# Electronic Supplementary Information

## Oxidation of Phosphinidene Oxide: Formation of Dioxaphosphirane Oxide with Oxygen Scrambling

Xianxu Chu, Chao Song, Yang Yang and Xiaoqing Zeng*

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123 China.

* E-mail: xqzeng@suda.edu.cn

**Table of Contents:**

**Experimental details**

**Sample preparation**. Fluorophosphoryl diazide, $FP(O)(N_3)_2$, was prepared and purified according to the published protocol.[1] Ar (≥ 99.999%, Messer), $N_2$ (≥ 99.999%, Messer), Ar (≥ 99.999%, Messer), Ne (≥ 99.999%, Messer), and $O_2$ (≥ 99.999%, Messer) gases were used without further purification. For the labeling experiments, $^{18}O_2$ (97 atom %, Aldrich) was used.

**Matrix IR spectra**

Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70V) in a reflectance mode using a transfer optic. A KBr beam splitter and wide band MCT detector were used in the mid-IR region (4000–400 $cm^{-1}$). Typically, 200 scans at a resolution of 0.5 $cm^{-1}$ were co-added for each spectrum. Fluorophosphoryl diazide was mixed by passing a flow of dilution gas (Ar, Ne, or $N_2$) through a U-trap (–55 °C) containing ca. 20 mg of the $FP(O)(N_3)_2$. Then the mixture (estimated 1:50:1000, azide: $O_2$: noble gas) was passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), deposited (2 mmol $h^{-1}$ ) in a high vacuum (~$10^{-6}$ pa) onto the Rh-plated Cu block matrix support (10K) using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled and monitored using a LakeShore 335 digital cryogenic temperature controller a Silicon Diode (DT-670). The voltage and current used in the pyrolysis experiments were 5.4 V and 3.96 A. Photolysis experiments were performed using an ArF excimer laser (Gamlaser EX5/250, 5 mJ, 3Hz), a $Nd^{3+}$:YAG laser (MPL-F-266, 10 mW), and an UV flashlight (Boyu T648, 30 W).

## Quantum chemical calculation methods and additional results

Structures and IR frequencies of stationary points and transient states were calculated using the DFT-B3LYP[2] and ab initio CCSD(T)[3] methods with the 6-311+G(3df)[4] and cc-pVTZ[5] basis sets, respectively. Local minima were confirmed by vibrational frequency analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.[6] Time-dependent (TD) DFT (B3LYP/6-311+G(3df)) calculations[7] were performed for the prediction of UV-Vis transitions. These computations were performed using the Gaussian 09 software package.[8] The CCSD(T) computations were performed using the CFOUR [9] packages. The minimum energy crossing point (MECP) is located at the B3LYP/6-311+G(3df) level using the Newton-Lagrange method, which was introduced by Koga and Morokuma.[12] The algorithm is based on the minimization of the Lagrangian function $L(R\lambda) = E_1(R) – \lambda[E_1(R) – E_2(R)]$, where R is nuclear coordinates, $E_1(R)$ and $E_2(R)$ are the energies of the states presently considered as functions of R, and λ is Lagrange multiplier. The energies, energy gradients, and Hessian matrices of both the two states need to be calculated, and the minimum point is found on the seam of intersection. These calculations are treated using a homemade program LookForMECP (version 1.0). This program can be obtained from the authors upon request. The early version of this program has been used successfully to search the MECP.[11]

