Table S1. Calculated molecular parameters (B3LYP/6-311+G(2d,p)) and heats of formation (CBS-Q) of stationary points on the OH + SiO potential energy surface.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Species</th>
<th>Geometry \textsuperscript{b}</th>
<th>Dipole moment \textsuperscript{c}</th>
<th>Rotational constants \textsuperscript{d}</th>
<th>Vibrational frequencies \textsuperscript{e}</th>
<th>$\Delta H_f^{\circ}(0 \text{ K})$ \textsuperscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSiO-\textit{cis} (2A') planar $C_s$</td>
<td>$r$(H-O)=0.968</td>
<td>2.696</td>
<td>55.69</td>
<td>278 (a')</td>
<td>-324.0</td>
</tr>
<tr>
<td></td>
<td>$r$(O-Si)=1.639</td>
<td></td>
<td>7.575</td>
<td>390 (a'')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$r$(Si-O)=1.534</td>
<td></td>
<td>6.668</td>
<td>763 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(H-O-Si)=117.43°</td>
<td></td>
<td></td>
<td>864 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(O-Si-O)=126.79°</td>
<td></td>
<td></td>
<td>1161 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>278 (a')</td>
<td>390 (a'')</td>
<td>763 (a')</td>
<td>-324.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>864 (a')</td>
<td>1161 (a')</td>
<td>3792 (a')</td>
<td></td>
</tr>
<tr>
<td>TS1 (2A) \textit{C}_1</td>
<td>$r$(H-O)= 0.964</td>
<td>4.018</td>
<td>63.89</td>
<td>-386 (a)</td>
<td>-311.7</td>
</tr>
<tr>
<td></td>
<td>$r$(O-Si)= 1.640</td>
<td></td>
<td>7.252</td>
<td>299 (a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$r$(Si-O)= 1.537</td>
<td></td>
<td>6.611</td>
<td>615 (a)</td>
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</tr>
<tr>
<td></td>
<td>$\angle$(H-O-Si)= 124.08°</td>
<td></td>
<td></td>
<td>829 (a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(O-Si-O)= 128.34°</td>
<td></td>
<td></td>
<td>1178 (a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(H-OSiO)= 93.17°</td>
<td></td>
<td></td>
<td>3853 (a)</td>
<td></td>
</tr>
<tr>
<td>HOSiO-\textit{trans} (2A') planar $C_s$</td>
<td>$r$(H-O)= 0.965</td>
<td>4.745</td>
<td>62.09</td>
<td>294 (a')</td>
<td>-323.6</td>
</tr>
<tr>
<td></td>
<td>$r$(O-Si)= 1.645</td>
<td></td>
<td>7.412</td>
<td>359 (a'')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$r$(Si-O)= 1.530</td>
<td></td>
<td>6.621</td>
<td>783 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(H-O-Si)= 118.19°</td>
<td></td>
<td></td>
<td>824 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\angle$(O-Si-O)= 124.62°</td>
<td></td>
<td></td>
<td>1178 (a')</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>294 (a')</td>
<td>359 (a'')</td>
<td>783 (a')</td>
<td>-323.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>824 (a')</td>
<td>1178 (a')</td>
<td>3842 (a')</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Symmetry</td>
<td>Bond Distances (Å)</td>
<td>Angles (°)</td>
<td>Frequencies (cm⁻¹)</td>
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<td>-----------------</td>
<td>----------</td>
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</tr>
<tr>
<td>TS2 ((^2\text{A}'))</td>
<td>planar C(_s)</td>
<td>(r(\text{H-O})= 1.470)</td>
<td>2.234</td>
<td>134.0</td>
<td>(-1255) (a')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{O-Si})= 1.590)</td>
<td>6.843</td>
<td>299</td>
<td>(a')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{Si-O})= 1.514)</td>
<td>6.517</td>
<td>333</td>
<td>(a'')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{H-O-Si})= 62.76°)</td>
<td></td>
<td></td>
<td>882</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{H-Si-O})= 153.41°)</td>
<td></td>
<td></td>
<td>1287</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
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<td>1825</td>
</tr>
<tr>
<td>HSiO(_2) ((^2\text{B}_2))</td>
<td>planar C(_{2v})</td>
<td>(r(\text{H-Si})= 1.468)</td>
<td>3.352</td>
<td>36.23</td>
<td>307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{Si-O})= 1.565)</td>
<td>8.982</td>
<td>546</td>
<td>(b(_2))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{O-Si-O})= 115.81°)</td>
<td>7.198</td>
<td>573</td>
<td>(b(_1))</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>912</td>
</tr>
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<td>1020</td>
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<td>2298</td>
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<tr>
<td>TS3 ((^2\text{A}'))</td>
<td>planar C(_s)</td>
<td>(r(\text{H-O})= 1.882)</td>
<td>0.315</td>
<td>299.9</td>
<td>(-596) (a')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{O-Si})= 1.523)</td>
<td>6.175</td>
<td>83</td>
<td>(a')</td>
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<tr>
<td></td>
<td></td>
<td>(r(\text{Si-O})= 1.513)</td>
<td>6.051</td>
<td>293</td>
<td>(a'')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{H-O-Si})= 137.41°)</td>
<td></td>
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<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{O-Si-O})= 175.53°)</td>
<td></td>
<td></td>
<td>955</td>
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<td></td>
<td>1402</td>
</tr>
<tr>
<td>HSiOO ((^2\text{A}'))</td>
<td>planar C(_s)</td>
<td>(r(\text{H-Si})= 1.518)</td>
<td>2.273</td>
<td>90.86</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{Si-O})= 1.692)</td>
<td>5.952</td>
<td>253</td>
<td>(a'')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r(\text{O-O})= 1.319)</td>
<td>5.586</td>
<td>643</td>
<td>(a')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{H-Si-O})= 89.63°)</td>
<td></td>
<td></td>
<td>824</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\angle(\text{Si-O-O})= 133.5°)</td>
<td></td>
<td></td>
<td>1156</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>2053</td>
</tr>
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</table>
The molecular parameters at the B3LYP/6-311+G(2d,p) level of theory and heats of formation at the CBS-Q level of theory for SiO, SiO₂, SiH, SiH₂(1A₁) and SiC were benchmarked against experimental data in the ESI of Part I of this series.¹ The accuracy of the ab initio results is stated following the convention of the CCCBDB-NIST database.² This is also broadly consistent with the accuracy of the experimental data reported for the silicon benchmarking species.¹ The geometric parameters: \( r \) in Å and \( \angle \) in degrees. Geometrical parameters:

