

**Phosphorus Chemistry in the Earth's Upper Atmosphere**

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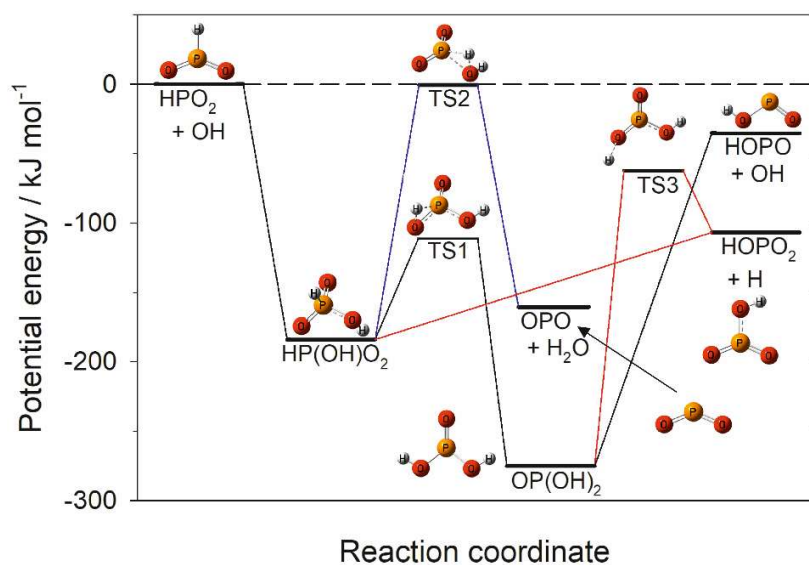
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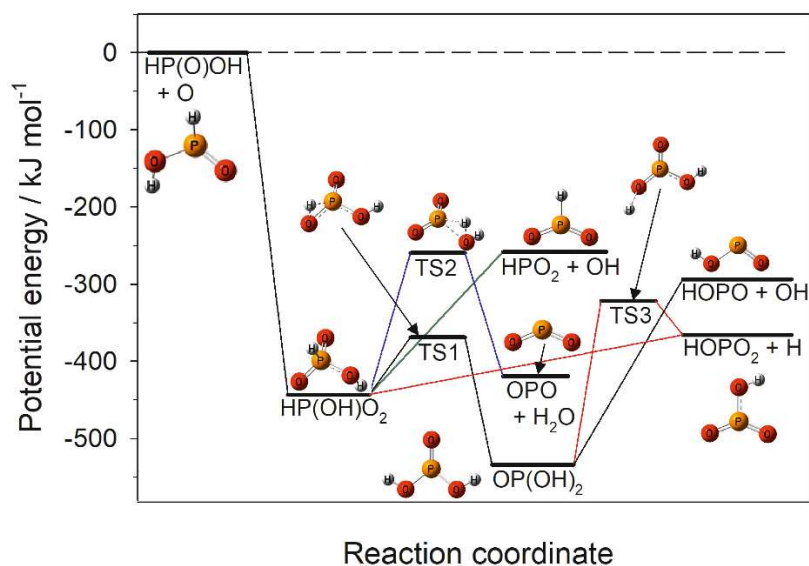
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## Introduction

