Theoretical Studies of the RSOO, ROSO, RSO₂ and HOOS (R = H, CH₃) Radicals

Dianna Laakso, C. E. Smith, A. Goumri, John-David R. Rocha and Paul Marshall

Department of Chemistry, University of North Texas

P.O. Box 5068, Denton, Texas 76203-5068, USA

Abstract:

The geometries of the radicals HSOO, HOSO, HSO₂ and HOOS have been optimized at the MP2=FULL/6-31G* level, and energies obtained with Gaussian-2 theory. Internal rotations and vibrational frequencies are analyzed. The results yield values of ΔHᵣ,298 for the four doublet radicals of 111.5, -241.4, -141.4 and 58.9 kJ mol⁻¹, respectively. Implications for reactions of interest in combustion and atmospheric chemistry are discussed. The results are employed to derive ΔHᵣ,₀ for CH₃SOO, CH₃OSO and CH₃SO₂ of 91.8, -222.6 and -199.4 kJ mol⁻¹, respectively. The calculated CH₃S-OO bond strength is in excellent accord with a recent measurement.
1. Introduction

SH radicals are a major product of H$_2$S oxidation, but their fate in flames or in the atmosphere is unclear [1]. One reaction pathway that has been considered is formation of thiyperoxyl radicals:

$$\text{SH} + \text{O}_2 \rightarrow \text{HSO}$$  \hspace{1cm} (1)

At room temperature the reaction of SH with O$_2$ to any products is very slow [2], and only an upper limit to the recombination rate constant $k_1$ of $< 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ is available at 298 K [3], based on the assumption that the reverse reaction is negligible (this in fact is probably not the case, as argued below). By contrast, the analogous reaction of CH$_3$S to form methanethiyperoxyl

$$\text{CH}_3\text{S} + \text{O}_2 \rightarrow \text{CH}_3\text{SO}$$  \hspace{1cm} (2)

has been characterized both theoretically and experimentally [4][5][6][7]. Modified Gaussian-1 (G1) theory yielded a binding energy at 298 K of about 37 kJ mol$^{-1}$ for the peroxyl adduct [6], in accord with the measured value of 49 kJ mol$^{-1}$ [7]. Here the thermochemistry of reaction (1), which has not been analyzed previously, is investigated at the G2 level of calculation, and the results then employed to analyze reaction (2).

This same approach is applied to the HOSO (hydroxysulfinyl, sulfonyl or sulfur hydroxide oxide) and HSO$_2$ (sulfinyl or sulfur hydride oxide) radicals, which are thought to be important in the SO$_2$-catalyzed removal of H atoms in flames [8], and are possible products of the reactions of HSO with NO$_2$ and O$_3$ [9][10]. If the second reaction is exothermic then it may participate in the atmospheric chemistry of sulfur, where the cycle HS + O$_3 \rightarrow$ HSO + O$_2$ and HSO + O$_3 \rightarrow$ HS + 2 O$_2$ has been suggested as a potential route for removal of odd
oxygen [11]. HSO₂ has been identified by ESR spectroscopy [12], while HOSO and HSO₂ have been the subject of earlier \textit{ab initio} studies [13][14][15], carried out with limited basis sets. Here the thermochemistry of HOSO, HSO₂ and their methyl analogues, which have been investigated very recently [16], is derived.

We also characterize the novel HOOS radical for the first time. For all four isomers MP2/6-31G* vibrational frequencies and G2 barriers to internal rotation are characterized.

2. Methodology

Geometries and vibrational frequencies for the doublet sulfur species, scaled by the usual factors of 0.893 (HF) and 0.95 (MP2), were calculated with spin-unrestricted HF/6-31G*, MP2=FULL/3-21G(*) and MP2=FULL/6-31G* theories using standard methods [17][18] implemented with the GAUSSIAN90 and 92 programs [19][20]. The MP2=FULL results include a partial correction for electron correlation effects with all orbitals active. The zero-point vibrational energy ΔE(ZPE) was derived from the MP2=FULL/6-31G* frequencies\#1, and the HF wavefunctions were verified to be stable [21] at the MP2=FULL/6-31G* geometries.

