The Observed Shortening of the Oxygen–Oxygen Bond in the Hydrogen Peroxide Molecule in Solids

By Berit F. Pedersen

Sentralinstitutt for Industriell Forskning, Blindern, Oslo 3, Norway

The observed, uncorrected oxygen–oxygen distance in hydrogen peroxide molecules in solids is generally observed to be shorter than the corresponding distance observed in organic peroxides and peroxo compounds. The presence of water molecules on hydrogen peroxide molecule sites has been detected in ammonium oxalate monoperhydrate. This substitutional disorder will lead to a decrease in the observed oxygen–oxygen distance in perhydrates. Correction for this effect in ammonium oxalate monoperhydrate reduces the shortening, but a difference of 0·020(3) Å still remains.

The accepted oxygen–oxygen single bond distance is 1·48 Å. Values close to this have been observed in several organic peroxides and peroxocompounds. In perhydrates on the other hand, the O–O distance seems to be systematically smaller as shown by the data in Table 1. The question arises whether this shortening of the oxygen–oxygen bond is significant or not.

Table 1. *Observed intramolecular oxygen–oxygen distances in solids* (Å)

Perhydrates	Peroxoacids	Organic peroxides	Peroxo compounds
1·453 (7)[a]	1·48 (2)[i]	1·45 (2)[l]	1·500 (15)[h]
1·481 (9)[b]	1·478 (7)[j]	1·48 (2)[m]	1·500 (15)[h]
1·460[c]	1·442 (12)[k]	1·460 (15)[n]	1·470 (15)[h]
1·439 (11)[d]		1·48 (1)[o]	1·500 (15)[h]
1·466 (9)[e]		1·478 (2)[p]	1·500 (15)[h]
1·441 (9)[f]		1·468 (3)[q]	1·470 (15)[h]
1·443 (12)[f]		1·470 (2)[r]	1·480 (15)[s]
1·452 (1)[g]			1·480 (15)[s]
1·450 (15)[h]			1·497 (8)[t]

Table 1 (cont.)

a	H_2O_2	Busing & Levy (1965)
b	$H_2O_2.2H_2O$	Olovsson & Templeton (1960)
c	$(NH_2)_2CO.H_2O_2$	Lu, Hughes & Giguère (1941)
d	$Li_2C_2O_4.H_2O_2$	Pedersen (1969c)
e	$Na_2C_2O_4.H_2O_2$	Pedersen & Pedersen (1964)
f	$K_2C_2O_4.H_2O_2$	Pedersen (1967)
f	$Rb_2C_2O_4.H_2O_2$	
g	$(NH_4)_2C_2O_4.H_2O_2$	Present paper
h	Potassium triperoxo-o-phenanthrolineniobate trihydrate and its H_2O_2 adduct	Mathern, Weiss & Rohmer (1970)
i	p-Nitroperoxybenzoic acid	Kim, Chu & Jeffrey (1970)
j	o-Nitroperoxybenzoic adid	Sax, Beurskens & Chu (1965)
k	Peroxypelargonic acid	Belitskus & Jeffrey (1965)
l	2,2-Dichlorodibenzoyl peroxide	Gougoutas & Clardy (1970)
m	4,4-Dichlorodibenzoyl peroxide	Caticha-Ellis & Abrahams (1968)
n	Dibenzoyl peroxide	Sax & McMullan (1967)
o	3,6-Diphenyl-1,2,4,5-tetraoxacyclohexane	Groth (1967)
p	Dimeric cyclohexanone peroxide	Groth (1967)
q	Dimeric cycloheptanone peroxide	Groth (1967)
r	Dimeric cyclooctanone peroxide	Groth (1967)
s	Ammonium diperoxodioxalatoniobate monohydrate	Mathern, Weiss & Rohmer (1969)
t	$(NH_4)_2S_2O_8$	Sivertsen & Sørum (1969)

Fig. 1. $(NH_4)_2C_2O_4.xH_2O_2.(1-x)H_2O$. The discrepancy factor R, and r(O–O) as functions of x(left). The isotropic temperature factor of the water molecule, BO_w, as a function of x(right). [Diagrams based on photographic film data (Pedersen, 1969b)].

We will in this note discuss two sources of systematic errors that will contribute to this effect. The perhydrates are unstable compounds, preventing in general the highly accurate determination of their structures. However, ammonium oxalate monoperhydrate seems to be an exception to the rule, and we have just completed a thorough refinement based on diffractometer measured intensities.

A preliminary investigation of this compound (Pedersen, 1969a) indicated r(O–O) to be less than 1·40 Å. However, we became aware of one possible explanation foɪ this apparent shortening (Pedersen,

1969b). The exchange of some of the H_2O_2 molecules with water molecules could account for the discrepancy as shown in Fig. 1. To pursue the reliability of this explanation a new set of intensity data was carefully collected on an automated four-circle diffractometer, and pertinent details of this analysis will be given here. The full account of the crystal structure will be published in a separate paper.