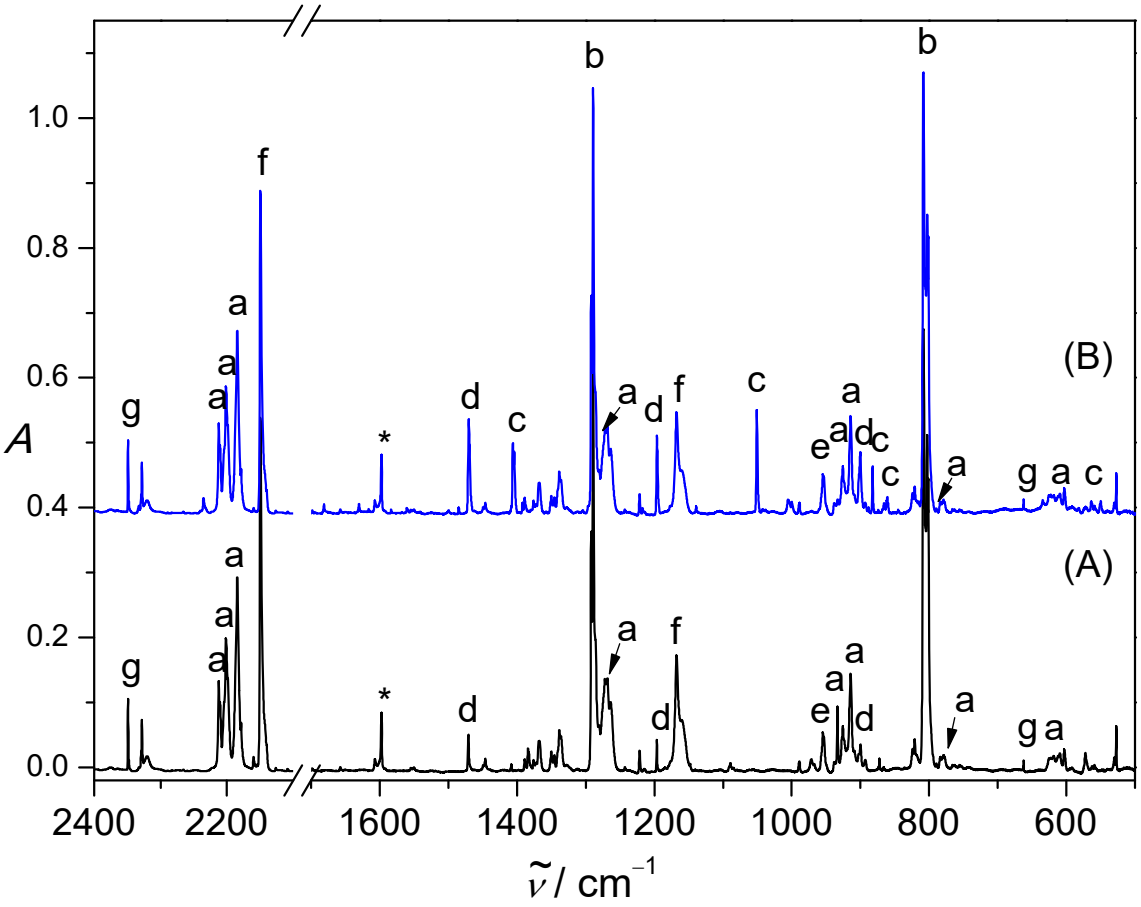


**Figure S1.** A) IR spectrum of the flash vacuum pyrolysis products of a mixture of $FP(=O)(N_3)_2$, $O_2$, and $N_2$ (ca. 1:50:1000) at 10 K. B) IR spectrum of the matrix after 266 nm laser photolysis (50 minutes) at 10 K. The IR bands of $FP(=O)(N_3)_2$ (a), FP=O (b), cyclic $FP(=O)(O_2)$ (c), $FP(=O)_2$ (d), $F_3P=O$ (e), $HN_3$ (f), $CO_2$ (g), and $H_2O$ (*) are labeled.