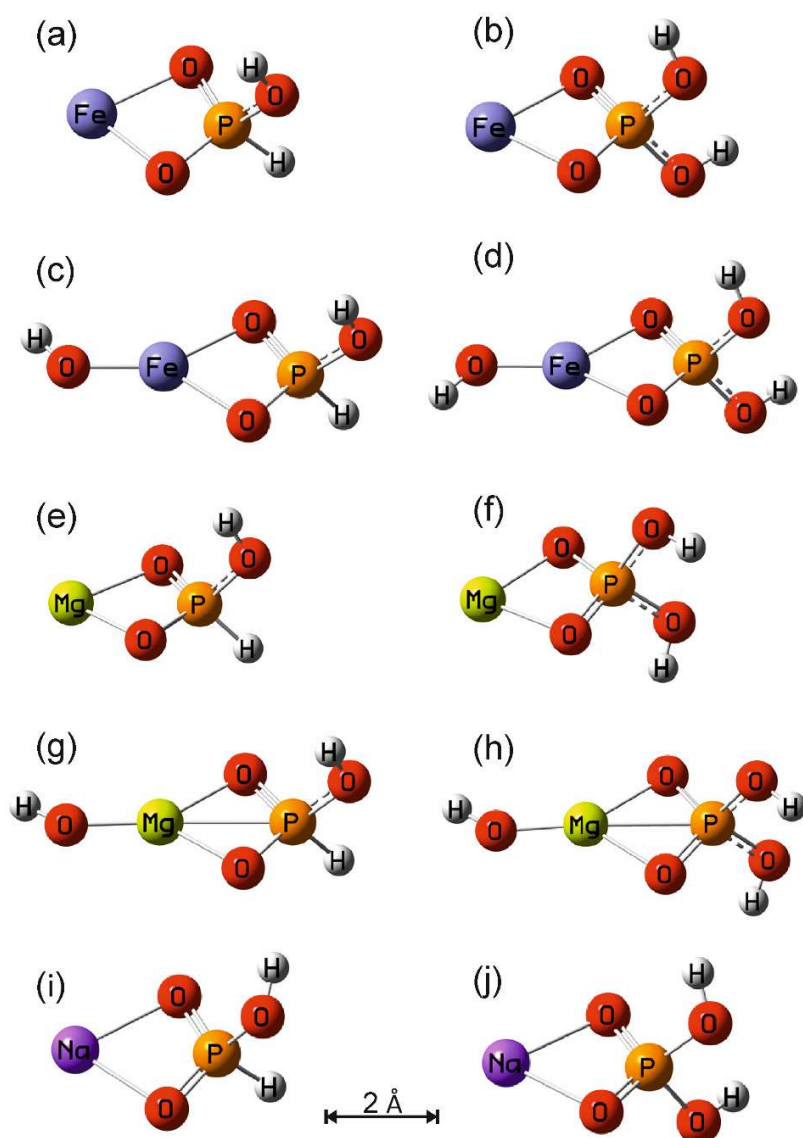
The three Figures and nine Tables and are all referred to in the main paper, and the figure and table captions describe the methods employed.



**Figure S1.** Potential energy surface for the reaction  $\text{HPO}_2 + \text{OH}$ , with energies at the CBS-QB3 level of theory [Montgomery *et al.*, 2000]. Production of OPO, HOPO<sub>2</sub> and HOPO are shown by the blue, red and black pathways, respectively.



**Figure S2.** Potential energy surface for the reaction  $\text{HP(O)OH} + \text{O}$ , with energies at the CBS-QB3 level of theory [Montgomery *et al.*, 2000]. Production of HPO<sub>2</sub>, HOPO<sub>2</sub> and HOPO are shown by the green, red and black pathways, respectively.



**Figure S3.** Structures of Fe-, Mg- and Na-salts formed from condensation reactions of FeOH, Fe(OH)<sub>2</sub>, MgOH, Mg(OH)<sub>2</sub> and NaHCO<sub>3</sub> with H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>: (a) FeH<sub>2</sub>PO<sub>3</sub>; (b) FeH<sub>2</sub>PO<sub>4</sub>; (c) HOFeh<sub>2</sub>PO<sub>3</sub>; (d) HOFeh<sub>2</sub>PO<sub>4</sub>; (e) MgH<sub>2</sub>PO<sub>3</sub>; (f) MgH<sub>2</sub>PO<sub>4</sub>; (g) HOMgH<sub>2</sub>PO<sub>3</sub>; (h) HOMgH<sub>2</sub>PO<sub>4</sub>; (i) NaH<sub>2</sub>PO<sub>3</sub>; (j) NaH<sub>2</sub>PO<sub>4</sub>.