Two procedures were used in the last cycles of the full-matrix least-squares refinement. Firstly we included variable fractions of oxygen atoms from H_2O_2 and H_2O molecules, and secondly no water was included. The results are:

H_2O_2: 88·9 (7)%; H_2O: 6·4 (6)%; $R_w = 4·6$%, $R = 4·2$%; $r(O-O) = 1·452$ (1) Å. H_2O_2: 100%; H_2O: 0%; $R_w = 5·5$%; $R = 4·8$%; $r(O-O) = 1·434$ (1) Å.

Further experimental evidence for the presence of H_2O molecules is found in the difference Fourier map. We observe one peak of 0·50 (5) e.Å^{-3} on the twofold axis of the H_2O_2 molecule, at a distance of 0·25 Å from the midpoint of the O–O bond. This peak cannot solely be due to bonding electrons, which should be centred on the bond, but to some extra scattering matter which is believed to be water molecules. These water molecules fit into the lattice of the compound, making hydrogen bonds of 3·12 and 3·00 Å to appropriate acceptor molecules, and have tetrahedral coordination.

This substitutional disorder could be present in other perhydrates as well, but the quality of the diffraction data prohibits a detailed analysis being made. Both the potassium and the rubidium oxalate monoperhydrates have isostructural hydrates and the explanation for the remarkably short O–O bonds observed in these compounds (Pedersen, 1967) might be similar.

Introducing a fraction of H_2O molecules on H_2O_2 sites in $(NH_4)_2C_2O_4 . H_2O_2$ increases the O–O distance by 0·018 Å to 1·452 (1) Å. This value compares favourably with $r(O-O)$ determined for solid H_2O_2 from a neutron diffraction study, 1·453 (7) Å, but is still considerably and significantly shorter than $r(O-O)$ determined for organic peroxides, and also seems to be shorter than $r(O-O)$ in peroxocompounds.

However, one surce of systematic error likely to be more pronounced in perhydrates than in peroxides and peroxocompounds remains. The experimentally observed interatomic distances are always distances averaged in a specific way over the motions of the atoms in the solid. As shown by Cruickshank, (1956, 1961) and by Busing & Levy (1964) an observed interatomic distance in a diffraction study is *always smaller* than the true mean value. For rigid molecules it is possible to apply corrections to the observed bond lengths (Cruickshank, 1956, 1961; Schomaker & Trueblood, 1967). For the organic peroxides sited above, this correction is found to be about 0·004 Å.

A well founded correction for $r(O-O)$ in the H_2O_2 molecule cannot easily be computed as there are too few parameters available to allow a rigid body analysis. We can however, make an estimate of the magnitude of the correction from the thermal parameters derived for this oxygen atom.

The root-mean-square (r.m.s.) thermal displacements along the principal axes of the thermal ellipsoid and their direction cosines relative to the crystallographic axes, a, b, c, are:

r.m.s. (Å)	Direction cosines		
0·261	0·1962	0·3970	0·8965
0·165	0·5076	−0·8234	0·2535
0·154	0·8386	0·4054	−0·3632

From these data we calculate that the r.m.s. displacement along O–O is 0·176 Å, along the z axis, 0·244 Å, and normal to these two directions, 0·169 Å. In simple terms the r.m.s. displacements can be regarded as superpositions of contributions from two librational and three translational vibrations. The component along O–O should then be purely translational, and if the translational motion is isotropic this displacement should be the smallest. However, the calculated r.m.s. displacements show that the component along $r(O-O)$ is not the smallest, and the translational motion is therefore not isotropic. The detected anisotropy is therefore partly due to anisotropic translations and partly due to librational vibrations. The magnitude and degree of anisotropy found in this study of H_2O_2 is similar to that observed in organic peroxides [r.m.s. amplitudes from 0·184 to 0·277 Å (Groth, 1967)]. No indication is therefore found on a more pronounced thermal motion in the perhydrate, and we estimate the corrections to be of similar magnitude, about 0·004 Å.

As the comparisons we make are between values which have all been obtained from diffraction studies, and the estimated thermal corrections are of similar magnitude, the *differences* between the uncorrected distances should be a proper measure of a significant change in the interatomic distance.

The difference between the observed and uncorrected $r(O-O)$ distances in the organic peroxides (Groth, 1967) and in ammonium oxalate monoperhydrate is 0·020 (3) Å, or about seven times the standard deviation. According to normal criteria this difference should be highly significant. Hence, we conclude that $r(O-O)$ in hydrogen peroxide molecules in solids [1·456 (1) Å] seems to be significantly shorter than $r(O-O)$ in organic peroxides [1·476 (3) Å] and also shorter than the most accurate value of $r(O-O)$ reported for a peroxocompound [1·497 (8) Å] (Sivertsen & Sørum, 1969).