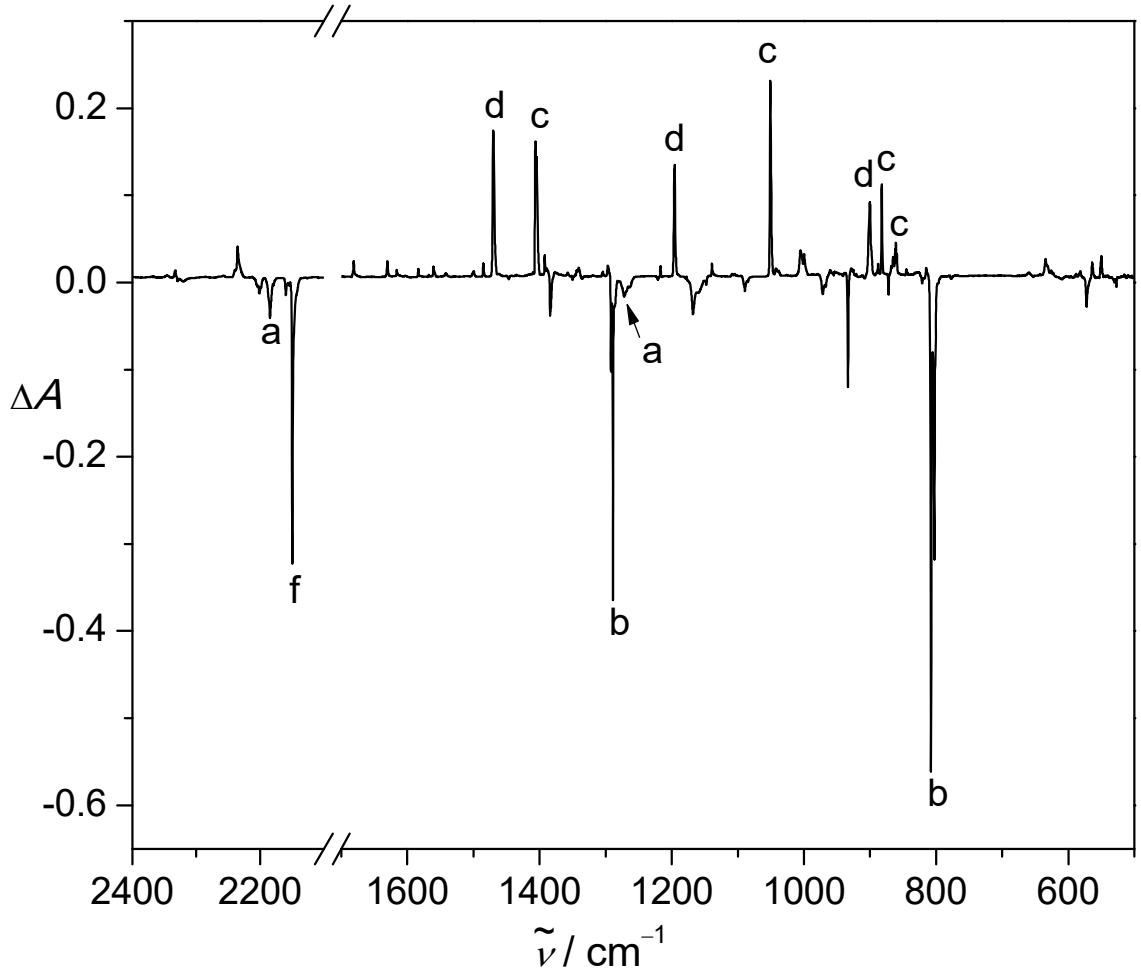


**Figure S2.** IR difference spectrum showing of the change of the matrix containing the flash vacuum pyrolysis products of a mixture of $FP(=O)(N_3)_2$, $O_2$, and $N_2$ (ca. 1:50:1000) upon a 266 nm laser photolysis.

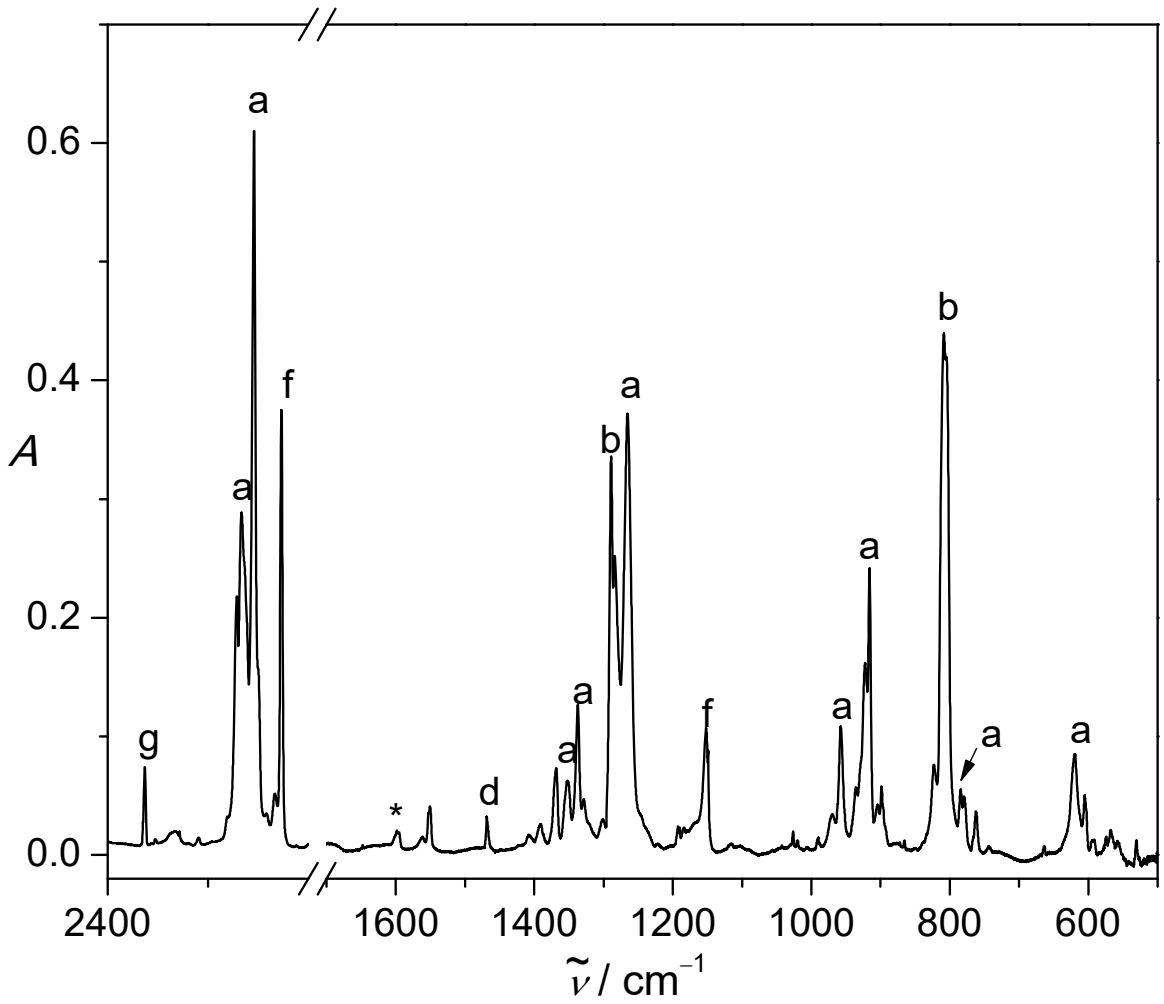


**Figure S3.** IR spectrum of the flash vacuum pyrolysis products of a mixture of $FP(=O)(N_3)_2$, $O_2$, and Ne (ca. 1:50:1000) at 10 K.