**Table S1.** Molecular properties and heats of formation (at 0 K) of the stationary points on the OPO + H potential energy surface (doublet spin multiplicity). The geometries are illustrated in Figure 2a in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0\text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
OPO ( <sup>2</sup> A <sub>1</sub> )	P, 0.0, 0., 0.295 O, 0.0, 1.360, -0.278 O, 0.0, -1.360, -0.278	97.649 8.5398 7.8530	381, 1060, 1305	-290
HPO <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	P, 0.0, , 0.236 O, 0.0, 1.349, -0.323 O, 0.0, -1.349, -0.323 H, 0.0, 0.0, 1.639	65.391 8.6851 7.6668	456, 612, 988, 1137, 1449, 2462	-407
TS from HPO <sub>2</sub> to HOPO (TS1)	P, 0.044, 0.298, 0.002 O, -1.305, -0.409, -0.0 O, 1.384, -0.284, -0.0 H, -1.260, 1.049, 0.008	64.902 8.4887 7.5069	-1601i, 272, 405, 1072, 1339, 2105	-215
HOPO ( <sup>1</sup> A')	P, -0.129, 0.462, 0.0 O, 1.250, -0.414, 0.0 O, -1.264, -0.469, 0.0 H, 2.043, 0.142, 0.0	39.236 9.1542 7.4224	407, 481, 803, 950, 1278, 3782	-442

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{H}) = 216.0\text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{OH}) = 38.4\text{ kJ mol}^{-1}$  from Chase *et al.* [1985] and  $\Delta_f H^\circ(\text{OPO}) = -290\text{ kJ mol}^{-1}$  from Douglas *et al.* [2020].

**Table S2.** Molecular properties and heats of formation (at 0 K) of the stationary points on the  $\text{HPO}_2 + \text{H}_2\text{O}$  potential energy surface (singlet spin multiplicity). The geometries are illustrated in Figure 2b in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> )
$\text{HPO}_2$ ( <sup>1</sup> A <sub>1</sub> )	P, 0.0, , 0.236 O, 0.0, 1.349, -0.323 O, 0.0, -1.349, -0.323 H, 0.0, 0.0, 1.639	65.391 8.6851 7.6668	456, 612, 988, 1137, 1449, 2462	-407 <sup>b</sup>
$\text{HPO}_2\text{-H}_2\text{O}$ complex	P, 0.429, 0.351, 0.289 O, -0.485, 1.386, -0.202 O, 1.612, -0.283, -0.300 H, 0.344, 0.163, 1.673 O, -0.946, -1.362, -0.010 H, -0.451, -1.962, -0.588 H, -1.673, -0.993, -0.533	7.5681 5.9108 3.7098	158, 191, 231, 308, 446, 568, 615, 761, 1002, 1128, 1414, 1621, 2483, 3742, 3844	-687 <sup>b</sup>
TS from $\text{HPO}_2\text{H}_2\text{O}$ to $\text{H}_3\text{PO}_3$ (TS1)	P, 0.333, 0.218, 0.373 O, -0.500, 1.259, -0.229 O, 1.494, -0.544, -0.261 H, 0.508, 0.352, 1.752 O, -0.478, -1.444, 0.356 H, 0.569, -1.524, -0.183 H, -1.260, -1.477, -0.217	9.5914 6.3404 4.3914	-1490i, 269, 434, 510, 542, 716, 842, 886, 1015, 1064, 1319, 1353, 2005, 2501, 3762	-644 <sup>c</sup>
$\text{H}_3\text{PO}_3$	P, -0.013, 0.112, 0.274 H, 0.08, -0.032, 1.656 O, -0.424, 1.424, -0.245 O, -0.991, -1.093, -0.156 O, 1.442, -0.419, -0.122 H, 1.698, -0.190, -1.026 H, -1.802, -0.750, -0.555	8.0192 7.6065 4.4569	143, 256, 376, 408, 466, 843, 893, 949, 993, 1047, 1085, 1292, 2533, 3808, 3815	-819 <sup>b</sup>

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}) = -238.9 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985] and  $\Delta_f H^\circ(\text{OPO}) = -290 \text{ kJ mol}^{-1}$  from Douglas *et al.* [2020].