Approximate QCISD(T)/6-311+G(3df,2p) energies were calculated at these geometries using the Gaussian-2 (G2) methodology [22][23][24]. Briefly, the MP4/6-311G** energy is modified with a series of additive corrections defined as follows: ΔE(+) = E(MP4/6-311+G**) - E(MP4/6-311G**), ΔE(2df) = E(MP4/6-311G**(2df)) - E(MP4/6-311G**), ΔE(QCI) = E(QCISD(T)/6-311G**) - E(MP4/6-311G**) and ΔE(HLC) = -0.00019 n_{unpair} -

\#1 This is a modification to the original G2 method based instead on HF/6-31G* frequencies.
0.00614 \text{n}_{\text{pair}} \text{ au} (1 \text{ au} \approx 2625 \text{ kJ mol}^{-1})$, where $n_{\text{unpair}}$ and $n_{\text{pair}}$ represent the numbers of unpaired valence electrons and valence pairs, respectively. The G1 energy is defined as $E(\text{G1}) = E(\text{MP4/6-311G}^{**}) + \Delta E(+) + \Delta E(2\text{df}) + \Delta E(\text{QCI}) + \Delta E(\text{HLC}) + \Delta E(\text{ZPE})$. The further term $\Delta = E(\text{MP2/6-311+G(3df,2p)}) - E(\text{MP2/6-311G}^{**}(2\text{df}) - E(\text{MP2/6-311+G}^{**}) + E(\text{MP2/6-311G}^{**})$ leads to the G2 energy as $E(\text{G2}) = E(\text{G1}) + \Delta + 0.00114 \text{n}_{\text{pair}} \text{ au}$. The spin contamination in the systems studied here is negligible.

3. **Results and Discussion**

3.1 **Geometries and Internal Motions**

Figure 1 shows the molecular geometries obtained with MP2=FULL/3-21G*, HF/6-31G* and MP2=FULL/6-31G* theories. For the two molecules with cis and trans isomers the lowest energy form is shown, although the uncertainty of the energy calculations means this assignment is not definitive. Generally the MP2=FULL/6-31G* bond lengths fall between those estimated at the other levels, and we consider them the most reliable and employ them in the calculations below, although it should be noted that lengths of multiple bonds in these open shell systems are probably less certain than the single bond lengths.

The staggered structure for HSOO is analogous to that reported recently by McKee [6] for CH$_3$SOO, with a similar overlap of half-occupied p orbitals on S and O to form a $\sigma$ S-O bond, and the unpaired electron spin density is located largely on the terminal O atom. The S-O bond is significantly extended compared to a normal $\sigma$ bond, with an MP2=FULL/6-31G* length of 1.75 Å cf the experimental value of 1.57 Å for the single S-O bonds in H$_2$SO$_4$ [25], while the O-O distance of 1.31 Å indicates some multiple bond character and falls
between those measured for O₂ (1.21 Å) and H₂O₂ (1.48 Å) [26]. The barrier E₀ to rotation about the S-O bond was investigated by optimizing the geometry at the rotational transition state (TS) and calculating E₀ as the increase in E(G2), excluding the ΔE(ZPE) terms. The results are listed in Table 1, and show there is almost free rotation about the S-O bond. Vibrational data are summarized in Table 2, where the dominant contributions to each normal mode were visualized with the NorMode program [27]. The most reliable results are probably those obtained at the MP2=FULL/6-31G* level, although it may be seen that for the purpose of, e.g., estimating ΔE(ZPE) generally similar results would be obtained with the other, less computationally expensive, methods.

The HF/6-31G* and MP2=FULL/3-21G* geometries of HOSO and HSO₂ have been discussed previously. The HF minimum is staggered but when electron correlation is taken into account the minimum energy MP2 conformation of HOSO is predicted to be cis, with a trans TS for internal rotation. The central S-O separation of 1.66 Å at the MP2=FULL/6-31G* level is closer to that of a normal σ bond than the distance in HSOO, and is consistent with the modest rotational barrier (Table 1). The other S-O distance of 1.48 Å is close to the experimental value of 1.43 Å for SO₂ [26], that corresponds to a partial ψ bond. The spin density is located at the S and terminal O atoms. The S-O distance in HSO₂ of 1.48 Å is consistent with a degree of multiple bonding, and the spin density is spread across the S and both O atoms.