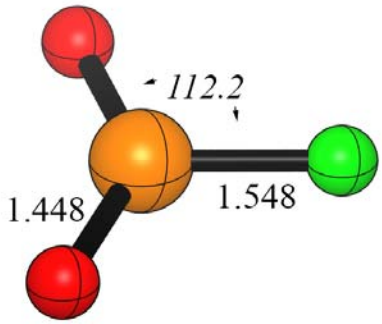


**Figure S4.** RB3LYP/6-311+G(3df) calculated bond lengths (Å) and angle (°) of singlet $FPO_2$.

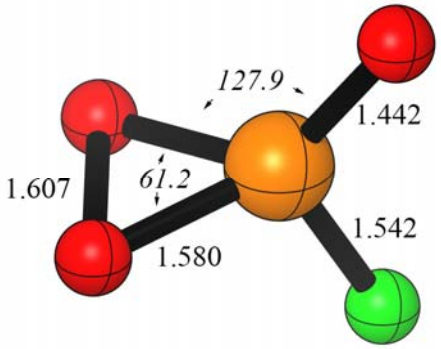


**Figure S5.** RB3LYP/6-311+G(3df) calculated bond lengths (Å) and angle (°) of close-shell singlet $FPO_3$.

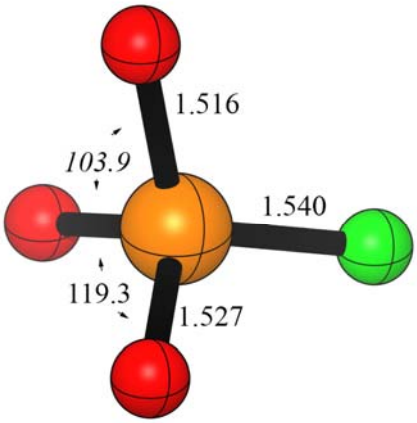


**Figure S6.** UB3LYP/6-311+G(3df) calculated bond lengths (Å) and angle (°) of triplet $FPO_3$.

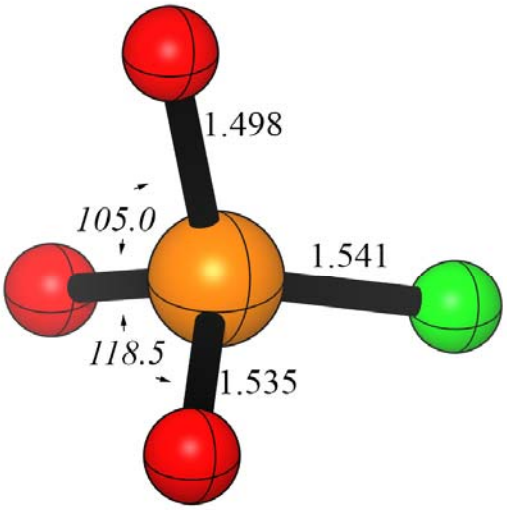


**Figure S7.** UB3LYP/6-311+G(3df) (guess=mix) calculated bond lengths (Å) and angle (°) of open-shell singlet $FPO_3$.

**Table S1.** Calculated IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$, in parentheses) of $FPO_n$ (n=2, 3) species at B3LYP/6-311+G(3df) level.

| Triplet-FP(=O)$(O)_2$ | FOP$(=O)_2$ | FOP=O | FP(=$^{16}$O)$^{16}$O$^{16}$O-syn | FP(=$^{16}$O)$^{18}$O$^{18}$O-syn | FP(=$^{16}$O)$^{16}$O$^{16}$O-anti | FP(=$^{16}$O)$^{18}$O$^{18}$O-anti |
|---|---|---|---|---|---|---|
| 1077.2 (129) | 1493.4 (147) | 1303.7 (89) | 1315.2 (114) | 1314.2 (113) | 1316.5 (122) | 1316.4 (122) |
| 897.6 (105) | 1179.6 (80) | 875.0 (24) | 1039.6 (133) | 982.7 (113) | 989.6 (108) | 937.6 (75) |
| 860.3 (130) | 942.9 (9) | 682.5 (72) | 881.1 (182) | 879.2 (187) | 901.0 (164) | 896.1 (182) |
| 844.3 (49) | 792.0 (82) | 495.3 (41) | 621.8 (31) | 596.1 (26) | 621.0 (28) | 598.5 (24) |
| 422.4 (28) | 469.2 (38) | 244.9 (10) | 463.4 (5) | 450.6 (6) | 479.5 (7) | 464.2 (7) |
| 371.9 (0) | 409.4 (51) | 181.8 (2) | 349.2 (19) | 344.2 (19) | 352.9 (24) | 348.6 (24) |
| 324.7 (3) | 390.3 (19) | | 266.9 (41) | 256.3 (43) | 230.8 (46) | 223.4 (48) |
| 292.3 (6) | 231.9 (3) | | 189.1 (49) | 186.0 (46) | 191.2 (25) | 186.9 (28) |
| 246.7 (1) | 166.2 (1) | | 162.8 (9) | 157.9 (7) | 165.2 (35) | 161.0 (27) |