<table>
<thead>
<tr>
<th>Species</th>
<th>( r(\text{H-Si}) )</th>
<th>( r(\text{Si-O}) )</th>
<th>( r(\text{O-O}) )</th>
<th>( \angle(\text{H-Si-O}) )</th>
<th>( \angle(\text{Si-O-O}) )</th>
<th>( \text{Heat of Formation} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>planar ( C_3 )</td>
<td>1.524</td>
<td>1.675</td>
<td>1.427</td>
<td>91.85°</td>
<td>93.60°</td>
<td>(-357 ) (( a' ))</td>
</tr>
<tr>
<td>TS4 (( ^2\text{A}' ))</td>
<td>2.403</td>
<td>8.536</td>
<td>6.965</td>
<td>798 (( a' ))</td>
<td>922 (( a' ))</td>
<td>1992 (( a' ))</td>
</tr>
</tbody>
</table>

The symmetry of the vibration is shown in parenthesis. Geometrical parameters: \( r \) in Å and \( \angle \) in degrees. Geometrical parameters:

\[ r(\text{H-Si})= 1.524 \quad 2.403 \quad 37.85 \quad -357 \quad (a') \quad 200.2 \]
\[ r(\text{Si-O})= 1.675 \quad 8.536 \quad 602 \quad (a'') \]
\[ r(\text{O-O})= 1.427 \quad 6.965 \quad 692 \quad (a') \]
\[ \angle(\text{H-Si-O})= 91.85^\circ \quad 798 \quad (a') \]
\[ \angle(\text{Si-O-O})= 93.60^\circ \quad 922 \quad (a') \]
\[ 1992 \quad (a') \]

References:


Figure S1. Stationary points on the SiO + OH potential surface, using the data in Table S1.
Table 2. Calculated molecular parameters (B3LYP/6-311+G(2d,p)) and heats of formation (CBS-Q) for stationary points on the SiO + H2O potential energy surface

<table>
<thead>
<tr>
<th>Species</th>
<th>Geometry</th>
<th>Dipole moment</th>
<th>Rotational constants</th>
<th>Vibrational frequencies</th>
<th>$\Delta H_f^{\circ}(0 \text{ K})$ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS5 ($^1$A)</td>
<td></td>
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</tr>
<tr>
<td>C$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(OH)$_2$ ($^1$A')</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>planar C$_s$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(H-O)= 0.967</td>
<td>2.996</td>
<td>19.23</td>
<td>-1358 (a)</td>
<td>-330.8</td>
<td></td>
</tr>
<tr>
<td>$r$(O-Si)=1.966</td>
<td>10.11</td>
<td></td>
<td>418 (a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(Si-O)=1.583</td>
<td>6.712</td>
<td></td>
<td>474 (a)</td>
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<td></td>
</tr>
<tr>
<td>$r$(O-H)= 1.343</td>
<td></td>
<td></td>
<td>692 (a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\angle$(H-O-Si)= 123.87°</td>
<td>696 (a)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\angle$(O-Si-O)= 79.43°</td>
<td>1064 (a)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\angle$(Si-O-H)= 80.16°</td>
<td>1315 (a)</td>
<td></td>
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</tr>
<tr>
<td>$\angle$(H-SiO)= -113.1°</td>
<td>1912 (a)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3800 (a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(H-O)= 1.267</td>
<td>1.826</td>
<td>26.08</td>
<td>321 (a')</td>
<td>-498.3</td>
<td></td>
</tr>
<tr>
<td>$r$(O-Si)=1.652</td>
<td>8.834</td>
<td></td>
<td>443 (a'')</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r$(Si-O)=1.675</td>
<td>6.599</td>
<td></td>
<td>515 (a'')</td>
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<td></td>
</tr>
<tr>
<td>$r$(O-H)= 0.963</td>
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<td>778 (a')</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\angle$(H-O-Si)= 117.4°</td>
<td>797 (a')</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\angle$(O-Si-O)= 126.8°</td>
<td>832 (a')</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\angle$(Si-O-H)= 116.9°</td>
<td>893 (a')</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3794 (a')</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3859 (a')</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Units as indicated in the footnote to Table S1.
Figure S2. Stationary points on the SiO + H2O potential surface, using the data in Table S2.
Table S3. Calculated molecular parameters (B3LYP/6-311+G(2d,p)) and heats of formation (CBS-Q) of stationary points on the SiO₂ + O potential energy surface

