Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Spectroscopic Identification of Monomeric Methyl Metaphosphate

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Experimental details

Caution! *Covalent azides are potentially hazardous explosive. Although we have not experienced any incident during this work, safety precautions (face shields, leather gloves, and protective leather clothing) are recommended for handling* $CH_3P(O)(N_3)_2$.

Sample preparation. Methylphosphoryl diazide[1] and methyl 2-butenylphosphonate[2] were prepared and purified according to the published protocols. Ar (≥ 99.999%, Messer), N_2 (≥ 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}). For each spectrum, 200 scans at a resolution of 0.5 cm^{-1} were co-added. The gaseous sample was mixed by passing a flow of dilution gas (N_2, Ar or Ne) through a U-trap ($CH_3P(O)(N_3)_2$: –17 °C, methyl 2-butenylphosphonate: 60 °C) containing ca. 10 mg of the sample. Then the mixture (diazide : O_2 : inert gas, estimated ratio of 1:50:1000; methyl 2-butenylphosphonate : inert gas, estimated ratio of 1:1000) was passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), which can be heated over a length of ca. 25 mm by a tantalum wire (o.d. 0.4 mm, resistance 0.4 Ω) and immediately deposited (2 mmol h^{-1}) onto the Rh-plated copper block matrix support (N_2: 15 K, Ar: 10 K, Ne: 3 K) in a high vacuum (~10^{-6} Pa). While not directly measured, the expected residence time of the mixture in the pyrolysis tube is about a few milliseconds, and the pressure inside the pyrolysis tube is about 10 mbar. The electric power (voltage/current) used in the pyrolysis experiments was 5.4 V/3.6 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 calculations

Structures, IR frequencies and energies were calculated using the DFT-B3LYP[3] method with the 6-311++G(3df,3pd)[4] basis set. The natural population analysis (NPA) charges were calculated with the NBO 7.0 program.[5] Structures, IR frequencies, energies and the molecular electrostatic potential maps were performed using Gaussian 09 software package.[6]