**Table S2.** Calculated IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$, in parentheses) of close shell singlet FP(=O)$(O_2)$ isotopomers.

| FP(=$^{16}$O)($^{16}$O$^{16}$O) CCSD(T)/cc-pVTZ | CCSD(T)/cc-pVTZ | B3LYP/6-311+G(3df) | FP(=$^{16}$O)($^{18}$O$^{18}$O) B3LYP/6-311+G(3df) | FP(=$^{18}$O)($^{16}$O$^{18}$O) B3LYP/6-311+G(3df) | FP(=$^{18}$O)($^{18}$O$^{18}$O) B3LYP/6-311+G(3df) |
|---|---|---|---|---|---|
| $\nu_{anharm}$ | $\nu_{harm}$ | $\nu_{harm}$ | $\nu_{harm}$ | $\nu_{harm}$ | $\nu_{harm}$ |
| 1402.3 (166) | 1424.2 (178) | 1420.2 (205) | 1416.6 (201) | 1378.8 (203) | 1376.6 (201) |
| 1044.4 (168) | 1063.2 (176) | 1062.2 (147) | 1036.0 (168) | 1045.1 (160) | 1032.4 (171) |
| 874.6 (42) | 885.1 (48) | 879.0 (78) | 865.0 (58) | 868.4 (62) | 858.1 (51) |
| 847.9 (15) | 860.6 (15) | 841.0 (15) | 805.1 (16) | 819.6 (16) | 805.0 (16) |
| 553.2 (25) | 567.5 (28) | 629.7 (31) | 602.3 (30) | 613.6 (29) | 599.7 (29) |
| 430.4 (41) | 433.8 (41) | 434.4 (40) | 427.8 (38) | 426.2 (38) | 422.7 (37) |
| 411.4 (33) | 413.9 (33) | 412.5 (32) | 407.1 (30) | 400.5 (30) | 396.9 (30) |
| 399.4 (13) | 402.6 (13) | 399.9 (14) | 393.7 (14) | 392.2 (13) | 390.1 (12) |
| 265.9 (0) | 269.1 (0) | 268.9 (0) | 257.8 (0) | 261.2 (1) | 255.8 (1) |

**Table S3.** Calculated IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$, in parentheses) of close shell singlet $FP(O)_2$ isotopomers.

| $FP(=^{16}O)(=^{16}O)$ CCSD(T)/cc-pVTZ | CCSD(T)/cc-pVTZ | B3LYP/6-311+G(3df) | $FP(=^{16}O)(=^{18}O)$ B3LYP/6-311+G(3df) | $FP(=^{18}O)(^{18}O)$ B3LYP/6-311+G(3df) |
|---|---|---|---|---|
| $\nu_{anharm}$ | $\nu_{harm}$ | $\nu_{harm}$ | $\nu_{harm}$ | $\nu_{harm}$ |
| 1457.9 (129) | 1478.2 (135) | 1478.4 (176) | 1457.1 (173) | 1435.0 (170) |
| 1177.3 (97) | 1193.0 (101) | 1193.3 (101) | 1166.3 (109) | 1145.9 (116) |
| 889.4 (98) | 899.2 (100) | 873.9 (110) | 867.2 (102) | 862.5 (93) |
| 431.6 (36) | 434.0 (37) | 434.2 (37) | 428.3 (31) | 421.8 (53) |
| 426.5 (19) | 428.9 (20) | 429.6 (55) | 425.6 (54) | 416.9 (34) |
| 421.9 (50) | 425.7 (51) | 426.5 (18) | 418.0 (22) | 415.9 (17) |

**Table S4.** Calculated vertical transition energies (nm) and oscillator strength (in parentheses) at TD-B3LYP/6-311+G(3df) level.

| FP=O | | $FP(=O)_2$ | | cyclic $FP(=O)(O)_2$ | | FP(=O)OO | |
|---|---|---|---|---|---|---|---|
| energy (nm) | oscillator strength | energy (nm) | oscillator strength | energy (nm) | oscillator strength | energy (nm) | oscillator strength |
| 264 | 0.0181 | 225 | 0.0033 | 373 | 0.0006 | 1410 | 0.0003 |
| 212 | 0.0156 | 180 | 0.0411 | 254 | 0.0038 | 402 | 0.1140 |
| 180 | 0.0226 | 163 | 0.0020 | 187 | 0.0006 | 311 | 0.0022 |
| 151 | 0.1010 | 160 | 0.0041 | 185 | 0.0001 | 258 | 0.0191 |
| 147 | 0.1078 | 157 | 0.0504 | 176 | 0.0018 | 203 | 0.0067 |
| 143 | 0.0100 | 140 | 0.2121 | 173 | 0.0027 | 192 | 0.0506 |
| 142 | 0.0742 | 134 | 0.0095 | 165 | 0.0236 | 186 | 0.0020 |
| 138 | 0.0241 | | | 159 | 0.0110 | 184 | 0.0204 |
| 134 | 0.0022 | | | 141 | 0.0171 | 180 | 0.0231 |
| 132 | 0.0372 | | | | | 178 | 0.0215 |

**References:**


1 S. R. O'Neill and J. M. Shreeve, *Inorg. Chem*., 1972, **11**, 1629–1631.

2 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648−5652.