<sup>c</sup> Calculated at the CCSD(T)//B3LYP/aug-cc-pVQZ level of theory [Frisch *et al.*, 2016] (see text)

**Table S3.** Molecular properties and heats of formation (at 0 K) of the stationary points on the HOPO + OH potential energy surface (doublet spin multiplicity). The geometries are illustrated in Figure 3a in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0\text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
HOPO ( <sup>1</sup> A')	P, -0.129, 0.462, 0.0 O, 1.250, -0.414, 0.0 O, -1.264, -0.469, 0.0 H, 2.043, 0.142, 0.0	39.236 9.1542 7.4224	407, 481, 803, 950, 1278, 3782	-442
OP(OH) <sub>2</sub>	P, -0.032, 0.100, 0.104 O, -0.375, 1.455, -0.388 O, -1.045, -1.105, -0.279 O, 1.304, -0.591, -0.500 H, 2.026, 0.049, -0.571 H, -1.967, -0.824, -0.197	8.4581 7.7964 4.3821	130, 272, 351, 391, 457, 798, 830, 1018, 1031, 1211, 3808, 3809	-644
TS from OP(OH) <sub>2</sub> to HP(OH)O <sub>2</sub> (TS1)	P, 0.0160, 0.114, -0.138 O, -0.830, 1.288, 0.095 O, 1.509, -0.081, 0.276 O, -0.720, -1.293, 0.068 H, -1.682, -1.182, 0.108 H, 1.270, -0.064, -1.061	8.8076 7.8778 4.3727	-1493i, 336, 373, 430, 466, 571, 830, 946, 1054, 1295, 1879, 3781	-479
HP(OH)O <sub>2</sub>	P, -0.039, 0.0, 0.287 O, -0.817, -1.193, -0.246 O, 1.500, -0.0, -0.120 O, -0.817, 1.194, -0.246 H, 1.653, -0.0, -1.076 H, 0.109, -0.0, 1.672	9.3207 7.3433 4.7798	241, 336, 376, 451, 790, 872, 964, 969, 1063, 1115, 2542, 3789	-553
TS from HP(OH)O <sub>2</sub> to OPO + H <sub>2</sub> O (TS2)	P, -0.208, -0.012, 0.093 O, -0.864, -1.313, 0.236 O, 1.587, -0.304, -0.364 O, -0.584, 1.292, -0.469 H, 1.896, 0.549, -0.730 H, 1.205, 0.034, 0.881	8.21475 7.3725 4.0516	-1279i, 270, 312, 433, 461, 503, 901, 1075, 1100, 1394, 1608, 3674	-396
OPO ( <sup>2</sup> A <sub>1</sub> )	P, 0.0, 0., 0.295 O, 0.0, 1.360, -0.278 O, 0.0, -1.360, -0.278	97.649 8.5398 7.8530	381, 1060, 1305	-290
TS from OP(OH) <sub>2</sub> to HOPO <sub>2</sub> + H (TS3)	P, 0.009, 0.238, 0.214 O, -0.520, 1.600, 0.110 O, -0.953, -0.889, -0.369 O, 1.357, -0.307, 0.484 H, 2.476, -0.512, -0.687 H, -1.808, -0.520, -0.639	9.0044 7.5904 4.2706	-1006i, 169, 277, 387, 434, 485, 503, 861, 1049, 1127, 1383, 3770	
HOPO <sub>2</sub> ( <sup>1</sup> A')	H, 0.607, -1.912, 0.0 P, 0.0, 0.140, 0.0 O, -0.234, -1.431, 0.0	9.4944 8.6070 4.5145	397, 427, 439, 523, 882, 1066,	-693

	O, 1.410, 0.524, 0.0 O, -1.253, 0.881, 0.0		1171, 1445, 3774	
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<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{OH}) = 38.4 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}) = -238.9 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985] and  $\Delta_f H^\circ(\text{OPO}) = -290 \text{ kJ mol}^{-1}$  from Douglas *et al.* [2020].