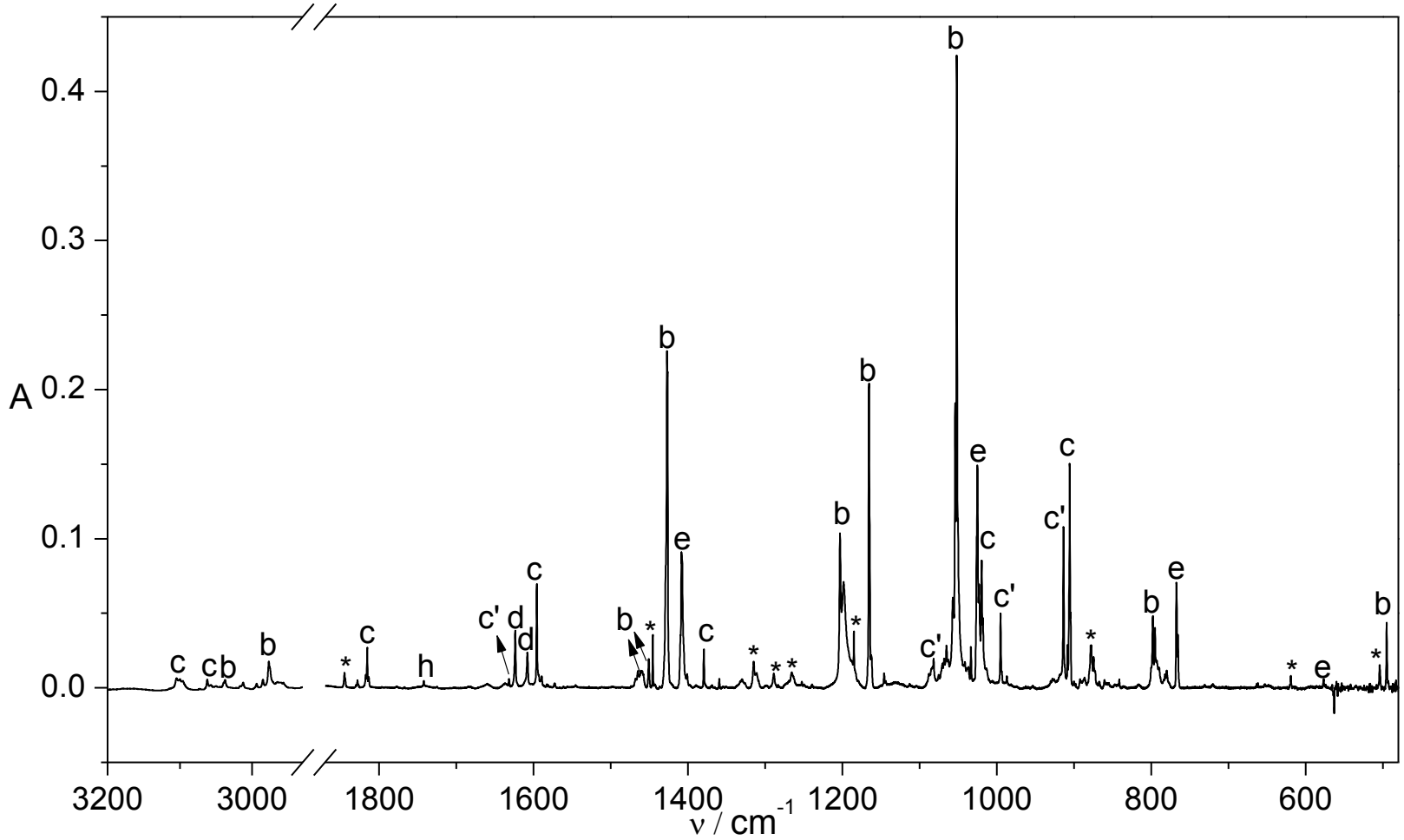

Figure S1. IR spectrum (3200-480 cm^{-1}) of Ar-matrix isolated high-vacuum flash pyrolysis (HVFP, ca. 1000 K) products of methyl 2-butenylphosphonate at 10 K. The IR bands of CH_3OPO_2 (b), 1,3-butadiene (*trans*: c; *gauche*: c'), H_2O (d), P_4O_{10} (e), H_2CO (h) and unknown species (*) are labeled.