3 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.,* 1989, **157**, 479−483.

4 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265–3269.

5 a) T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023. b) R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796−6806.

6 a) K. Fukui, *Acc. Chem. Res*., 1981, **14**, 363−368. b) H. P. Hratchian and H. B. Schlegel, *J.Chem. Theory Comput*., 2005, **1**, 61−69.

7 a) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys*., 1998, **109**, 8218−8224. b) J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, *J. Phys. Chem.,* 1992, **96**, 135−149.

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.2, Gaussian, Inc., Wallingford CT, 2009.

9 J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, C. Huber, T. -C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, F. Lipparini, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf, and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen for the current version, see http://www.cfour.de.

10 N. Koga and K. Morokuma, *Chem. Phys. Lett*., 1985, **119**, 371−374.

11 a) H. Zhao, W. Bian and K. Liu, *J. Phys. Chem. A*, 2006, **110**, 7858−7866. b) S. Zhao, W. Wu, H. Zhao, H. Wang, C. Yang, K. Liu and H. Su, *J. Phys. Chem. A*, 2009, **113**, 23−34. c) K. Liu, Y. Li, J. Su and B. Wang, *J. Comput. Chem*., 2014, **35**, 703–710.

**Calculated structures, atomic coordinates (in Angstroms), and energies (in Hartrees) for all optimized species at B3LYP/6-311+G(3df)**

**Closed-shell singlet $FP(=O)(O)_2$**

| | | | |
|---|---|---|---|
| 8 | -1.113460 | 1.210398 | 0.000000 |
| 8 | -0.102777 | -1.178031 | 0.803827 |
| 8 | -0.102777 | -1.178031 | -0.803827 |
| 15 | -0.102777 | 0.181925 | 0.000000 |
| 9 | 1.343751 | 0.715160 | 0.000000 |

Zero-point correction= 0.014461 (Hartree/Particle)
Thermal correction to Energy= 0.018944
Thermal correction to Enthalpy= 0.019888
Thermal correction to Gibbs Free Energy= -0.013431
Sum of electronic and zero-point Energies= -666.983003
Sum of electronic and thermal Energies= -666.978520
Sum of electronic and thermal Enthalpies= -666.977576
Sum of electronic and thermal Free Energies= -667.010895

**Triplet $FP(=O)(O)_2$**

| | | | |
|---|---|---|---|
| 8 | -0.544825 | 1.399871 | -0.000000 |
| 8 | -0.544825 | -0.601343 | 1.318148 |
| 8 | -0.544825 | -0.601343 | -1.318148 |
| 15 | -0.031208 | -0.026889 | 0.000000 |
| 9 | 1.504880 | -0.130461 | 0.000000 |

Zero-point correction= 0.012162 (Hartree/Particle)
Thermal correction to Energy= 0.017141
Thermal correction to Enthalpy= 0.018085
Thermal correction to Gibbs Free Energy= -0.017203
Sum of electronic and zero-point Energies= -666.979570
Sum of electronic and thermal Energies= -666.974591
Sum of electronic and thermal Enthalpies= -666.973647
Sum of electronic and thermal Free Energies= -667.008935

**Open-shell singlet $FP(=O)(O)_2$**

| | | | |
|---|---|---|---|
| 8 | -0.540132 | 1.403194 | 0.000000 |
| 8 | -0.540132 | -0.609496 | 1.319140 |
| 8 | -0.540132 | -0.609496 | -1.319140 |
| 15 | -0.035349 | -0.007571 | 0.000000 |
| 9 | 1.499266 | -0.151117 | -0.000000 |

Zero-point correction= 0.012248 (Hartree/Particle)
Thermal correction to Energy= 0.017196

| | |
|---|---|
| Thermal correction to Enthalpy= | 0.018140 |
| Thermal correction to Gibbs Free Energy= | -0.016044 |
| Sum of electronic and zero-point Energies= | -666.978341 |
| Sum of electronic and thermal Energies= | -666.973393 |
| Sum of electronic and thermal Enthalpies= | -666.972448 |
| Sum of electronic and thermal Free Energies= | -667.006633 |