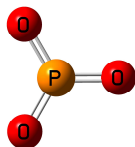
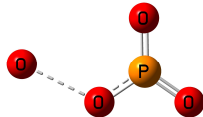
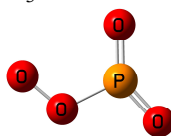
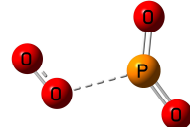
**Table S4.** Molecular properties and heats of formation (at 0 K) of the stationary points on the HOPO<sub>2</sub> + H<sub>2</sub>O potential energy surfaces (singlet spin multiplicity). The geometries are illustrated in Figure 3b in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0\text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
HOPO <sub>2</sub> ( <sup>1</sup> A')	H, 0.607, -1.912, 0.0 P, 0.0, 0.140, 0.0 O, -0.234, -1.431, 0.0 O, 1.410, 0.524, 0.0 O, -1.253, 0.881, 0.0	9.4944 8.6070 4.5145	397, 427, 439, 523, 882, 1066, 1171, 1445, 3774	-693
HOPO <sub>2</sub> -H <sub>2</sub> O complex	P, 0.385, 0.050, 0.418 O, 0.604, 1.320, -0.270 O, 0.616, -1.344, 0.024 H, 0.233, -0.603, 2.448 O, -1.754, 0.001, 0.081 H, -1.866, -0.750, -0.518 H, -1.912, 0.805, -0.435 O, 0.263, 0.250, 1.993	4.4988 3.8590 3.6727	175, 184, 211, 225, 386, 430, 438, 483, 610, 671, 873, 1065, 1157, 1419, 1623, 3741, 3798, 3839	-982
TS from HOPO <sub>2</sub> -H <sub>2</sub> O to H <sub>3</sub> PO <sub>4</sub>	P, -0.248, -0.046, 0.088 O, 0.032, 1.441, 0.217 O, -0.526, -1.025, 1.138 H, -1.407, -1.193, -1.296 O, 1.518, -0.127, -0.424 H, 2.055, -0.600, 0.230 H, 1.253, 0.985, -0.125 O, -1.002, -0.314, -1.283	5.1195 4.2684 3.8541	-1482i, 233, 325, 365, 419, 441, 549, 577, 718, 871, 911, 1046, 1115, 1332, 1361, 2025, 3774, 3804	-934
H <sub>3</sub> PO <sub>4</sub>	P, 0.0, 0.0, 0.112 O, 0.005, -0.004, 1.579 O, -0.572, 1.314, -0.589 O, 1.419, -0.161, -0.599 O, -0.854, -1.148, -0.594 H, -0.827, -1.973, -0.094 H, -1.297, 1.702, -0.083 H, 2.122, 0.270, -0.097	4.5083 4.4603 4.4596	161, 162, 314, 370, 370, 448, 450, 450, 823, 910, 911, 1054, 1060, 1060, 1304, 3824, 3824, 3826	-1119

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{H}) = 216.0\text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{OH}) = 38.4\text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}) = -238.9\text{ kJ mol}^{-1}$  from Chase *et al.* [1985] and  $\Delta_f H^\circ(\text{OPO}) = -290\text{ kJ mol}^{-1}$  from Douglas *et al.* [2020].

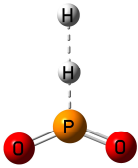
**Table S5.** Molecular properties and heats of formation (at 0 K) of the stationary points on the  $\text{PO}_3 + \text{O}$  potential energy surface (double spin multiplicity).

Molecule	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
$\text{PO}_3$ 	P, 0.000, 0.000, 0.002 O, 0.000, 0.000, 1.479 O, 1.278, 0.000, -0.742 O, -1.278, 0.000, -0.742	9.64387 9.64387 4.82194	192, 192, 434, 1015, 1123, 1123	-447
TS from $\text{PO}_3 + \text{O}$ to $\text{PO}_3\text{-O}$ 	P, -0.162, -0.766, -2.453 O, -0.151, -1.205, -1.016 O, -0.146, 0.639, -2.854 O, -0.183, -1.923, -3.384 O, -0.3669, 0.402, 0.709	8.93193 2.52293 1.97041	68 <i>i</i> , 42, 70, 247, 262, 423, 953, 1027, 1253	-193 <sup>c</sup>
$\text{PO}_3\text{-O}$ 	P, 0.527, 0.127, -0.004 O, -0.835, -0.854, 0.009 O, 0.255, 1.554, -0.009 O, 1.690, -0.745, -0.006 O, -1.996, -0.194, 0.012	8.44965 3.86590 2.65238	134, 242, 378, 386, 485, 682, 1078, 1149, 1468	-379
TS from $\text{PO}_3\text{-O}$ to $\text{OPO} + \text{O}_2$ 	P, 0.734, 0.037, 0.079 O, -1.532, -0.686, 0.007 O, 0.805, 1.502, -0.025 O, 1.687, -1.075, -0.045 O, -2.365, 0.200, -0.021	8.01272 2.52723 1.92463	158 <i>i</i> , 42, 73, 85, 330, 396, 1080, 1360, 1490	-287

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{O}) = 246.8 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985] and  $\Delta_f H^\circ(\text{PO}_3) = -447 \text{ kJ mol}^{-1}$  from Douglas *et al.* [2020]. <sup>c</sup> Determined at the G4 level of theory.

