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Structures and Energies of Intermediates in the Reactions of Singlet Oxygen with Organic Phosphines and Sulfides

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Abstract: Structures, energies, and vibrational frequencies of various intermediates and transition states in the reaction between phosphines and singlet oxygen have been calculated using ab initio methods, including RHF, MP2, and CASSCF optimizations, and energy evaluations using various basis sets including electron correlation. A surprising result is that the only intermediate located for the first step of the reaction has the cyclic phosphadioxirane structure. An acyclic intermediate is not stable. This result contrasts strongly with the reaction of sulfides, where both cyclic and open structures are stable. Improved calculations for thiadioxirane and peroxy sulfoxide are reported. Transition structures leading to the phosphadioxirane intermediate and its reactions with water and phosphines have also been examined, as has the rotational barrier of the intermediate.

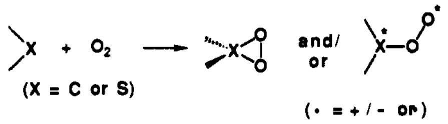
Introduction

The high oxygen affinity of trivalent phosphorus drives a variety of interesting reactions.[1] Reduction of peroxy species by phosphines has been used extensively in synthetic chemistry.[2] Usually a phosphine oxide and a reduced form of the peroxy compound are formed. This process, especially when metal-catalyzed, has been studied mechanistically.[3] The simplest oxidations of organophosphines involve singlet or triplet oxygen. Dioxygen and 2 equiv of the phosphine eventually give 2 equiv of the phosphine oxide. The few mechanistic studies of this reaction[4,5] indicate that initial formation of a phosphine–dioxygen complex is followed by reaction with a second phosphine molecule to give two phosphine oxides:

$$R_3P + O_2 \rightarrow (R_3P\text{–}O_2) + PR_3 \rightarrow 2R_3PO$$

This mechanism is similar to those of the oxidation of sulfides with singlet oxygen[6] and the formation of methylene peroxides and dioxiranes from carbenes and dioxygen,[7] which have been extensively studied both experimentally and theoretically. Kinetic studies of the oxidation of sulfides have suggested two different intermediates in some solvent systems. Only the open peroxy sulfoxide was located by early ab initio quantum mechanical calculations,[6k] but recent reports indicate that cyclic and acyclic intermediates have similar energies.[6l,m] Both methylene peroxide and dioxirane have been located by ab initio studies and detected experimentally.[7]

The corresponding reactions of phosphorus compounds with singlet oxygen have not attracted much attention to date. Two of us recently showed that the higher oxygen affinity of phosphorus compounds compared to the related sulfur species extends to their reactions with singlet oxygen; trimethyl phosphite has over 100 times higher reactivity than diethyl sulfide toward the peroxy intermediate formed from singlet oxygen and diethyl sulfide.[5] In an extension of this work, we have now performed a theoretical study of the reaction of phosphines with singlet oxygen. Here, we report the structures and energies of various intermediates, including the transition structures from the reaction of single oxygen with PH_3 and PMe_3 at the Hartree–Fock (HF) and Møller–Plesset (MP) levels of theory. Some stable structures have been further studied with the CASSCF (complete active space SCF) multiconfiguration method.



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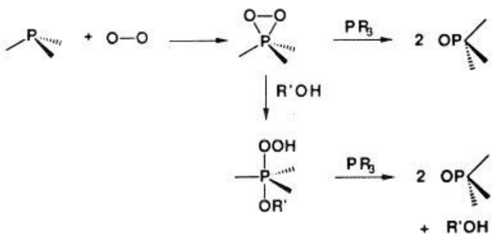
Scheme I



We also reinvestigated the adducts of H_2S and $^1O_2$ using the methods employed here, which are superior to those employed in our original work.[6c] During the course of this work, Sawaki[6l] and Jensen[6m] have reported calculations on these adducts.

Calculations

Initial calculations were carried out with the restricted Hartree–Fock (RHF) procedure.[8] The structures reported in this paper have been optimized fully with analytical gradient procedures,[9] and the stationary points on the potential surface were characterized by harmonic vibrational frequency calculations. Several basis sets[10] (STO-3G(*), 3-21G(*), and 6-31G*) were used. The (*) basis sets have d orbitals on phosphorus or sulfur but not on C or O and provide the necessary orbitals for adequate calculation of hypervalent compounds.[11] The effects of electron correlation were calculated by means of second-order Møller–Plesset perturbation (MP2) theory.[12] Frequency calculations were performed using an analytical method at the HF level and by numerically differentiating the analytical gradients at the MP2 and CASSCF levels. Single-determinant and Møller–Plesset calculations[12d] were done with the GAUSSIAN 86 program package,[13] and CASSCF calculations[14a] were performed with the GAMESS program.[14b] The IRC (intrinsic reaction coordinate)[15] option of GAMESS was used to confirm that the transition states on the potential energy surfaces connect with the stable structures in the fashion described in the text.