<table>
<thead>
<tr>
<th>Species</th>
<th>Geometry</th>
<th>Dipole moment</th>
<th>Rotational constants</th>
<th>Vibrational frequencies</th>
<th>ΔHf°(0 K) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS6 (3A&quot;)</td>
<td>planar Cs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r(O-O)= 1.702</td>
<td>1.760</td>
<td>21.960</td>
<td>-773 (a')</td>
<td></td>
<td>57.6</td>
</tr>
<tr>
<td>r(O-Si)= 1.591</td>
<td>3.545</td>
<td>111 (a')</td>
<td>324 (a')</td>
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<td></td>
</tr>
<tr>
<td>r(Si-O)= 1.518</td>
<td>3.052</td>
<td>225 (a&quot;)</td>
<td>787 (a')</td>
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<td></td>
</tr>
<tr>
<td>∠(O-O-Si)= 118.89°</td>
<td></td>
<td></td>
<td>1265 (a')</td>
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<td></td>
</tr>
<tr>
<td>∠(O-Si-O)= 151.76°</td>
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</tr>
<tr>
<td>TS7 (3A)</td>
<td>C₁</td>
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</tr>
<tr>
<td>r(O-O)= 1.348</td>
<td>2.305</td>
<td>28.769</td>
<td>-160 (a)</td>
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<td>-18.8</td>
</tr>
<tr>
<td>r(O-Si)= 1.756</td>
<td>3.788</td>
<td>78 (a)</td>
<td>624 (a)</td>
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<tr>
<td>r(Si-O)= 1.529</td>
<td>3.669</td>
<td>252 (a)</td>
<td>1092 (a)</td>
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<tr>
<td>∠(O-O-Si)= 100.6°</td>
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<tr>
<td>∠(O-Si-O)= 120.8°</td>
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</tr>
<tr>
<td>∠(OOSi-O)= 126.1°</td>
<td></td>
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</tr>
<tr>
<td>TS8 (1A)</td>
<td>C₁</td>
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<tr>
<td>r(O-O)= 1.391</td>
<td>2.853</td>
<td>24.568</td>
<td>-317 (a)</td>
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<td>-7.1</td>
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<tr>
<td>r(O-Si)= 1.664</td>
<td>4.074</td>
<td>99 (a)</td>
<td>634 (a)</td>
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<tr>
<td>r(Si-O)= 1.519</td>
<td>3.610</td>
<td>165 (a)</td>
<td>913 (a)</td>
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<tr>
<td>∠(O-O-Si)= 104.5°</td>
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<tr>
<td>∠(O-Si-O)= 143.1°</td>
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</tr>
<tr>
<td>∠(OOSi-O)= -70.96°</td>
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</tr>
<tr>
<td></td>
<td>( r(\text{O-Si}) )</td>
<td>( r(\text{O-Si}) )</td>
<td>( \angle(\text{O-Si-O}) )</td>
<td>258</td>
<td>(( a_1 ))</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>-----------------------------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>( \text{OSiO}_2 \left( ^3B_1 \right) )</td>
<td>1.511</td>
<td>1.556</td>
<td>13.180</td>
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<tr>
<td>( C_{2v} )</td>
<td>1.632</td>
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<td>6.269</td>
<td>282</td>
<td>(( b_2 ))</td>
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<td>4.249</td>
<td>288</td>
<td>(( b_1 ))</td>
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<td>843</td>
<td>(( a_1 ))</td>
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<td>918</td>
<td>(( b_2 ))</td>
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<td></td>
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<td>1301</td>
<td>(( a_1 ))</td>
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</tbody>
</table>

\(^a\) Units as indicated in the footnote to Table S1.
Figure S4. Stationary points on the SiO$_2$ + O potential surface, using the data in Table S3.