P$_4$O$_{18}$—The First Binary Phosphorus Oxide Ozonide**

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It was reported as early as 1961 that ozone reacts with the esters of *ortho*phosphoric acid ((RO)$_3$P) at low temperatures to form thermolabile ozonide products of the type (RO)$_3$PO$_3$, which were classified as phosphite ozonides [Eq. (1)].[1] These phosphite ozonides were shown to decompose to yield the corresponding stable phosphates and singlet oxygen (^{1}O$_2$), and are very convenient precursors for the generation of ^{1}O$_2$ [Eq. (2)].

$$(RO)_3P + O_3 \rightarrow (RO)_3PO_3 \qquad (1)$$

$$(RO)_3PO_3 \rightarrow (RO)_3PO + {}^1O_2 \qquad (2)$$
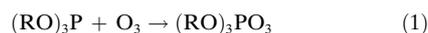
However, it was not until very recently that Dimitrov and Seppelt were able for the first time to unequivocally answer the question as to whether these ozonides definitely contained a four-membered PO$_3$ ring.[2] Crystal-structure analysis of C$_2$H$_5$C(CH$_2$O)$_3$PO$_3$ showed that this ozonide does in fact contain a symmetric, almost planar, four-membered PO$_3$ ring (Figure 1).

Despite the knowledge and the recent structural characterization of C$_2$H$_5$C(CH$_2$O)$_3$PO$_3$, there have been no sound reports regarding binary phosphorus oxide ozonides containing a PO$_3$ unit. However, in 2003 Meisel and co-workers applied the synthetic strategy of

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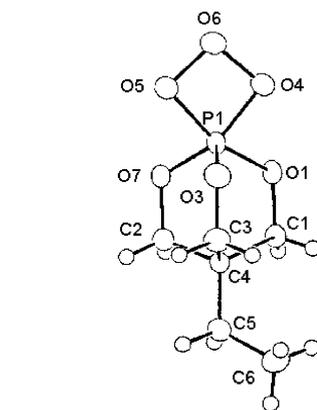
Figure 1. Molecular structure of the first structurally characterized phosphite ozonide C$_2$H$_5$C(CH$_2$O)$_3$PO$_3$.[2]

making organic phosphite ozonides to the synthesis of inorganic phosphorus oxide ozonides.[3] Quite recently, the low-temperature reaction of P$_4$O$_6$ with ozone in CH$_2$Cl$_2$, as well as the formation [Eq. (3)] and subsequent structural characterization of the tetraozonide P$_4$O$_{18}$ was reported.[3]

$$P_4O_6 + 4\,O_3 \rightarrow P_4O_{18} \qquad (3)$$
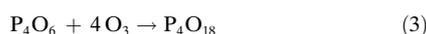
This novel phosphorus oxide ozonide P$_4$O$_{18}$ can be regarded as the [1+3] cycloaddition product of phosphorus(III) oxide and ozone. The tetraozonide P$_4$O$_{18}$ can be isolated at −78 °C as a white powder which slowly decomposes at temperatures above −35 °C in CH$_2$Cl$_2$ solution with elimination of oxygen. However, the neat material tends to decompose explosively upon warming.

The structure of P$_4$O$_{18}$ is (as are the structures of P$_4$O$_6$ and P$_4$O$_{10}$) based on a P$_4$ tetrahedron. Every P atom is coordinated with five O atoms in a distorted quadratic pyramidal arrangement. Similar to the above mentioned phosphite ozonide C$_2$H$_5$C(CH$_2$O)$_3$PO$_3$, the P$_4$O$_{18}$

molecule also contains four four-membered PO$_3$ rings and can therefore be regarded as a covalent phosphorus(V) oxide ozonide (Figure 2).
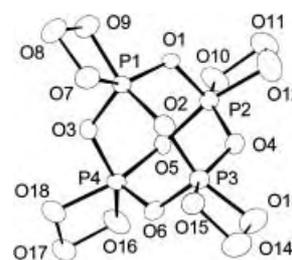
*Figure 2.* Molecular structure of the first binary phosphorus oxide ozonide P$_4$O$_{18}$.[3]

Not only is the synthesis of the first binary phosphorus oxide ozonide by Meisel and co-workers highly interesting in its own right, but the decomposition of the P$_4$O$_{18}$ molecule is also of great interest. P$_4$O$_{18}$ liberates oxygen in a controlled reaction in solution or suspension above −35 °C, and forms the thermodynamically favorable P$_4$O$_{10}$ and singlet oxygen [Eq. (4)]. Reaction (4) is thermodynamically allowed, with $\Delta H = -26.9$ kcal mol^{-1} (MPW1PW91/cc-pVDZ).[4]

$$P_4O_{18} \rightarrow P_4O_{10} + 4\,{}^1O_2 \qquad (4)$$
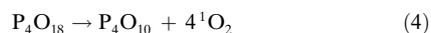
The most intense band in the low-temperature (−80 °C) Raman spectrum of P$_4$O$_{18}$ at 901 cm^{-1} corresponds to an asymmetric O-O-O stretch of the PO$_3$ ring. This value was also calculated to be the most intense Raman-active band (970 cm^{-1} at the MPW1PW91/cc-pvDZ level of theory). This band was shown to decrease significantly in intensity at −30 °C and indicates the loss of dioxygen from the PO$_3$ unit.