For the calculations of the ground-state singlet oxygen molecule, complex molecular orbitals were used in order to properly describe a closed-shell singlet species. Electron correlation calculations were also carried out at the MP2 level using complex orbitals. Ground-state $^1O_2$ with this complex wave function was optimized numerically at both the RHF and the MP2 levels.

The processes studied are presented in Scheme I. The optimized geometries of energy minima and transition structures are shown in Figure 1, the calculated total energies are listed in Table I, and the reaction energetics are tabulated in Table II. The addition of alcohols to the phosphine–oxygen adduct was included because this reaction is thought to be important with sulfides.[6k]

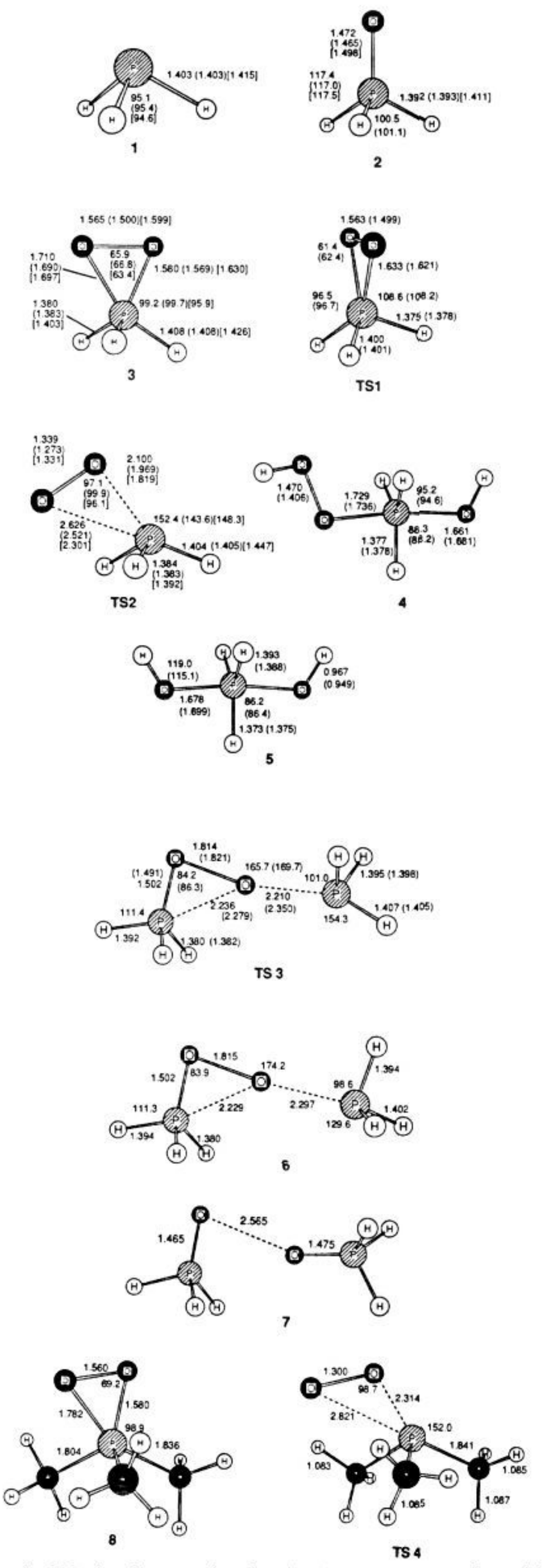


Figure 1. Calculated geometries of various intermediates and transition states for the oxidation of PH_3 with singlet oxygen at RHF/3-21G(*) (RHF/6-31G*) [MP2/6-31G*] levels. Bond lengths are in angstroms, bond angles are in degrees.