**Table S6.** Molecular properties and heats of formation (at 0 K) of the stationary points on the  $\text{HPO}_2 + \text{H}$  potential energy surface (singlet spin multiplicity).

Molecule	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
$\text{HPO}_2$ ( <sup>1</sup> A <sub>1</sub> )	P, 0.0, , 0.236 O, 0.0, 1.349, -0.323 O, 0.0, -1.349, -0.323 H, 0.0, 0.0, 1.639	65.391 8.6851 7.6668	456, 612, 988, 1137, 1449, 2462	-407
TS from $\text{HPO}_2$ + H to OPO + H <sub>2</sub> 	P,0,0.0001651477,0.13704175 84,0.0000114544 O,0,1.349446813,- 0.4238493771,0.0000036489 O,0,-1.3496978088,- 0.4224492896,0.0000036572 H,0,0.0009141816,1.57910945 96,0.0000321866 H,0,0.0016896664,3.08458844 87,0.000052053	27.94088 8.67387 6.61907	-488.51 154.47 208.94 447.15 693.07 1005.12 1124.23 1439.24 1890.17	-179
OPO ( <sup>2</sup> A <sub>1</sub> )	P, 0.0, 0., 0.295 O, 0.0, 1.360, -0.278 O, 0.0, -1.360, -0.278	97.649 8.5398 7.8530	381, 1060, 1305	-290

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with a reference value for  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985].

**Table S7.** Molecular properties and heats of formation (at 0 K) of the stationary points on the  $\text{HPO}_2 + \text{OH}$  potential energy surface (doublet spin multiplicity). The molecular geometries are illustrated in Figure S1.

Molecule	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
$\text{HPO}_2$ ( <sup>1</sup> A <sub>1</sub> )	P, 0.0, , 0.236 O, 0.0, 1.349, -0.323 O, 0.0, -1.349, -0.323 H, 0.0, 0.0, 1.639	65.391 8.6851 7.6668	456, 612, 988, 1137, 1449, 2462	-407
$\text{HP(OH)O}_2$	P, -0.039, 0.0, 0.287 O, -0.817, -1.193, -0.246 O, 1.500, -0.0, -0.120 O, -0.817, 1.194, -0.246 H, 1.653, -0.0, -1.076 H, 0.109, -0.0, 1.672	9.3207 7.3433 4.7798	241, 336, 376, 451, 790, 872, 964, 969, 1063, 1115, 2542, 3789	-553
TS from $\text{HP(OH)O}_2$ to $\text{OP(OH)}_2$ (TS1)	P, 0.0160, 0.114, -0.138 O, -0.830, 1.288, 0.095 O, 1.509, -0.081, 0.276 O, -0.720, -1.293, 0.068 H, -1.682, -1.182, 0.108 H, 1.270, -0.064, -1.061	8.8076 7.8778 4.3727	-1493i, 336, 373, 430, 466, 571, 830, 946, 1054, 1295, 1879, 3781	-479
TS from $\text{HP(OH)O}_2$ to $\text{OPO} + \text{H}_2\text{O}$ (TS2)	P, -0.208, -0.012, 0.093 O, -0.864, -1.313, 0.236 O, 1.587, -0.304, -0.364 O, -0.584, 1.292, -0.469 H, 1.896, 0.549, -0.730 H, 1.205, 0.034, 0.881	8.21475 7.3725 4.0516	-1279i, 270, 312, 433, 461, 503, 901, 1075, 1100, 1394, 1608, 3674	-396
$\text{OPO}$ ( <sup>2</sup> A <sub>1</sub> )	P, 0.0, 0., 0.295 O, 0.0, 1.360, -0.278 O, 0.0, -1.360, -0.278	97.649 8.5398 7.8530	381, 1060, 1305	-290
TS from $\text{OP(OH)}_2$ to $\text{HOPO}_2 + \text{H}$ (TS3)	P, 0.009, 0.238, 0.214 O, -0.520, 1.600, 0.110 O, -0.953, -0.889, -0.369 O, 1.357, -0.307, 0.484 H, 2.476, -0.512, -0.687 H, -1.808, -0.520, -0.639	9.0044 7.5904 4.2706	-1006i, 169, 277, 387, 434, 485, 503, 861, 1049, 1127, 1383, 3770	-431
$\text{HOPO}_2$ ( <sup>1</sup> A')	H, 0.607, -1.912, 0.0 P, 0.0, 0.140, 0.0 O, -0.234, -1.431, 0.0 O, 1.410, 0.524, 0.0 O, -1.253, 0.881, 0.0	9.4944 8.6070 4.5145	397, 427, 439, 523, 882, 1066, 1171, 1445, 3774	-693
$\text{HOPO}$ ( <sup>1</sup> A')	P, -0.129, 0.462, 0.0 O, 1.250, -0.414, 0.0 O, -1.264, -0.469, 0.0 H, 2.043, 0.142, 0.0	39.236 9.1542 7.4224	407, 481, 803, 950, 1278, 3782	-442