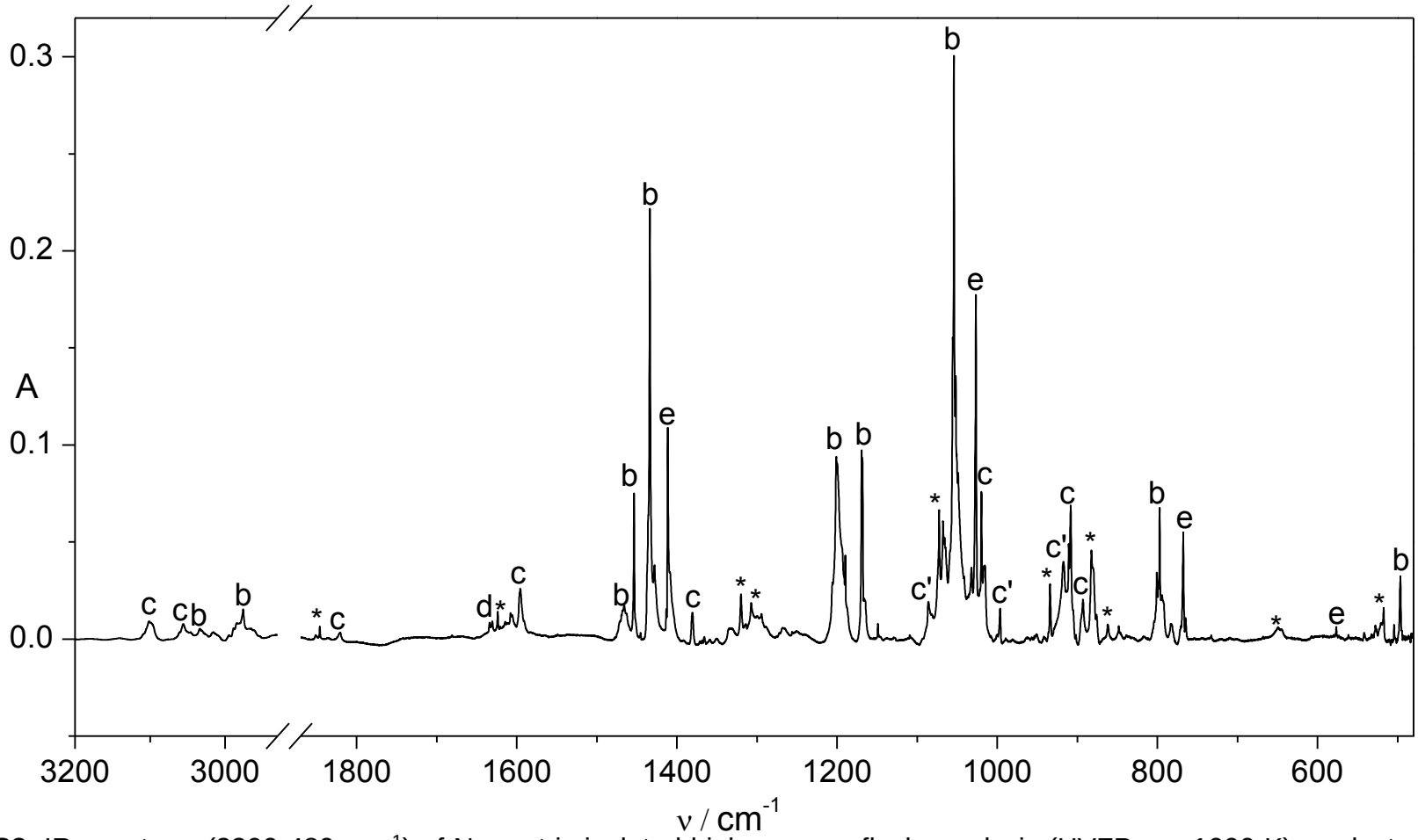

Figure S2. IR spectrum (3200-480 cm^{-1}) of Ne-matrix isolated high-vacuum flash pyrolysis (HVFP, ca. 1000 K) products of methyl 2-butenylphosphonate at 3 K. The IR bands of CH_3OPO_2 (b), 1,3-butadiene (*trans*: c; *gauche*: c'), H_2O (d), P_4O_{10} (e) and unknown species (*) are labeled.