**MECP $FP(=O)(O)_2$**

| | | | |
|---|---|---|---|
| 8 | 1.183563 | -1.085882 | 0.000228 |
| 8 | -1.078575 | -0.141007 | -0.994142 |
| 8 | -1.078046 | -0.140089 | 0.994579 |
| 15 | 0.126312 | -0.088388 | -0.000111 |
| 9 | 0.654420 | 1.362405 | -0.000406 |

| | |
|---|---|
| Zero-point correction= | 0.011823 (Hartree/Particle) |
| Thermal correction to Energy= | 0.016412 |
| Thermal correction to Enthalpy= | 0.017356 |
| Thermal correction to Gibbs Free Energy= | -0.017310 |
| Sum of electronic and zero-point Energies= | -666.964092 |
| Sum of electronic and thermal Energies= | -666.959503 |
| Sum of electronic and thermal Enthalpies= | -666.958559 |
| Sum of electronic and thermal Free Energies= | -666.993225 |

**Syn FP(=O)OO**

| | | | |
|---|---|---|---|
| 15 | -0.425458 | 0.115139 | 0.255378 |
| 8 | 1.006756 | -0.616456 | 0.019409 |
| 8 | -0.777785 | 1.460762 | -0.172238 |
| 8 | 2.108809 | 0.114242 | -0.113884 |
| 9 | -1.368929 | -1.043941 | -0.188552 |

| | |
|---|---|
| Zero-point correction= | 0.012049 (Hartree/Particle) |
| Thermal correction to Energy= | 0.017408 |
| Thermal correction to Enthalpy= | 0.018352 |
| Thermal correction to Gibbs Free Energy= | -0.017069 |
| Sum of electronic and zero-point Energies= | -666.881066 |
| Sum of electronic and thermal Energies= | -666.875707 |
| Sum of electronic and thermal Enthalpies= | -666.874763 |
| Sum of electronic and thermal Free Energies= | -666.910184 |

**Anti FP(=O)OO**

| | | | |
|---|---|---|---|
| 15 | -0.494140 | -0.067796 | -0.225640 |
| 8 | 0.942653 | -0.756059 | -0.015662 |
| 8 | -1.714259 | -0.715027 | 0.234180 |
| 8 | 2.060712 | -0.025491 | 0.114594 |

| | | | |
|---|---|---|---|
| 9 | -0.322305 | 1.443284 | 0.079967 |

| | |
|---|---|
| Zero-point correction= | 0.011955 (Hartree/Particle) |
| Thermal correction to Energy= | 0.017343 |
| Thermal correction to Enthalpy= | 0.018287 |
| Thermal correction to Gibbs Free Energy= | -0.017159 |
| Sum of electronic and zero-point Energies= | -666.880310 |
| Sum of electronic and thermal Energies= | -666.874922 |
| Sum of electronic and thermal Enthalpies= | -666.873978 |
| Sum of electronic and thermal Free Energies= | -666.909424 |

**$FP(=O)_2$**

| | | | |
|---|---|---|---|
| 15 | 0.000000 | 0.000000 | 0.129076 |
| 8 | 0.000000 | 1.340792 | 0.677144 |
| 8 | -0.000000 | -1.340792 | 0.677144 |
| 9 | -0.000000 | -0.000000 | -1.418937 |

| | |
|---|---|
| Zero-point correction= | 0.011017 (Hartree/Particle) |
| Thermal correction to Energy= | 0.014775 |
| Thermal correction to Enthalpy= | 0.015719 |
| Thermal correction to Gibbs Free Energy= | -0.015063 |
| Sum of electronic and zero-point Energies= | -591.823031 |
| Sum of electronic and thermal Energies= | -591.819273 |
| Sum of electronic and thermal Enthalpies= | -591.818329 |
| Sum of electronic and thermal Free Energies= | -591.849111 |

**FOP=O**

| | | | |
|---|---|---|---|
| 8 | -0.853151 | -0.655815 | -0.000040 |
| 15 | 0.787366 | -0.467878 | 0.000021 |
| 8 | 1.226781 | 0.923741 | -0.000022 |
| 9 | -1.644393 | 0.541640 | 0.000020 |

| | |
|---|---|
| Zero-point correction= | 0.008619 (Hartree/Particle) |
| Thermal correction to Energy= | 0.012953 |
| Thermal correction to Enthalpy= | 0.013897 |
| Thermal correction to Gibbs Free Energy= | -0.018882 |
| Sum of electronic and zero-point Energies= | -591.668245 |
| Sum of electronic and thermal Energies= | -591.663911 |
| Sum of electronic and thermal Enthalpies= | -591.662967 |
| Sum of electronic and thermal Free Energies= | -591.695746 |

**FP=O**

| | | | |
|---|---|---|---|
| 15 | 0.000000 | 0.470675 | 0.000000 |
| 8 | 1.305190 | -0.176320 | 0.000000 |

| | | | |
|---|---|---|---|
| 9 | -1.160169 | -0.627729 | 0.000000 |

| | |
|---|---|
| Zero-point correction= | 0.005702 (Hartree/Particle) |
| Thermal correction to Energy= | 0.008934 |
| Thermal correction to Enthalpy= | 0.009878 |
| Thermal correction to Gibbs Free Energy= | -0.019551 |
| Sum of electronic and zero-point Energies= | -516.563925 |
| Sum of electronic and thermal Energies= | -516.560693 |
| Sum of electronic and thermal Enthalpies= | -516.559749 |
| Sum of electronic and thermal Free Energies= | -516.589178 |