The dimensions of the free H_2O_2 molecule in the gas-phase is not accurately known. From the infrared and microwave spectra the three moments of inertia have been determined. However, as the skew chain configuration of the H_2O_2 molecule is determined by

four parameters, more information is needed. Reding-ton, Olson & Cross (1962) chose an OH distance of 0·95 Å and obtained an O–O distance of 1·475 (4) Å from their infrared spectra. Busing & Levy (1965) feel that a more reasonable choice would be 0·96 Å, giving $r(O–O) = 1·467$ (4) Å. The microwave data of Oelfke & Gordy (1969) lead to $r(O–O) = 1·470$ Å for $r(OH) = 0·96$ Å.

The value of $r(O–O)$ in $(NH_4)_2C_2O_4.H_2O_2$ uncorrected for librational motion [1·452 (1) Å] is significantly shorter than the gas-phase value. Based on our estimate of the librational correction, about 0·004 Å, the difference between solid- and gas-phase O–O distances will barely be significant, [1·467 (4) − 1·456 (1)] Å = 0·011 (4) Å. We therefore feel that more reliable gas-phase data and a rigorous correction for thermal motion in the solid are needed to settle this question.

References

BELITSKUS, B. & JEFFREY, G. A. (1965). *Acta Cryst.* **18**, 458.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

BUSING, W. R. & LEVY, H. A. (1965). *J. Chem. Phys.* **42**, 3054.

CATICHA-ELLIS, S. & ABRAHAMS, S. C. (1968). *Acta Cryst.* **B24**, 277.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.

CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.

GOUGOUTAS, J. Z. & CLARDY, J. C. (1970). *Acta Cryst.* **B26**, 1999.

GROTH, P. (1967). *Acta Chem. Scand.* **21**, 2608, 2631, 2695, 2711.

KIM, H. S., CHU, S. & JEFFREY, G. A. (1970). *Acta Cryst.* **B26**, 896.

LU, C. S., HUGHES, E. W. & GIGUÈRE, P. A. (1941). *J. Amer. Chem. Soc.* **63**, 1507.

MATHERN, G., WEISS, R. & ROHMER, R. (1969). *Chem. Commun.* p. 70.

MATHERN, G., WEISS, R. & ROHMER, R. (1970). *Chem. Commun.* p. 153.

OELFKE, W. C. & GORDY, W. (1969). *J. Chem. Phys.* **51**, 5336.

OLOVSSON, I. & TEMPLETON, D. H. (1960). *Acta Chem. Scand.* **14**, 1325.

PEDERSEN, B. F. (1967). *Acta Chem. Scand.* **21**, 779.

PEDERSEN, B. F. (1969a). *Acta Chem. Scand.* **23**, 342.

PEDERSEN, B. F. (1969b). *Structural Aspects of Perhydrates*, p. 12. Oslo: Universitetsforlaget.

PEDERSEN, B. F. (1969c). *Acta Chem. Scand.* **23**, 1871.

PEDERSEN, B. F. & PEDERSEN, B. (1964). *Acta Chem. Scand.* **18**, 1454.

REDINGTON, R. L., OLSON, W. B. & CROSS, P. C. (1962). *J. Chem. Phys.* **36**, 1311.

SAX, M., BEURSKENS, P. & CHU, S. (1965). *Acta Cryst.* **18**, 252.

SAX, M. & McMULLAN, R. K. (1967). *Acta Cryst.* **22**, 281.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.

SIVERTSEN, B. K. & SØRUM, H. (1969). *Z. Kristallogr.* **130**, 449.

On the Structures of $Y_2Zn_{\sim 9}$, $Gd_2Zn_{\sim 9}$, and Related Compounds*

BY DON T. CROMER AND ALLEN C. LARSON

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, U.S.A.

A number of $M_2X_{\sim 9}$ compounds exist where M is a rare-earth or Pu atom and X is Zn or Cd. They all have a hexagonal cell, or subcell, with a about 14 to 15·5 Å and c/a about 0·98. Many of the compounds have a superlattice which increases the a axis and may or may not lower the symmetry. $Gd_2Zn_{\sim 9}$ is an ordered example of the parent structure. $Y_2Zn_{\sim 9}$ has an occupational disorder but does not have a superlattice. $Pu_2Zn_{\sim 9}$, $Y_2Cd_{\sim 9}$ and $Ce_2Cd_{\sim 9}$ each have different superlattices, but so far none of these superstructures has been solved.

Introduction

Several $M_2X_{\sim 9}$ compounds are known where M is a large rare-earth or plutonium atom and X is a smaller zinc or cadmium atom. The structure of the compound $Pu_2Zn_{\sim 9}$ has been reported by Larson & Cromer (1966, 1967). Cramer & Wood (1967) in their study of the Pu–Zn system have designated this phase as η, and

we use their nomenclature for $Pu_2Zn_{\sim 9}$ and similar phases. The η phase has a hexagonal subcell, probable space group $P6_3/mmc$. The previous work on ηPu–Zn gave what is best described as the average structure for the subcell, for it was recognized that the true cell has a doubled a axis.

By coincidence, at about the time the work on ηPu–Zn was started, Elliott & Lemons (1964) were making vapor pressure measurements on the Ce–Cd system at approximately the η composition. To interpret their data they proposed the existence of a large