the principal diffractor in this crystal it was possible to estimate its location by an investigation of first the h00, 0k0 and 00l data, and then a set of h0l and hk0 data. This position had parameters that were less than 0.04 different from that found for I in HIO_3 .

An electron density projection using 55 non-zero hk0 terms with signs based on Xe only was calculated. The three largest peaks exclusive of the Xe peak were observed to occur at positions not far different from those of oxygen in HIO_3 . We estimated the third parameter of each from the iodic acid positions.

(4) P. Gantzel, R. Sparks, and K. Trueblood, private communication (1961).

(5) "International Tables for X-ray Crystallography", Vol. 3, Kynoch Press, Birmingham (1962).

(6) J. D. Donnay and W. Nowacki, "Crystal Data", Memoir 30, The Geological Society of America, New York (1954).

Least squares refinement proceeded as follows. Four cycles of least squares using 297 reflections and isotropic temperature factors resulted in $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.24$. More data were added to make a total of 386, and another 4 cycles reduced R to 0.19. With all 482 reflections and 6 more cycles R was 0.17. The data were corrected for obvious blunders by remeasurement of a few reflections that showed very bad agreement. The reflections were separated into 12 groups, and a scaling factor was determined for each from the sums of observed and calculated structure factors. Six cycles of refinement reduced R to 0.11.

A second rescaling was done and the number of scale factors increased to 15. The beginning and end of each group could be correlated with an event in the data taking, e. g., a new crystal was put on, the crystal was realigned, a fragment of the crystal dropped off, etc.

The final result after six more iterations, with $R = 0.098$, is shown in Table 1 with all of the pertinent crystal structure data. Attempts to refine the xenon atom with anisotropic temperature factors did not improve the agreement and furthermore is of doubtful validity considering the method of scaling. Any attempt at a thermal description other than isotropic is not warranted from these data. The standard deviations listed in Table 1 are those estimated by the method of least squares. The accuracy cannot be expected to be this good, at least for the thermal parameter of xenon.

The 15 scale factors that were applied to the intensities are shown in Table 2. Observed and calculated structure factors are listed in Table 3, in the order in which they were measured. A list of interatomic distances is given in Table 4.

STOICHIOMETRY OF XeO_3

Although the structures of HIO_3 and XeO_3 are closely related, there are significant differences that forced us to conclude that the structure we had just analyzed was xenon trioxide rather than "xenic acid". Iodic acid has one hydrogen bond as deduced by Wells⁷ from the x-ray structure determination by Rogers and Helmholtz.⁸ Garrett⁹ did a neutron diffraction study of HIO_3 and confirmed the basic structure as well as the location of the hydrogen bond as suggested by Wells.⁷ In iodic acid this hydrogen bond distance is 2.69 Å, and the corresponding distance in xenon trioxide is 3.19 Å, far too long to be considered as a hydrogen bond. This is consistent with the observation that though HIO_3 is a larger molecule than XeO_3 , its crystal volume is smaller due to the contraction by hydrogen bonding. Furthermore, we find no evidence of a hydrogen bond elsewhere in the structure. The structures of the two substances are otherwise so similar that we could not believe that the xenon compound would not make a hydrogen bond if it contained hydrogen. Structural data for XeO_3 and HIO_3 are compared in Table 5.

This formulation as XeO_3 was shortly after confirmed by chemical analysis.¹⁻³

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

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

(9) B. S. Garrett, Oak Ridge National Laboratory Report 1745, 97 (1954).

Abstracted in Structure Reports 18, 393 (1954).

DISCUSSION

The arrangement of molecules in the unit cell is shown in Fig. 1. The dimensions found for the molecule are shown in Fig. 2. No correction has been made for thermal motion. While we do not have an accurate description of this motion, we estimate that it affects bond distances by less than 0.01 Å.

Standard deviations of coordinates correspond to 0.002 Å for xenon and 0.03 Å for oxygen. Because of the unorthodox method of scaling, the true accuracy may not be this good. Thus we have no basis for claiming any significant deviation of the dimensions of the molecule from three-fold symmetry, and we report the average bond distance as 1.76 Å and the average bond angle as 103° . These dimensions may be compared with 1.82 Å and 97° reported for the isoelectronic iodate ion.¹⁰

Each xenon has three close oxygen neighbors from other molecules, at an average distance of 2.86 Å. The interaction of these atoms is analogous to the situation in HIO_3 , which has been discussed in terms of "weak secondary bonds".^{7,8} Whatever its nature, this interaction presumably is an important part of the explanation of the similarity of the two crystal structures.