Results and Discussion

Structures and Bonding. The geometries of PH_3 and OPH_3 have been previously optimized at various levels.[16] The structure of PH_3 at the RHF/3-21G(*) level is almost identical with the previous one[16] and has a P–H bond of 1.403 Å and HPH angle

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Table I. Total Energies of Various Substrates (in hartrees, all values are negative)

substrates	HF/STO-3G(*)	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*//6-31G*[a]	MP2/6-31G*
$^1O_2$	147.578 51	148.712 20	149.557 49	149.901 22	149.917 50
H_2O	74.965 90	75.585 96	76.010 75	76.195 96	76.199 24
PH_3 (**1**)	338.685 95	340.813 99	342.447 96	342.551 51	342.562 26
OPH_3 (**2**)	412.570 21	415.266 04	417.306 81	417.593 69	417.609 65
H_3POO (**3**)	486.362 89	489.599 38	492.028 19[b]	492.507 00	492.530 79
H_3POO (**TS1**)		489.595 28	492.024 38[b]	492.505 22	
H_3POO (**TS2**)		489.476 18	491.924 65[b]	492.422 25	492.440 28
H_3POO-PH_3 (**TS3**)	825.006 21[c]	830.395 46	834.447 60[b]	835.010 39	
H_3POO-PH_3 (**6**)[b]	825.005 07[c]	830.394 20[c]			
$H_3P(OH)(OOH)$ (**4**)	561.375 94	565.229 84	568.070 60[c]	568.728 52	
$H_3P(OH)_2$ (**5**)	487.572 69	490.859 19	493.307 10[c]	493.784 12	493.803 60
Me_3P	454.461 85	457.300 60	459.567 37	460.068 19	
Me_3POO (**8**)[b]	602.154 96	606.121 93	609.174 69	610.053 13	
Me_3POO (**TS4**)[b]	601.988 82	605.979 87			
Me_3PO	528.371 74	531.800 17	534.464 33	535.148 66	

[a] Single-point calculation at the MP2(FC)/6-31G* level on the RHF/6-31G* geometry. [b] Using C_s symmetry. [c] Two imaginary frequencies.

Table II. Reaction Energies (kcal/mol)

		RHF			MP2	
entry	reaction	STO-3G(*)	3-21G(*)	6-31G*	single-point[a]	6-31G*
1	$2PH_3 + {}^1O_2 \rightarrow 2H_3PO$	−119.2	−120.4	−100.5	−114.9	−111.2
2	$PH_3 + {}^1O_2 \rightarrow H_3POO$ (**3**)	−61.8	−45.9	−14.3	−34.1	−32.0
3	H_3POO (**3**) → H_3POO (**TS1**)		2.6	2.4	1.1	
4	$PH_3 + {}^1O_2 \rightarrow H_3POO$ (**TS2**)		31.4	60.7	19.1	24.8
5	**3** + $H_2O \rightarrow H_3P(OH)(OOH)$ (**4**)	−29.6	−27.8	−19.9	−16.0	
6	**4** + $PH_3 \rightarrow H_3P(OH)_2 + H_3PO$	−50.8	−51.1	−59.8	−61.4	
7	$H_3P(OH)_2 \rightarrow H_3PO + H_2O$	23.0	4.5	−6.6	−3.5	−3.3
8	**3** + $PH_3 \rightarrow H_3POO$-PH_3 (**TS3**)	26.7	11.2	17.9	30.2	
9	**3** + $PH_3 \rightarrow 2OPH_3$	−57.5	−74.5	−86.3	−80.9	−79.2
10	$2Me_3P + {}^1O_2 \rightarrow 2Me_3PO$	−151.4	−180.1	−148.4	−163.0	
11	$Me_3P + {}^1O_2 \rightarrow Me_3POO$ (**8**)	−71.9	−68.5	−31.3	−52.5	
12	$Me_3P + {}^1O_2 \rightarrow Me_3POO$ (**TS4**)	32.3	20.7			

[a] Single-point calculation at the MP2(FC)/6-31G* level on the RHF/6-31G* geometry.

Table III. Geometries of H_3PO_2 (**3**) with the Various Basis Sets[a]

geometry	HF/STO-3G(*)	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*	CASSCF/6-31G*[b]
E (hartrees)	−486.362 89	−489.599 38	−492.028 19	−492.530 79	−492.127 98
O–O[c]	1.482	1.565	1.500	1.599	1.630
O_1–P[c]	1.657	1.710	1.690	1.697	1.681
O_2–P[c]	1.580	1.580	1.569	1.630	1.622
P–H_4[c]	1.393	1.408	1.408	1.426	1.410
P–H_5[c]	1.379	1.380	1.383	1.403	1.385
$\angle O_1O_2P$[d]	65.4	65.9	66.8	63.4	62.3
$\angle O_2PH_4$[d]	100.3	99.2	99.7	95.9	96.5
$\angle O_2PH_5$[d]	123.9	122.6	122.3	124.5	124.0
$\omega(O_1O_2PH_5)$	75.4	75.4	74.4	77.0	77.3

[a] These structures have C_s symmetry. The O_1–O_2–P–H_4 dihedral angles are 180°, and all four atoms are located on the symmetry plane. [b] A 12-orbital CASSCF was implemented with 10 filled and 2 virtual orbitals; see text. [c] Bond length, Å. [d] Angle, deg.