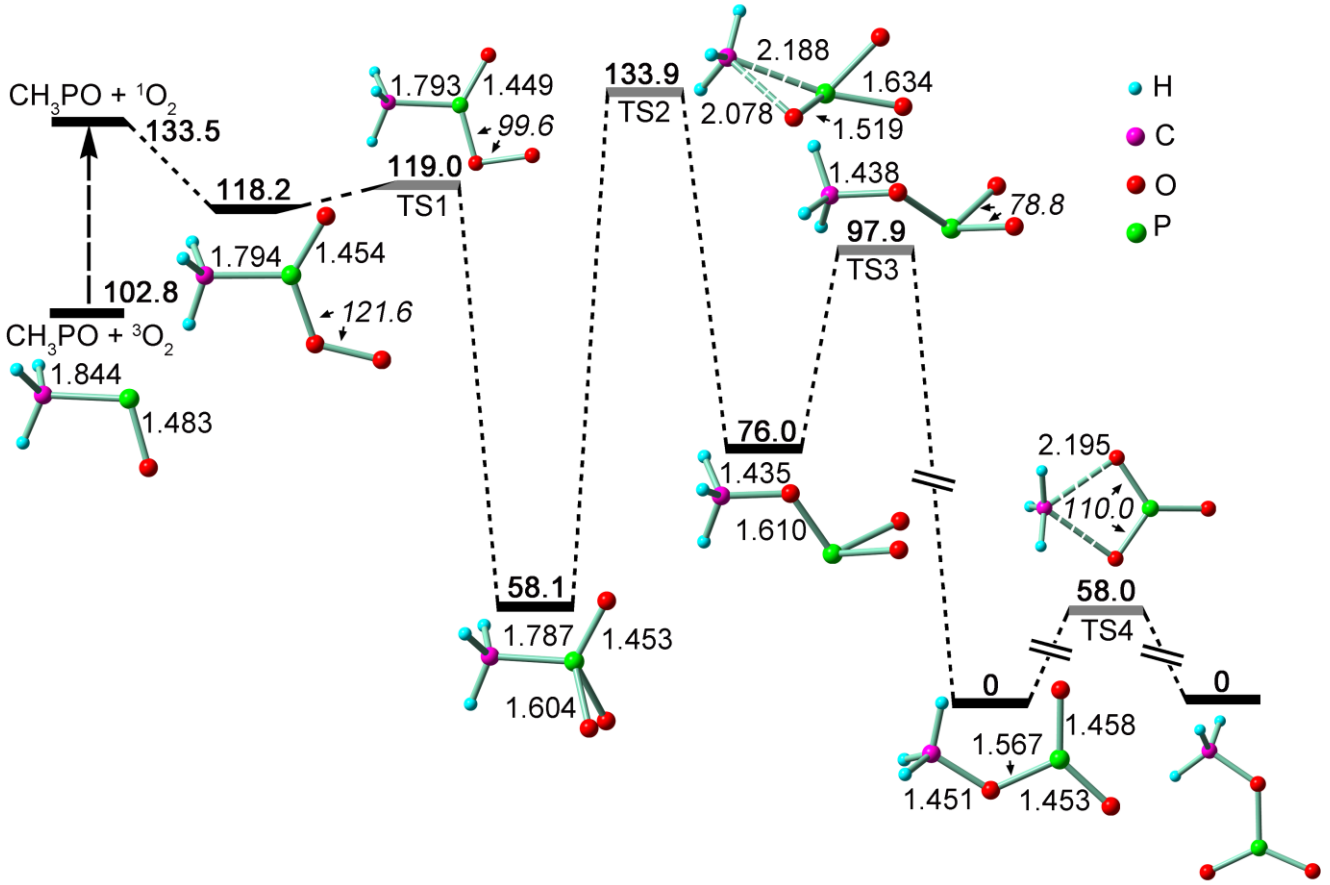

Figure S3. Calculated potential energy profile (ΔG in kcal mol^{-1}) for the oxidation of CH_3PO by O_2 at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(3df,3pd) level. The calculated bond lengths (Å), bond angles (º, italics) at B3LYP/6-311++G(3df,3pd) level and relative energies (bold) are given.

Table S1. Computed IR frequencies (cm^{-1}) and intensity (km mol^{-1}, in parentheses) of cyclic $CH_3P(=O)(O_2)$ and acyclic $CH_3P(=O)OO$ at the B3LYP/6-311++G(3df,3pd) level.

cyclic $CH_3P(=O)(O_2)$	*cis*-$CH_3P(=O)OO$	*trans*-$CH_3P(=O)OO$
3162.3 (< 1)	3169.3 (3)	3170.8 (6)
3130.9 (< 1)	3125.7 (2)	3121.1 (7)
3057.3 (< 1)	3052.1 (2)	3050.0 (12)
1458.1 (2)	1452.1 (3)	1422.6 (1)
1456.1 (7)	1443.1 (11)	1409.8 (13)
1371.2 (200)	1369.9 (145)	1357.4 (188)
1343.5 (27)	1327.7 (1)	1315.2 (10)
1023.3 (101)	969.8 (14)	1016.0 (53)
920.1 (5)	900.4 (19)	915.6 (3)
902.2 (14)	876.1 (3)	851.5 (8)
773.7 (12)	755.7 (88)	711.0 (29)
761.6 (45)	709.5 (16)	693.5 (12)
631.6 (20)	445.9 (29)	384.6 (33)
410.3 (50)	309.7 (8)	291.0 (1)
370.1 (19)	272.8 (< 1)	271.7 (9)
291.1 (< 1)	150.7 (8)	237.1 (22)
254.9 (< 1)	133.9 (4)	194.9 (10)
128.3 (< 1)	38.9 (2)	94.8 (5)

Table S2. Computed IR data of CH_3OPO_2 at the B3LYP/6-311++G(3df,3pd) level.