Since the generation of singlet oxygen (^{1}O$_2$) by direct electronic excitation

of the triplet ground state ($^3O_2$) is spin forbidden, singlet oxygen is usually prepared either 1) by chemical reactions that form intermediates which spontaneously eliminate $^1O_2$, or 2) from compounds which decompose to give $^1O_2$. The most well-known example of the latter method is the reaction of basic hydrogen peroxide (BHP) with Cl_2[5] or the above-mentioned decomposition of phosphite ozonides.[1, 6] Further work has to be carried out to evaluate the suitability of using P_4O_{18} as a potential source of singlet oxygen. In this context, the very recent report by Alfano and Christe on the first feasible production of $^1O_2$ from a gas–solid reaction should be mentioned [Eq. (5)].[7]

$$Na_2O_2 + 2\,HCl \rightarrow H_2O + 2\,NaCl + 1/2\,^1O_2 \tag{5}$$
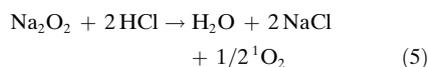
Equally interesting is the structure and bonding in the P_4O_{18} molecule which contains four essentially equivalent (approximate D_2 symmetry) hypercoordinate P atoms. Similar to the phosphite ozonide $C_2H_5C(CH_2O)_3PO_3$,[2] the P atom in the P_4O_{18} molecule forms a distorted square pyramid arrangement with the O atoms, with the apical P–O bonds being slightly shorter (1.59 Å) than the four basal P–O bonds (1.63–1.65 Å). The O–O bond lengths in the covalently bound ozonide ligands correspond to typical O–O single bonds (1.45 Å).[3] Since bonding-wise the model compound $(HO)_3PO_3$ (see resonance structures) with a five-coordinate phos-

phorus atom can best be described as a molecule with an axial 3-center-4-electron bonding unit (see for example, ref. [8]), the possibility exists that at least one 3-center-4-electron bonding unit also exists in P_4O_{18} (O···P···O) and is associated with each P atom. Further theoretical studies are needed to fully understand the structure and bonding in this highly interesting phosphorus oxide ozonide molecule.
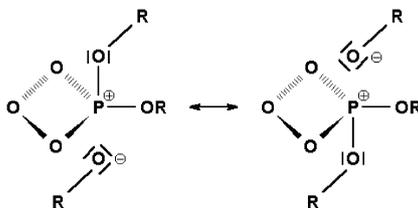
[1] Q. E. Thompson, *J. Am. Chem. Soc.* **1961**, *83*, 846–851.
[2] A. Dimitrov, K. Seppelt, *Eur. J. Inorg. Chem.* **2001**, 1929–1932.
[3] A. Dimitrov, B. Ziemer, W.-D. Hunnius, M. Meisel, *Angew. Chem.* **2003**, *115*, 2588–2590; *Angew. Chem. Int. Ed.* **2003**, *42*, 2484–2486.
[4] MPW1PW91/cc-pVTZ: P_4O_{18}, $E = -2718.676900$ au, zpe $= 50.2$ kcal mol^{-1}; P_4O_{10}, $E = -2117.805845$ au, zpe $= 31.9$ kcal mol^{-1}; $^1O_2$ ($^1\Delta$), $E = -150.228341$ au, zpe $= 2.4$ kcal mol^{-1}.
[5] a) A. U. Kahn, M. Kasha, *J. Chem. Phys.* **1963**, *39*, 2105; b) E. McKeown, W. A. Waters, *J. Chem. Soc. B* **1966**, 1040.
[6] N. J. Turro, V. Ramamurthy, K.-C. Liu, A. Krebs, R. Kemper, *J. Am. Chem. Soc.* **1976**, *98*, 6758–6761.
[7] A. J. Alfano, K. O. Christe, *Angew. Chem.* **2002**, *114*, 3386–3388; *Angew. Chem. Int. Ed.* **2002**, *41*, 3252–3254.
[8] a) "Qualitative Valence Bond Descriptions of Electron-Rich Molecules": R. D. Harcourt, *Lect. Notes Chem.* **1982**, *30*; b) R. D. Harcourt in *Quantum Chemical Methods in Main Group Chemistry* (Eds.: T. M. Klapötke, A. Schulz), Wiley, Chichester, **1998**, pp. 217–253; and references therein; c) R. D. Harcourt, *Eur. J. Inorg. Chem.* **2000**, 1901.

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