of 95.1°. These values correspond quite well to the experimental data, $d(\text{P–H}) = 1.412$ Å and $\angle HPH = 93.4°$.[17] The angle between the C_3 axis and the P–H bond is 121.6°. The calculated dipole moment is 0.87 D, whereas the experimental value is 0.57 D.[18]

The geometry of OPH_3 is not known, but the calculated structures can be compared with the experimentally-known structures of trimethylphosphine oxide. The calculated P–O distance in H_3PO is 1.472 Å at the 3-21G(*) level, which is very close to the experimental value of 1.480 Å in trimethylphosphine oxide.[19] The RHF/6-31G* structures are very similar, and the vibrational frequencies of PH_3 and OPH_3 calculated previously at the same level are in good agreement with the experimental data for PH_3 and $OP(Me)_3$.[16a,b,d]

We then searched for stable intermediates formed from the reaction of PH_3 and $^1O_2$. Cyclic phosphadioxirane (**3**) was found easily, and the optimized bond lengths and angles are summarized in Table III. The equilibrium structure has C_s symmetry with both oxygens located in the symmetry plane. A frequency calculation showed that this structure is a minimum. At the 3-21G(*) level, there is a large difference in the P–O bond lengths, 1.580 and 1.710 Å (see below). The POO bond angles are 65.9° and 57.5°; the O–O bond length is 1.565 Å at the same level, but it shortens to 1.500 Å with the 6-31G* basis set. On the other hand, the geometry of phosphadioxirane is somewhat different at the MP2/6-31G* level, where the O–O bond length increases to 1.599 Å, while the difference between the two P–O bonds drops to 0.067 Å. For comparison, the experimental O–O length in methylene dioxirane is 1.516 Å and has been calculated to be 1.529 Å at the MP2/6-31G* level.[7]

The open peroxide, which is a stationary structure[6k] in the reaction of sulfides with $^1O_2$, could not be located in the phosphine oxidation, and this "closed" phosphadioxirane (**3**) appears to be the only stationary point on the PES. As the POO angle was

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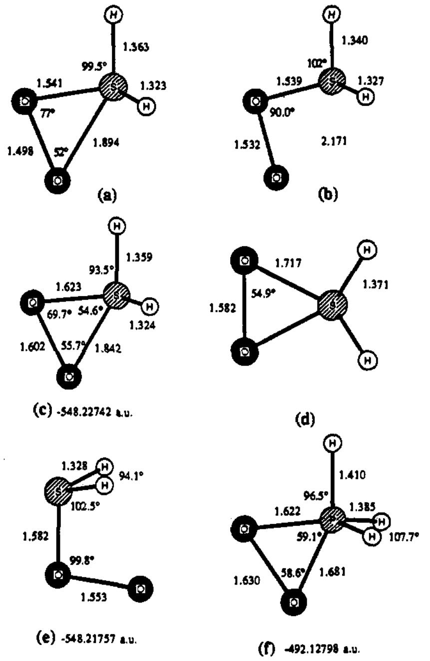

Figure 2. Structure of the thiadioxirane optimized at the RHF/3-21G* (a), RHF/6-31G* (b), CASSCF/6-31G* (c), and MP2/6-31G* (d) levels. Also shown are the CASSCF/6-31G* geometries of peroxy sulfide (e) and phosphadioxirane (f). Bond lengths are in angstroms and bond angles are in degrees.

increased intentionally, the total energy increased gradually, but no second minimum could be located.

Because of the surprising difference between the sulfur and phosphorus cases, higher level calculations were carried out using the complete active space SCF (CASSCF) method on both phosphadioxirane and thiadioxirane and the corresponding acyclic species. This multifigurational technique is expected to give a better treatment of species with biradical character, if this should be present in the acyclic species. The active space includes all 20 valence electrons in 12 orbitals in both cases. The 12 active orbitals include all valence orbitals except the antibonding H–S orbitals for the thiadioxirane and the antibonding H–P orbitals for the phosphadioxirane. The results of CASSCF calculations with the 6-31G* basis set are shown in Figure 2.

For the reaction of singlet oxygen with hydrogen sulfide, the peroxy sulfoxide was reported originally to be the only intermediate at the RHF/3-21G(*) level, because other minima located had one long S–O bond and were dismissed as rotational isomers of the peroxy sulfoxide.[6k] Sawaki and co-workers carried out calculations with the 3-21G* basis set, including d orbitals on both sulfur and oxygen, and found a cyclic thiadioxirane structure to be more stable than the peroxy sulfoxide intermediate.[6l] The discrepancy between the earlier results[6k] and Sawaki's findings[6l] prompted us and Jensen[6m] to carry out further studies using higher level computational methods.