ν_{calcd}[a]				$\Delta\nu$[b]	$\Delta\nu$[c]	$\Delta\nu$[d]
$CH_3O_\alpha P(O_\beta O_\gamma)$	$CH_3{}^{18}O_\alpha P({}^{18}O_\beta O_\gamma)$	$CH_3{}^{18}O_\alpha P(O_\beta{}^{18}O_\gamma)$	$CH_3O_\alpha P({}^{18}O_\beta{}^{18}O_\gamma)$			
3164.0 (1)	3164.0 (1)	3164.0 (1)	3164.0 (1)	0	0	0
3153.2 (8)	3153.2 (8)	3153.2 (8)	3153.2 (8)	0	0	0
3066.0 (29)	3065.9 (29)	3066.0 (29)	3066.0 (29)	< 0.5	0	0
1500.3 (7)	1499.9 (7)	1499.8 (7)	1500.2 (8)	< 0.5	0.5	< 0.5
1499.2 (7)	1499.1 (7)	1499.1 (7)	1499.2 (7)	< 0.5	< 0.5	0
1479.5 (4)	1476.0 (1)	1476.8 (2)	1478.1 (< 1)	3.5	2.7	1.4
1443.3 (191)	1427.4 (190)	1421.8 (183)	1402.2 (186)	15.9	21.5	41.1
1215.5 (119)	1202.1 (49)	1202.2 (54)	1211.5 (72)	13.4	13.3	4.0
1179.6 (< 1)	1177.0 (< 1)	1177.0 (< 1)	1179.6 (< 1)	2.6	2.6	0
1175.9 (122)	1151.9 (175)	1156.6 (180)	1140.6 (236)	24.0	19.3	35.3
1061.6 (173)	1025.4 (171)	1024.6 (165)	1050.8 (108)	36.2	37.0	10.8
787.4 (45)	767.7 (43)	768.6 (44)	779.9 (40)	19.7	18.8	7.5
493.0 (14)	476.7 (11)	480.8 (14)	482.7 (11)	16.3	12.2	10.3
435.7 (50)	429.6 (48)	430.0 (48)	428.1 (47)	6.1	5.7	7.6
419.9 (45)	413.2 (43)	406.7 (42)	404.4 (43)	6.7	13.2	15.5
234.9 (6)	230.0 (6)	232.6 (5)	229.3 (5)	4.9	2.3	5.6
145.1 (1)	141.3 (1)	139.7 (1)	143.3 (1)	3.8	5.4	1.8
20.0 (< 1)	19.3 (< 1)	20.0 (< 1)	19.4 (< 1)	0.7	0	0.6

[a] Calculated harmonic frequencies and IR intensities (km mol^{-1}, in parentheses) at B3LYP/6-311++G(3df,3pd) level. [b] B3LYP/6-311++G(3df,3pd) calculated doubly-^{18}O-labeled isotopic shifts (cm^{-1}) for $CH_3{}^{18}O_\alpha P({}^{18}O_\beta O_\gamma)$. [c] B3LYP/6-311++G(3df,3pd) calculated doubly-^{18}O-labeled isotopic shifts (cm^{-1}) for $CH_3{}^{18}O_\alpha P(O_\beta{}^{18}O_\gamma)$. [d] B3LYP/6-311++G(3df,3pd) calculated doubly-^{18}O-labeled isotopic shifts (cm^{-1}) for $CH_3O_\alpha P({}^{18}O_\beta{}^{18}O_\gamma)$.

Table S3. Computed vertical transitions for CH_3OPO_2, acyclic $CH_3P(=O)OO$ and cyclic $CH_3P(=O)(O_2)$ at the TD-B3LYP/6-311++G(3df,3pd) level.

CH_3OPO_2		*cis*-$CH_3P(=O)OO$		*trans*-$CH_3P(=O)OO$		cyclic $CH_3P(=O)(O_2)$	
energy (nm)	oscillator strength (*f*)	energy (nm)	oscillator strength (*f*)	energy (nm)	oscillator strength (*f*)	energy (nm)	oscillator strength (*f*)
217	0.0039	411	0.0100	456	0.0001	338	0.0009
202	0.0002	398	0.0013	429	0.0200	240	0.0041
188	0.0019	335	0.1255	394	0.0009	175	0.0012
188	0.0031	269	0.0013	347	0.0347	174	0.0023
180	0.0406	268	0.0014	288	0.0015	167	0.0049
165	0.0007	231	0.0006	273	0.0009	164	0.0687
161	0.0001	225	0.0040	213	0.0034	162	0.0006
156	0.0324	209	0.0002	210	0.0006		
153	0.0051	206	0.0046	203	0.0075		
148	0.1402			197	0.0052		

References

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Computed atomic coordinates (in Angstroms) and energies (in Hartrees) for all optimized structures.