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{OH}) = 38.4 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}) = -238.9 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985].

**Table S8.** Molecular properties and heats of formation (at 0 K) of the stationary points on the HOPO<sub>2</sub> + H potential energy surface (doublet spin multiplicity). The molecular geometries are illustrated in Figure S1, where the reaction proceeds from the right-hand side of the figure.

Molecule	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
HOPO <sub>2</sub> ( <sup>1</sup> A')	H, 0.607, -1.912, 0.0 P, 0.0, 0.140, 0.0 O, -0.234, -1.431, 0.0 O, 1.410, 0.524, 0.0 O, -1.253, 0.881, 0.0	9.4944 8.6070 4.5145	397, 427, 439, 523, 882, 1066, 1171, 1445, 3774	-693
HP(OH)O <sub>2</sub>	P, -0.039, 0.0, 0.287 O, -0.817, -1.193, -0.246 O, 1.500, -0.0, -0.120 O, -0.817, 1.194, -0.246 H, 1.653, -0.0, -1.076 H, 0.109, -0.0, 1.672	9.3207 7.3433 4.7798	241, 336, 376, 451, 790, 872, 964, 969, 1063, 1115, 2542, 3789	-553
TS from HOPO <sub>2</sub> + H to OP(OH) <sub>2</sub> (TS3)	P, 0.009, 0.238, 0.214 O, -0.520, 1.600, 0.110 O, -0.953, -0.889, -0.369 O, 1.357, -0.307, 0.484 H, 2.476, -0.512, -0.687 H, -1.808, -0.520, -0.639	9.0044 7.5904 4.2706	-1006i, 169, 277, 387, 434, 485, 503, 861, 1049, 1127, 1383, 3770	-431
OP(OH) <sub>2</sub>	P, -0.032, 0.100, 0.104 O, -0.375, 1.455, -0.388 O, -1.045, -1.105, -0.279 O, 1.304, -0.591, -0.500 H, 2.026, 0.049, -0.571 H, -1.967, -0.824, -0.197	8.4581 7.7964 4.3821	130, 272, 351, 391, 457, 798, 830, 1018, 1031, 1211, 3808, 3809	-644
TS from HP(OH)O <sub>2</sub> to OP(OH) <sub>2</sub> (TS1)	P, 0.0160, 0.114, -0.138 O, -0.830, 1.288, 0.095 O, 1.509, -0.081, 0.276 O, -0.720, -1.293, 0.068 H, -1.682, -1.182, 0.108 H, 1.270, -0.064, -1.061	8.8076 7.8778 4.3727	-1493i, 336, 373, 430, 466, 571, 830, 946, 1054, 1295, 1879, 3781	-479

<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with a reference value for  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985].

**Table S9.** Molecular properties and heat of formation (at 0 K) of the stationary points on the HP(O)OH + O potential energy surface (doublet spin multiplicity). The molecular geometries are illustrated in Figure S2.