The structure of the thiadioxirane is very sensitive to the level of theory used. At the RHF/3-21G* level, the two S–O bond lengths are 1.541 and 1.894 Å and the two SOO bond angles are 52° and 77°, as shown in Figure 2a.[6l] At the RHF/6-31G* level, the S–O bond lengths change to 1.539 and 2.171 Å, respectively, with an open 90° SOO angle (Figure 2b). The RHF/6-31G* structure is intermediate between an acyclic and a cyclic species. Inclusion of nondynamical correlation between (CASSCF) with the 6-31G* basis set gave a closed structure (Figure 2c), of which the two S–O bond lengths are 1.623 and 1.842 Å. On the other hand, these two S–O bonds were found to be identical (1.717 Å), leading to a cyclic thiadioxirane of C_s symmetry, at the MP2/6-31G* level (Figure 2d). Frequency calculations at the CASSCF level confirmed that both thiadioxirane and peroxy sulfoxide are minima, and the former is predicted to be 6 kcal/mol more stable, in agreement with Sawaki's results.[6l] Jensen reported an energy difference of 6–9 kcal/mol with several basis sets and MP4 correlation energy corrections.[6m] Likewise, the cyclic C_s structure was confirmed to be a minimum on the MP2/6-31G* potential energy surface, and single-point energy calculations at higher Møller–Plesset levels with larger basis sets also show that the C_s cyclic thiadioxirane is more stable than the peroxy sulfoxide.[6m]

The cyclic phosphadioxirane was located easily at all levels of theory, and all attempts to locate the acyclic peroxy species led to only phosphadioxirane. Why are two minima present in the sulfur species and only one in the phosphorus? The stable acyclic peroxy sulfoxide has the terminal oxygen anti to the sulfur lone pair. When rotated to a structure with the terminal oxygen anti to an S–H bond, cyclization occurs spontaneously. On the other hand, in the various peroxyphosphine oxides, the terminal oxygen is always in an apical position anti to one of the P–H bonds. According to the Westheimer model[20] for substitution on phosphorus, nucleophiles attack phosphorus centers at the apical position, and the terminal oxygen is ideally placed for this attack to give the phosphadioxirane intermediate with the trigonal bipyramidal configuration.

Few experimental data exist for a three-membered POO ring. During photolysis of the phosphine–ozone complex in solid argon,[21] IR spectra of an intermediate believed to be the cyclic $HP(O_2)O$ were detected. The structure assigned from the spectra has a cyclic P–O bond length of 1.60 Å and an O–O length of 1.48 Å, substantially different from the computed structures.[21]

Since pseudorotation of pentavalent phosphorus compounds is very common,[1a,20,22] the turnstile rotation of the phosphadioxirane was investigated. When the HPOO dihedral angle was varied from 180° to 120°, the total energy went through a maximum, but the total variation was less than 3 kcal/mol. The transition structure (**TS1**) for the turnstile-type pseudorotation of **3** was located at the RHF/3-21G(*) level. As expected, **TS1** also has a plane of symmetry (C_s) with the O–O bond perpendicular to the symmetry plane. There is little change in the O–O bond length compared to that of **3** at the same basis set, even though those lengths change with different basis sets. The optimized structure of **TS1** shows relatively small changes in the P–O length and the POO angle during this turnstile rotation.

The pseudorotation of **3** via **TS1** is predicted to have a low activation energy. The MP2 single-point calculations show an activation energy of about 1 kcal/mol, which is lower than those calculated from the Berry rotation and the turnstile of PH_5 (2.0 and 9.1 kcal/mol, respectively),[23] where only one genuine saddle point has been located, which corresponds to C_{4v} geometry. The actual rotation of **3** is more similar to turnstile rotation than to Berry rotation.[22c] The low barrier for the pseudorotation of **3** can be partially explained by the fact that the OPO angle of **3** is constrained to a small angle by the ring and relatively little distortion is required to rotate. **TS1** resembles the transition structure for the turnstile rotation of PH_5, with a small angle between the rotating apical and equatorial hydrogens.[22b]

The transition structure (**TS2**) for the addition of singlet oxygen to PH_3 leading to phosphadioxirane (**3**) was located initially at the RHF/3-21G(*) level. Only one negative eigenvalue was observed in the vibrational frequency calculation, suggesting that it is a true transition state. The transition structure has C_s symmetry, with one of the POO angles equal to 97.1°. The O–O and O–P lengths are 1.339 and 2.100 Å, respectively. On the symmetry plane, the OPH angle of **TS2** is 152.4°, which shows