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 preparation and analysis.

(10) J. A. Ibers, *Acta Cryst.* 2, 225 (1956).

Table 1: Crystal Structure Data for XeO₃ .

Cell data

Orthorhombic

Space Group P2₁2₁2₁ (D₂⁴)

a = 6.163 ± .008 Å

b = 8.115 ± .010 Å

c = 5.234 ± .008 Å

Z = 4

V = 261.8 Å³

Molecular weight = 179.30

X-ray density = 4.55 g/ml

Atomic parameters - all atoms in the general position

4a x,y,z; 1/2-x, \bar{y} , 1/2+z; 1/2+x, 1/2-y, \bar{z} ; \bar{x} , 1/2+y, 1/2-z .

	<u>x</u>	<u>y</u>	<u>z</u>	<u>B(Å⁻²)</u>
Xe	.9438 ± .0003	.1496 ± .0003	.2192 ± .0004	1.34 ± .04
O1	.537 ± .004	.267 ± .004	.066 ± .006	2.3 ± .5
O2	.171 ± .005	.096 ± .004	.406 ± .006	2.2 ± .5
O3	.142 ± .004	.454 ± .003	.142 ± .006	1.8 ± .4

Table 2: Scaling factors applied to the raw intensities. These correlate

to those referred to in Table 3.

No.	Scale Factor	No.	Scale Factor	No.	Scale Factor
1	0.62	6	1.12	11	0.71
2	0.49	7	1.72	12	0.47
3	1.17	8	0.60	13	1.00
4	1.95	9	0.85	14	0.85
5	1.41	10	1.41	15	0.97

Table 3: Observed and calculated structure factors for XeO₃. The order of the reflections is that of taking the data. The phase angle phi is given in terms of thousandths of a circle.

SCALE FACTOR 1						SCALE FACTOR 5						SCALE FACTOR 10						SCALE FACTOR 11						SCALE FACTOR 12						SCALE FACTOR 13						SCALE FACTOR 14																																																																																																																																																																																																																																																																													
H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI	H	K	L	FOB	FCA	PHI																																																																																																																																																																																																																																																																								
1	5	1	38	49	783	2	2	2	21	29	310	4	1	0	92	99	000	6	2	4	37	32	771	8	2	0	15	17	000	10	2	2	53	57	712	12	2	2	53	57	712	14	2	2	53	57	712	16	2	2	53	57	712	18	2	2	53	57	712	20	2	2	53	57	712	22	2	2	53	57	712	24	2	2	53	57	712	26	2	2	53	57	712	28	2	2	53	57	712	30	2	2	53	57	712	32	2	2	53	57	712	34	2	2	53	57	712	36	2	2	53	57	712	38	2	2	53	57	712	40	2	2	53	57	712	42	2	2	53	57	712	44	2	2	53	57	712	46	2	2	53	57	712	48	2	2	53	57	712	50	2	2	53	57	712	52	2	2	53	57	712	54	2	2	53	57	712	56	2	2	53	57	712	58	2	2	53	57	712	60	2	2	53	57	712	62	2	2	53	57	712	64	2	2	53	57	712	66	2	2	53	57	712	68	2	2	53	57	712	70	2	2	53	57	712	72	2	2	53	57	712	74	2	2	53	57	712	76	2	2	53	57	712	78	2	2	53	57	712	80	2	2	53	57	712	82	2	2	53	57	712	84	2	2	53	57	712	86	2	2	53	57	712	88	2	2	53	57	712	90	2	2	53	57	712	92	2	2	53	57	712	94	2	2	53	57	712	96	2	2	53	57	712	98	2	2	53	57	712	100	2	2	53	57	712

Table 4: List of distances less than 3.5 Å in XeO₃. Asterisked values are intramolecular distances.