**$FOP(=O)_2$**

| | | | |
|---|---|---|---|
| 15 | -0.000000 | 0.547008 | 0.000000 |
| 8 | 1.445863 | 0.578512 | 0.000000 |
| 8 | -1.087448 | 1.505405 | 0.000000 |
| 8 | -0.692991 | -0.918600 | 0.000000 |
| 9 | 0.297401 | -1.947517 | 0.000000 |

| | |
|---|---|
| Zero-point correction= | 0.013840 (Hartree/Particle) |
| Thermal correction to Energy= | 0.018817 |
| Thermal correction to Enthalpy= | 0.019762 |
| Thermal correction to Gibbs Free Energy= | -0.014859 |
| Sum of electronic and zero-point Energies= | -666.929171 |
| Sum of electronic and thermal Energies= | -666.924193 |
| Sum of electronic and thermal Enthalpies= | -666.923249 |
| Sum of electronic and thermal Free Energies= | -666.957870 |

**Singlet $O_2$**

| | | | |
|---|---|---|---|
| 8 | 0.000000 | 0.000000 | 0.601398 |
| 8 | 0.000000 | 0.000000 | -0.601398 |

| | |
|---|---|
| Zero-point correction= | 0.003722 (Hartree/Particle) |
| Thermal correction to Energy= | 0.006085 |
| Thermal correction to Enthalpy= | 0.007030 |
| Thermal correction to Gibbs Free Energy= | -0.015201 |
| Sum of electronic and zero-point Energies= | -150.314432 |
| Sum of electronic and thermal Energies= | -150.312068 |
| Sum of electronic and thermal Enthalpies= | -150.311124 |
| Sum of electronic and thermal Free Energies= | -150.333355 |

**TS1: FP=O to FP(=O)OO**

| | | | |
|---|---|---|---|
| 15 | -0.651883 | 0.129675 | 0.402767 |
| 8 | 1.370318 | -0.556685 | 0.033623 |
| 8 | -0.983587 | 1.351995 | -0.321359 |

| | | | |
|---|---|---|---|
| 8 | 2.260047 | 0.265502 | -0.130949 |
| 9 | -1.266220 | -1.159069 | -0.299114 |

| | |
|---|---|
| Zero-point correction= | 0.010681 (Hartree/Particle) |
| Thermal correction to Energy= | 0.016285 |
| Thermal correction to Enthalpy= | 0.017229 |
| Thermal correction to Gibbs Free Energy= | -0.019469 |
| Sum of electronic and zero-point Energies= | -666.875876 |
| Sum of electronic and thermal Energies= | -666.870273 |
| Sum of electronic and thermal Enthalpies= | -666.869329 |
| Sum of electronic and thermal Free Energies= | -666.906026 |

**TS2: FP(=O)OO to FP(=O)(O)$_2$**

| | | | | |
|---|---|---|---|---|
| 8 | 0 | 1.303921 | 0.947086 | 0.000000 |
| 8 | 0 | -0.569774 | -1.054901 | 0.000000 |
| 8 | 0 | 0.622365 | -1.975586 | 0.000000 |
| 15 | 0 | 0.000000 | 0.336450 | 0.000000 |
| 9 | 0 | -1.205789 | 1.291163 | 0.000000 |

| | |
|---|---|
| Zero-point correction= | 0.011575 (Hartree/Particle) |
| Thermal correction to Energy= | 0.016566 |
| Thermal correction to Enthalpy= | 0.017510 |
| Thermal correction to Gibbs Free Energy= | -0.017532 |
| Sum of electronic and zero-point Energies= | -666.878351 |
| Sum of electronic and thermal Energies= | -666.873360 |
| Sum of electronic and thermal Enthalpies= | -666.872416 |
| Sum of electronic and thermal Free Energies= | -666.907458 |

**TS3: FP(=O)O(O)$_2$ scarambling**

| | | | |
|---|---|---|---|
| 8 | -0.539479 | 1.415338 | -0.000000 |
| 8 | -0.539479 | -0.692402 | 1.245921 |
| 8 | -0.539479 | -0.692402 | -1.245921 |
| 15 | -0.040131 | -0.009149 | 0.000000 |
| 9 | 1.505496 | -0.011892 | -0.000000 |

| | |
|---|---|
| Zero-point correction= | 0.012353 (Hartree/Particle) |
| Thermal correction to Energy= | 0.017045 |
| Thermal correction to Enthalpy= | 0.017989 |
| Thermal correction to Gibbs Free Energy= | -0.016492 |
| Sum of electronic and zero-point Energies= | -666.950355 |
| Sum of electronic and thermal Energies= | -666.945662 |
| Sum of electronic and thermal Enthalpies= | -666.944718 |
| Sum of electronic and thermal Free Energies= | -666.979199 |