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(22) For reviews, see: (a) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Ibid.* **1971**, *4*, 288. (b) Holmes, R. R. *Ibid.* **1979**, *12*, 257. (c) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(23) (a) Altmann, J. A.; Yates, K.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1976**, *98*, 1450. (b) Kutzelnigg, W.; Wasilewski, J. *J. Am. Chem. Soc.* **1982**, *104*, 953.

that singlet oxygen approaches the phosphorus atom from the side of the PH_3 pyramid, maintaining C_s symmetry. The geometry changes very little at higher levels. The Mulliken charges of **TS2** at the MP2/6-31G* geometry show that there is a significant charge transfer from the phosphine (+0.755) to two oxygens (−0.302 and −0.453). It is noteworthy that the terminal oxygen of **TS2** has more negative charge than the inner oxygen. This negatively charged terminal oxygen also approaches the phosphorus center from an apical position anti to one of the PH bond (**TS2**), indicating that there is some nucleophilic attack by oxygen on the phosphorus center, even though the overall reaction is nucleophilic attack on the singlet oxygen by phosphine at early stages of the reaction. Thus, the structure resembles a nucleophilic addition of the phosphine to singlet oxygen, with a simultaneous nucleophilic addition of the terminal oxygen to the phosphorus center.

Upon reaction with alcohols, phosphadioxirane (**3**) should open to a peroxide ($ROPH_2OOH$), which is expected to be further reduced to a hydroxyphosphorane ($ROPH_3OH$) by phosphine. To study this process, the water adduct **4** of phosphadioxirane (**3**) was optimized. This pentavalent structure also has C_s symmetry, i.e., the phosphorus, one hydrogen atom, the peroxide, and hydroxy group are located in the symmetry plane. The hydrogen on the peroxy group is placed away from the phosphorus atom.[24] In the symmetry plane, the angles HPO for hydroxy and peroxide groups are the same (83.3°), while the P–O bond lengths are 1.661 and 1.729 Å, respectively, at the 3-21G(*) level. These bonds are considerably longer than an ordinary P–O bond, consistent with the fact that apical groups have longer bond lengths than equatorial groups in pentacoordinate phosphorus compounds. For example, the structure of pentaphenoxyphosphorane has an apical P–O length of 1.662 Å and an equatorial P–O distance of 1.600 Å by X-ray crystallography.[25] As described, adduct **4** has a trigonal bipyramidal structure. The three hydrogens and the phosphorus atom almost form a plane. The two hydrogens not on the symmetry plane are located slightly toward the peroxide group but only by 2–3°. The O–O bond length was calculated to be 1.470 Å at the 3-21G(*) and shorter (1.406 Å) at the RHF/6-31G* level.

The dihydroxyphosphorane **5**, which can be derived from the peroxy adduct **4** by reduction, was calculated with C_{2v} symmetry. The apical P–O bonds are quite long (1.678 Å) at the RHF/3-21G(*) level and even longer (1.699 Å) at the RHF/6-31G* level. The OPO angle in **5** is 170°. There could be more energy minima possible by pseudorotation,[26] but no attempt was made to locate them.

One possible mechanism for formation of two moles of phosphine oxide from one dioxygen involves the attack of a phosphine on phosphadioxirane. The transition structure (**TS3**) for reaction of phosphadioxirane (**3**) with a second phosphine was located initially at the RHF/STO-3G(*) level. During the optimization, the C_s symmetry was maintained with the phosphine approaching one of the oxygens of **3** and bisecting the nearby HPH angle. A similar transition structure is found at the RHF/3-21G(*) and 6-31G* levels.[27] When the O–O–P–H dihedral angle is maintained at 0°, the optimized structure **6** is obtained with the 3-21G(*) basis set. This structure is only 0.6 kcal/mol above **TS3** but has two imaginary frequencies, one of which corresponds to rotation of the phosphine to form **TS3**. To confirm that **TS3** is the transition state for the reaction of interest, we performed an intrinsic reaction coordinate (IRC) analysis which follows a minimum energy pathway connecting reactants and products via the transition structure. The mode with the imaginary frequency at the saddle point determines the initial direction away from the transition state. A downhill stride of 0.15 Bohr amu$^{1/2}$ was used. After 22 steps in the reverse direction, the transition structure **TS3** gave structure **7**, which clearly shows that **TS3** is on the way to the formation of two phosphine oxides from **3** and the second phosphine molecule. Phosphadioxirane (**3**) and a separated phosphine were obtained after 15 steps of forward movement.