Xe - O ₁	1.74 ± .03 Å *	O ₁ - Xe	1.74 ± .03 Å *
O ₂	1.76 ± .03 Å *	O ₃	2.68 ± .04 Å *
O ₃	1.77 ± .03 Å *	O ₂	2.84 ± .04 Å *
O ₁	2.80 ± .03 Å	Xe	2.80 ± .03 Å
O ₃	2.89 ± .03 Å	O ₃	3.05 ± .04 Å
O ₃	2.90 ± .03 Å	O ₂	3.09 ± .04 Å
O ₂	3.31 ± .03 Å	2O ₁	3.17 ± .02 Å
		O ₂	3.19 ± .04 Å
		O ₂	3.22 ± .04 Å
		O ₃	3.23 ± .04 Å
		O ₂	3.32 ± .04 Å
		O ₃	3.33 ± .04 Å
		O ₃	3.43 ± .04 Å
O ₂ - Xe	1.76 ± .03 Å *	O ₃ - Xe	1.77 ± .03 Å *
Xe	3.31 ± .03 Å	Xe	2.89 ± .03 Å
O ₃	2.73 ± .04 Å *	Xe	2.90 ± .03 Å
O ₁	2.84 ± .04 Å *	O ₁	2.68 ± .04 Å *
O ₃	2.91 ± .04 Å	O ₂	2.73 ± .04 Å *
O ₁	3.09 ± .04 Å	O ₂	2.91 ± .04 Å
O ₃	3.12 ± .04 Å	2O ₃	3.03 ± .03 Å
O ₁	3.19 ± .04 Å	O ₁	3.05 ± .04 Å
2O ₂	3.20 ± .04 Å	O ₂	3.12 ± .04 Å
O ₁	3.22 ± .04 Å	O ₁	3.23 ± .04 Å
O ₁	3.32 ± .04 Å	O ₁	3.33 ± .04 Å
O ₃	3.46 ± .04 Å	O ₁	3.43 ± .04 Å
		O ₂	3.46 ± .04 Å

Table 5: XeO₃ and HIO₃ crystal structure comparison. The cell dimensions for HIO₃ are those given by Swanson et al¹¹, and the HIO₃ structural data are those of the neutron diffraction work of Garrett⁹.

Cell Dimensions:	<u>a</u>	<u>b</u>	<u>c</u>	<u>V</u>	<u>a/b</u>	<u>c/b</u>	Mol. Wt.	X-ray density
XeO ₃	6.163 Å	8.115 Å	5.234 Å	261.8 Å ³	.759	.645	179.3	4.55 g/ml
HIO ₃	5.888 Å	7.733 Å	5.538 Å	252.2 Å ³	.761	.716	175.9	4.63 g/ml

Atomic Parameters:

Heavy atom:	x	y	z	O ₁ :	x	y	z
XeO ₃	.9438	.1496	.2192		.537	.267	.066
HIO ₃	.914	.158	.204		.523	.243	.071
O ₂ :	x	y	z	O ₃ :	x	y	z
XeO ₃	.171	.096	.406		.142	.454	.389
HIO ₃	.198	.086	.334		.157	.448	.404
H:	x	y	z				
HIO ₃	.322	.135	.234				

Intramolecular distances and angles:

Heavy atom	to O ₁	to O ₂	to O ₃	O ₁ -O ₂	O ₁ -O ₃	O ₂ -O ₃
XeO ₃	1.74 Å	1.76 Å	1.77 Å	2.84 Å	2.68 Å	2.73 Å
HIO ₃	1.82 Å	1.90 Å	1.78 Å	2.80 Å	2.77 Å	2.69 Å
Angles	O ₁ - ^{Xe} I-O ₂		O ₁ - ^{Xe} I-O ₃		O ₂ - ^{Xe} I-O ₃	
XeO ₃	108°		100°		101°	
HIO ₃	98°		100°		94°	

Selected intermolecular distances:

Distance that is hydrogen bond in HIO ₃	Heavy atom to O ₁ '	to O ₃ '	to O ₃ ''
XeO ₃ 3.19 Å O ₂O ₁ '	2.80 Å	2.90 Å	2.89 Å
HIO ₃ 2.69 Å O ₂ —H.....O ₁ '	2.50 Å	2.87 Å	2.77 Å

¹¹H. E. Swanson, N. T. Gilfrich, and G. M. Ugrinic, Standard X-ray Diffraction Patterns, National Bureau of Standards Circular 539, 5, 28 (1955).

Figure 1: Molecular packing in XeO₃