Molecule	Geometry (Cartesian co-ordinates in Å) <sup>a</sup>	Rotational constants (GHz) <sup>a</sup>	Vibrational frequencies (cm <sup>-1</sup> ) <sup>a</sup>	$\Delta_f H^\circ(0\text{ K})$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
HP(O)OH	P, 0.643, -0.750, 0.042 O, 0.731, 0.724, -0.142 O, -0.616, -1.505, -0.669 H, 1.671, -1.480, -0.619 H, -1.447, -1.019, -0.575	34.10994 8.41204 7.02095	225, 390, 757, 816, 891, 1032, 1186, 2284, 3801	-358
HP(OH)O <sub>2</sub>	P, -0.039, 0.0, 0.287 O, -0.817, -1.193, -0.246 O, 1.500, -0.0, -0.120 O, -0.817, 1.194, -0.246 H, 1.653, -0.0, -1.076 H, 0.109, -0.0, 1.672	9.3207 7.3433 4.7798	241, 336, 376, 451, 790, 872, 964, 969, 1063, 1115, 2542, 3789	-553
HOPO <sub>2</sub> ( <sup>1</sup> A')	H, 0.607, -1.912, 0.0 P, 0.0, 0.140, 0.0 O, -0.234, -1.431, 0.0 O, 1.410, 0.524, 0.0 O, -1.253, 0.881, 0.0	9.4944 8.6070 4.5145	397, 427, 439, 523, 882, 1066, 1171, 1445, 3774	-693
TS from HP(OH)O <sub>2</sub> to OP(OH) <sub>2</sub> (TS1)	P, 0.0160, 0.114, -0.138 O, -0.830, 1.288, 0.095 O, 1.509, -0.081, 0.276 O, -0.720, -1.293, 0.068 H, -1.682, -1.182, 0.108 H, 1.270, -0.064, -1.061	8.8076 7.8778 4.3727	-1493i, 336, 373, 430, 466, 571, 830, 946, 1054, 1295, 1879, 3781	-479
TS from HOPO <sub>2</sub> + H to OP(OH) <sub>2</sub> (TS3)	P, 0.009, 0.238, 0.214 O, -0.520, 1.600, 0.110 O, -0.953, -0.889, -0.369 O, 1.357, -0.307, 0.484 H, 2.476, -0.512, -0.687 H, -1.808, -0.520, -0.639	9.0044 7.5904 4.2706	-1006i, 169, 277, 387, 434, 485, 503, 861, 1049, 1127, 1383, 3770	-431
OP(OH) <sub>2</sub>	P, -0.032, 0.100, 0.104 O, -0.375, 1.455, -0.388 O, -1.045, -1.105, -0.279 O, 1.304, -0.591, -0.500 H, 2.026, 0.049, -0.571 H, -1.967, -0.824, -0.197	8.4581 7.7964 4.3821	130, 272, 351, 391, 457, 798, 830, 1018, 1031, 1211, 3808, 3809	-644
TS from HP(OH)O <sub>2</sub> to OPO + H <sub>2</sub> O (TS2)	P, -0.208, -0.012, 0.093 O, -0.864, -1.313, 0.236 O, 1.587, -0.304, -0.364 O, -0.584, 1.292, -0.469 H, 1.896, 0.549, -0.730 H, 1.205, 0.034, 0.881	8.21475 7.3725 4.0516	-1279i, 270, 312, 433, 461, 503, 901, 1075, 1100, 1394, 1608, 3674	-396

OPO ( <sup>2</sup> A <sub>1</sub> )	P, 0.0, 0., 0.295 O, 0.0, 1.360, -0.278 O, 0.0, -1.360, -0.278	97.649 8.5398 7.8530	381, 1060, 1305	-290
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<sup>a</sup> Calculated at the B3LYP/6-311+g(2d,p) level of theory [Frisch *et al.*, 2016]

<sup>b</sup> Calculated at the CBS-QB3 level of theory [Montgomery *et al.*, 2000] with reference values for  $\Delta_f H^\circ(\text{O}) = 246.8 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{H}) = 216.0 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{OH}) = 38.4 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}) = -238.9 \text{ kJ mol}^{-1}$  from Chase *et al.* [1985].

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