Several structures derived from trimethylphosphine were also studied. The phosphadioxirane **8** of trimethylphosphine has a structure which is very similar to that of **3**. At the RHF/3-21G(*) level, the O–O length is 1.560 Å and the P–O lengths are 1.580 and 1.782 Å. The structure of **8** has C_s symmetry and all positive frequencies. The corresponding transition structure (**TS4**) for formation of **8** has a structure similar to that of **TS2**, but the P–O lengths of 2.314 and 2.821 Å are considerably longer (by about 0.2 Å) than those of **TS2** and the O–O length is shorter by 0.04 Å, which indicates looser binding, probably because the reaction is more exothermic. These structures were not studied at a higher level because the cost would be prohibitive.

Energetics. The calculated reaction energies at various levels of theory are summarized in Table II. The reaction between a singlet oxygen molecule and two phosphine molecules to give two phosphine oxides (entry 1) is predicted to be very exothermic, by at least 100 kcal/mol with various basis sets. This is reasonable since the reaction of PX_3 with dioxygen to OPX_3 is estimated to

$$2PX_3 + O_2 \rightarrow 2OPX_3 \qquad \text{(where X = F, Cl, Br)}$$

be exothermic by −139.8 (X = F), −132.6 (X = Cl), and −131.1 kcal/mol (X = Br).[28] Those processes are even more exothermic with singlet oxygen, which has 22.5 kcal/mol higher energy than ground-state dioxygen.

At the HF/3-21G(*) level, the formation of phosphadioxirane (**3**) from single oxygen and PH_3 (entry 2, Table II) is calculated to be exothermic by 46 kca/mol and to have a barrier of 31 kcal/mol via **TS2** (entry 4). The same reaction is predicted to be less exothermic (14 kcal/mol) and to have a higher barrier (51 kcal/mol) at the RHF/6-31G* level. However, the MP2/6-31G* calculation gives a heat of reaction of −32 kcal/mol and a lower barrier of 25 kcal/mol. Although the energy values are not consistent, the barrier is expected to be low. The experimental barrier is probably near 0 for all singlet oxygen reactions.[29]

The water adduct **4** is lower in energy than that of H_3POO and H_2O (entry 5, Table II). The reduction of the water adduct **4** by PH_3 (entry 6) is also predicted to be exothermic by at least 51 kcal/mol. This is not surprising, because many phosphines have been used to reduce peroxide and the redox process is very exothermic. Therefore, the whole process from phosphadioxirane (**3**) reacting with a second phosphine and an alcohol to form two phosphine oxides through adduct **4** (entry 5 and 6) is expected to be exothermic by >78 kcal/mol. However, cleavage of **5** to a phosphine oxide and a water molecule (entry 7) is calculated to slightly exothermic (−3.3 kcal/mol) at the MP2/6-31G* level.

The pathway from **3** and PH_3 through **TS3** to two phosphine oxides (entry 8 and 9) is predicted to be exothermic by 75 kcal/mol with a barrier of 11 kcal/mol at the RHF/3-21G* level. Although the barrier is predicted to be higher with the 6-31G* basis set, the phosphadioxirane intermediate (**3**) may not be easily detected experimentally.

Oxidation of trimethylphosphine with $^1O_2$ (entry 10, Table II) is predicted to be more exothermic than oxidation of PH_3, and formation of the corresponding phosphadioxirane **8** (entry 11) is favored by about 20 kcal/mol relative to the formation of **3** (entry

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(24) At the RHF/STO-3G(*) level, this hydrogen is not on the symmetry plane.

(25) Sarma, R.; Ramirez, F.; McKeever, B.; Marecek, J. F.; Lee, S. *J. Am. Chem. Soc.* **1976**, *98*, 581.

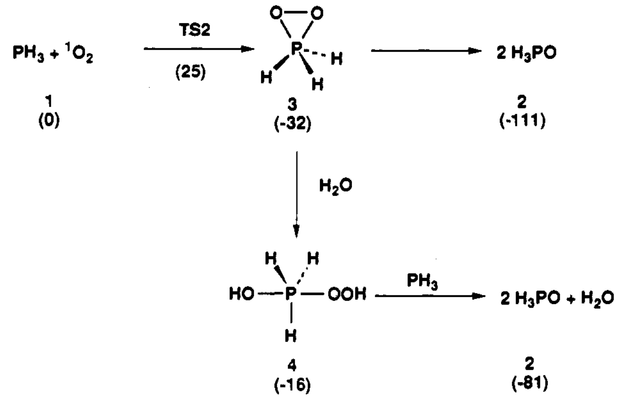
(26) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849.

(27) However, at the STO-3G(*) level the optimized structure showed two imaginary frequencies.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 85.

(29) Triphenylphosphine reacts rapidly with singlet oxygen even at −78 °C, Nahm, K.; Foote, C. S., unpublished results.