CH_3OPO_2

B3LYP/6-311++G(3df, 3pd)

O	-0.65626000	-0.84838200	0.00000000
C	0.11000200	-2.08088900	0.00000000
H	-0.17410900	-2.63366600	0.89071200
H	-0.17410900	-2.63366600	-0.89071200
H	1.17490300	-1.86900200	0.00000000
P	0.00000000	0.57433800	0.00000000
O	1.45822800	0.58496000	0.00000000
O	-0.98780500	1.63924700	0.00000000

Zero-point correction= 0.051199
Thermal correction to Energy= 0.057072
Thermal correction to Enthalpy= 0.058016
Thermal correction to Gibbs Free Energy= 0.020268
Sum of electronic and zero-point Energies= -607.079371
Sum of electronic and thermal Energies= -607.073498
Sum of electronic and thermal Enthalpies= -607.072554
Sum of electronic and thermal Free Energies= -607.110302

***cis*-$CH_3P(=O)OO$**

B3LYP/6-311++G(3df,3pd)

P	-0.32015300	0.18041700	-0.00005000
O	0.91274300	-0.72162500	-0.00004400
O	-0.44095300	1.62928500	0.00003300
O	2.22747600	-0.18510100	0.00005000
C	-1.76876400	-0.87766900	0.00003900
H	-1.45358400	-1.91662400	-0.00031100
H	-2.36260600	-0.65228900	0.88498300
H	-2.36306800	-0.65179900	-0.88446500

Zero-point correction= 0.046710
Thermal correction to Energy= 0.053232
Thermal correction to Enthalpy= 0.054176
Thermal correction to Gibbs Free Energy= 0.015560
Sum of electronic and zero-point Energies= -606.895270
Sum of electronic and thermal Energies= -606.888748
Sum of electronic and thermal Enthalpies= -606.887804
Sum of electronic and thermal Free Energies= -606.926419

***trans*-$CH_3P(=O)OO$**

B3LYP/6-311++G(3df,3pd)

P	-0.46664100	-0.10906900	-0.00000300
O	0.77958300	-0.98911700	-0.00001000
O	-1.83182200	-0.61173300	0.00000800
O	1.99023100	-0.14970500	0.00001000
C	-0.09010200	1.63087800	-0.00000200
H	0.52969600	1.83424600	0.87320900
H	0.52972300	1.83424000	-0.87319600
H	-1.02313700	2.18671900	-0.00001600

Zero-point correction= 0.046721
Thermal correction to Energy= 0.052993
Thermal correction to Enthalpy= 0.053937
Thermal correction to Gibbs Free Energy= 0.016792
Sum of electronic and zero-point Energies= -606.901366
Sum of electronic and thermal Energies= -606.895095
Sum of electronic and thermal Enthalpies= -606.894151
Sum of electronic and thermal Free Energies= -606.931296

cyclic $CH_3P(=O)(O_2)$

B3LYP/6-311++G(3df,3pd)

O	-0.46574000	1.60558600	0.00011100
O	1.17206900	-0.40060100	-0.78829500
O	1.17196100	-0.40082200	0.78826700
P	-0.08753800	0.20249600	-0.00001400
C	-1.43010000	-0.97743800	-0.00006900
H	-2.04575500	-0.80842900	0.88221200
H	-2.04722800	-0.80679400	-0.88099000
H	-1.03966800	-1.99089100	-0.00126500

Zero-point correction= 0.048859
Thermal correction to Energy= 0.054410
Thermal correction to Enthalpy= 0.055354
Thermal correction to Gibbs Free Energy= 0.019940
Sum of electronic and zero-point Energies= -606.982149
Sum of electronic and thermal Energies= -606.976598
Sum of electronic and thermal Enthalpies= -606.975654
Sum of electronic and thermal Free Energies= -607.011068

cyclic CH_3OPO_2

B3LYP/6-311++G(3df,3pd)

P	0.30915200	0.00022600	0.54135200
O	-0.91826800	-0.00030500	-0.49980600
O	1.51286800	-0.76843700	-0.26238800
O	1.51273700	0.76828000	-0.26292400
C	-2.27348200	0.00002400	-0.02719000
H	-2.31767300	0.00038800	1.06343400
H	-2.76870500	0.88919900	-0.41014600
H	-2.76870300	-0.88942800	-0.40947900