Scheme II



2). The reaction barrier via **TS4** (entry 12) is also lowered by 11 kcal/mol at the HF/3-21G(*) level. Charge transfer from phosphines to oxygens is expected to occur at the transition structure and phosphine oxides, and the methyl substituent should stabilize the intermediate better than the hydrogen substituent.

In summary, the computational results predict the facile reactions shown in Scheme II, which summarizes the intermediate and transition-state energies at the MP2/6-31G* level found in this work.

Infrared Spectra. Peroxy sulfoxides, methylene peroxide, and dioxirane have been identified by low-temperature matrix isolation experiments using FT-IR.[6j,7] We calculated the IR frequencies of intermediates **3** and **8** for use in indentification of intermediates in future matrix experiments. In general, IR frequencies calculated by ab initio calculations show some discrepancies with experimental data, but correlations can be found. The HF level usually overestimates the frequencies by 10–15% and the MP2 level by ~5%.[30]

The frequencies and intensities for the infrared spectrum of phosphadioxirane (**3**) were calculated and are listed in Table IV. At the RHF/6-31G* level, intermediate **3** is expected to show the asymmetric P–O stretch at 513 cm^{-1}, the asymmetric P–(O_2) stretch at 876 cm^{-1}, and the O–O stretch at 1130 cm^{-1}. The bands are predicted to have medium intensities. From the matrix isolation ozonolysis of phosphines, the asymmetric and symmetric P–(O_2) stretches of $HP(O_2)O$ were assigned at 833 and 974 cm^{-1}.[21] The frequencies of **3** were further calculated with ^{18}O; the expected differences are listed in the Table V. For Me_3PO_2 (**8**), the P–O and P–(O_2) stretching frequencies are calculated to appear at 419 and 893 cm^{-1}, respectively (Table IV).[31]

Conclusion. Whereas sulfides gave both cyclic and open intermediates, the only stable intermediate in the reaction of phosphines with singlet oxygen is predicted to have the closed phosphadioxirane structure, somewhat analogous to the cyclic trioxide formed with ozone.[32] The open peroxy phosphine oxide could not be located and was excluded as a possible intermediate. Both the initial dioxygen attachment to a phosphine and the oxygen atom sharing by the second phosphine are expected to by highly exothermic. This is not surprising because some alkyl phosphines are known to be reactive even with ground-state triplet oxygen and singlet oxygen is more reactive than the triplet ground state.

Table IV. Calculated Infrared Frequencies (ν, cm^{-1}) and Intensities (I, km/mol) for Phosphadioxirane (**3**) RHF/6-31G*) and Me_3POO (RHF/3-21G(*))

ν	I	ν	I	ν	I
		H_3POO (**3**)			
367	0.2	513	99	875	175
989	254	1016	66	1130	42
1195	225	1379	121	1409	425
2534	460	2729	141	2738	182
		Me_3POO			
70	0.0	112	0.7	223	0.6
235	2.7	268	0.1	319	32.7
336	0.3	343	1.6	377	34.5
419	26.4	694	1.4	766	62.8
846	29.5	893	57.7	930	0.0
975	4.8	1023	51.6	1047	7.0
1097	70.9	1100	64.6	1214	177.0
1522	54.7	1536	60.3	1547	22.5
1618	0.4	1629	15.9	1634	0.0
1637	4.8	1638	19.5	1648	2.9
3181	2.7	3207	0.6	3208	3.9
3248	12.2	3252	9.4	3276	2.3
3278	9.1	3282	1.5	3285	8.8

Table V. Calculated Oxygen Isotope Frequency Shifts (cm^{-1}) of Selected Bands Phosphadioxirane (**3**) at the RHF/3-21G(*) Level

H_3POO[a]	$H_3P^{18}O^{18}O$	$H_3P^{18}OO$	$H_3PO^{18}O$
513	−21	−6	−16
876	−37	−20	−17
1016	−6	−5	−2
1130	−35	−22	−9
1196	−17	−13	−7

[a] The terminal oxygen bisects one of the H–P–H angles, and the inner oxygen is near the hydrogen on the symmetry plane.

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(30) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(31) Dioxygenation of manganese dihalides–trimethylphosphine has been actively studied and is controversial. A recent IR experiment shows that at low temperatures, an O–O absorption peak of a dioxygen adduct appears at 898.4 cm^{-1}, which changed to 850.5 cm^{-1} with $^{18}O_2$. See: Burkett, H. D.; Worley, S. D. *J. Am. Chem. Soc.* **1989**, *111*, 5992 and references therein.

(32) Thompson, Q. E. *J. Am. Chem. Soc.* **1961**, *83*, 845.