Zero-point correction= 0.048943
Thermal correction to Energy= 0.054978
Thermal correction to Enthalpy= 0.055922
Thermal correction to Gibbs Free Energy= 0.018924
Sum of electronic and zero-point Energies= -606.949608
Sum of electronic and thermal Energies= -606.943573
Sum of electronic and thermal Enthalpies= -606.942629
Sum of electronic and thermal Free Energies= -606.979627

TS1

B3LYP/6-311++G(3df,3pd)

O	-0.23659900	1.60060300	-0.02529300
O	0.81423700	-0.92622500	-0.21838700
O	2.03457200	-0.14549100	0.21522000
P	-0.23946700	0.15247100	-0.07233000
C	-1.81964800	-0.67152200	0.12647800
H	-1.75707600	-1.67696400	-0.28151600
H	-2.03724000	-0.72903100	1.19434400
H	-2.59347000	-0.08303900	-0.35906000

Zero-point correction= 0.046432
Thermal correction to Energy= 0.052304
Thermal correction to Enthalpy= 0.053248
Thermal correction to Gibbs Free Energy= 0.016632
Sum of electronic and zero-point Energies= -606.891069
Sum of electronic and thermal Energies= -606.885197
Sum of electronic and thermal Enthalpies= -606.884253
Sum of electronic and thermal Free Energies= -606.920869

TS2

B3LYP/6-311++G(3df,3pd)

P	0.10971000	-0.08524200	-0.33114500
O	-0.74073600	-1.03230200	0.49863500
O	1.12258500	0.88891200	0.51325200
O	1.72509600	-0.31729500	-0.24643700
C	-1.98471500	0.51186000	-0.12443100
H	-2.37250100	0.16564600	-1.06856900
H	-2.50616400	0.16635900	0.75291400
H	-1.71425200	1.56094200	-0.09418200

Zero-point correction= 0.046139
Thermal correction to Energy= 0.051856
Thermal correction to Enthalpy= 0.052800
Thermal correction to Gibbs Free Energy= 0.016802
Sum of electronic and zero-point Energies= -606.861660
Sum of electronic and thermal Energies= -606.855943
Sum of electronic and thermal Enthalpies= -606.854999
Sum of electronic and thermal Free Energies= -606.890997

TS3

B3LYP/6-311++G(3df,3pd)

P	0.39090400	-0.07829800	0.41545000
O	-0.93870100	0.36208100	-0.37910900
O	1.36314900	-1.01513500	-0.30952400
O	1.48762900	0.96622200	-0.12669500
C	-2.24170500	-0.11053600	0.00435500
H	-2.19625800	-0.72245400	0.90526500
H	-2.87578200	0.75448100	0.17912300
H	-2.63790600	-0.69968100	-0.81964000

Zero-point correction= 0.047567
Thermal correction to Energy= 0.053452
Thermal correction to Enthalpy= 0.054397
Thermal correction to Gibbs Free Energy= 0.017559
Sum of electronic and zero-point Energies= -606.910190
Sum of electronic and thermal Energies= -606.904305
Sum of electronic and thermal Enthalpies= -606.903360
Sum of electronic and thermal Free Energies= -606.940198

TS4

B3LYP/6-311++G(3df,3pd)

O	0.30456500	-1.23110100	0.00666000
C	2.12223400	-0.00000200	-0.00747000
H	2.33732000	-0.92001100	-0.51996400
H	2.33734800	0.92027900	-0.51945700
H	2.19387900	-0.00030700	1.06629100
P	-0.55693400	0.00000200	-0.00117600
O	0.30453300	1.23112400	0.00665900
O	-2.01509100	-0.00002000	-0.00887100

Zero-point correction= 0.047970

Thermal correction to Energy= 0.053590

Thermal correction to Enthalpy= 0.054534

Thermal correction to Gibbs Free Energy= 0.018375

Sum of electronic and zero-point Energies= -606.992839

Sum of electronic and thermal Energies= -606.987218

Sum of electronic and thermal Enthalpies= -606.986274

Sum of electronic and thermal Free Energies= -607.022434