HOOS is a second example where HF theory predicts a staggered minimum energy geometry but MP2 theory supports a planar, in this case trans, structure. All the bond lengths agree with those expected for single σ bonds, consistent with the small barrier to rotation about the O-O bond, and the spin density is localized at the S atom.
3.2 Thermochemistry

Table 3 summarizes the components of the G2 energy for each radical. The original G2 approach yielded atomization enthalpies $\Delta H_a$ with a target accuracy of $\pm 8$ kJ mol$^{-1}$ and an average absolute deviation of $5$ kJ mol$^{-1}$ [24]. These $\Delta H_a$ can be combined with experimental enthalpies of formation $\Delta H_f$ for atoms to obtain molecular $\Delta H_f$. However, because the G2 $\Delta H_a$ for SO$_2$ is in significant error, by $21$ kJ mol$^{-1}$ [24], we instead analyze the following gas-phase processes:

\begin{align*}
\text{radical} & \rightarrow \text{SO}_2 + \text{H} \\
\text{radical} & \rightarrow \text{SO} + \text{OH} \\
\text{radical} & \rightarrow \text{SH} + \text{O}_2 \\
\text{radical} + 2\frac{1}{2} \text{H}_2 & \rightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O}
\end{align*}

All internal modes are treated as vibrations to obtain the changes in G2 energy $^\#$, which correspond to the enthalpy change at 0 K, $\Delta H_0$. For each process $\Delta H_{f,0}\text{(radical)}$ is obtained from $\Delta H_0$ and the measured $\Delta H_{f,0}$ of the other 1-3 atom species taken from the JANAF tables [28]. For SH we employ the enthalpy data of Nicovich et al. [29] which are consistent with other recent determinations [30][31]. Because $<S^2> = 0.76 - 0.78$, close to the ideal value of $0.75$ for the doublet sulfur radicals, we do not expect spin-contamination to cause significant errors in the ab initio energies.

The means of the four $\Delta H_{f,0}$ estimates for each radical are shown in Table 4; their

$^\#$ G2 energies for the 1-3 atom species from ref. 24, modified to incorporate $\Delta E$(ZPE) at the scaled MP2=FULL/6-31G* rather than HF/6-31G* level, are: $-548.01664$ (SO$_2$), $-0.50000$ (H), $-472.82978$ ($^3$SO), $-75.64394$ (OH), $-398.28687$ (SH), $-150.14922$ ($^3$O$_2$), $-1.16600$ (H$_2$), $-398.93048$ (H$_2$S) and $-76.33216$ (H$_2$O), in au.
standard deviations are 4.3 kJ mol\(^{-1}\) in each case. \(S_{298}, C_{p,298}\) and enthalpy corrections to 298 K are calculated via statistical mechanics, with the torsional modes in HSOO, HOSO and HOOS treated as hindered internal rotors and thermochemical properties interpolated from tables [32]. To use these tables, which apply only to symmetrical barriers, the barriers for HSOO are averaged to 2.5 kJ mol\(^{-1}\) and two-fold symmetry imposed.

There are no experimental enthalpies of formation for these radicals, although a recommendation for atmospheric modeling, based on HF/STO-3G(*) calculations by Boyd et al. [14], of \(\Delta H_{f,298}(\text{HSO}_2) = -222\ \text{kJ mol}^{-1}\) [33] appears to be significantly too negative. We believe our result is more accurate because of the much larger basis sets used here, and because electron correlation is taken into account. The reliability of the estimated \(\Delta H_0\) is checked by comparison with three known enthalpy changes. The G2 \(\Delta H_0\) for \(\text{SH} + \text{O}_2 \rightarrow \text{SO}_2 + \text{H}\) is -211.4 kJ mol\(^{-1}\) \(\text{cf}\) the experimental result -220.8 ± 3.0 kJ mol\(^{-1}\), the G2 \(\Delta H_0\) for \(\text{SH} + \text{O}_2 \rightarrow \text{SO} + \text{OH}\) is -98.8 kJ mol\(^{-1}\) \(\text{cf}\) the experimental value -99.1 ± 3.0 kJ mol\(^{-1}\), and the G2 \(\Delta H_0\) for \(\text{SO}_2 + 3 \text{H}_2 \rightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O}\) is -210.4 kJ mol\(^{-1}\) \(\text{cf}\) the experimental value -201.1 ± 0.8 kJ mol\(^{-1}\). Based on these comparisons we suggest approximate error limits of at least ±10 kJ mol\(^{-1}\) for our derived radical \(\Delta H_{f,298}\) in Table 4. Data are quoted to one decimal place to avoid accumulation of roundoff errors, without implication of this degree of accuracy.

The radical heats of formation can be combined with data for 1-3 atom species to obtain numerous bond dissociation enthalpies \(\Delta H_{298}\). Here we focus on plausible low energy dissociations. HOOS is predicted to be 14.9 kJ mol\(^{-1}\) endothermic with respect to \(\text{SO} + \text{OH}\) at 298 K, and therefore is likely to isolable only if there is a significant barrier to this dissociation. By contrast \(\Delta H_{298}(\text{H-OSO})\) and \(\Delta H_{298}(\text{H-SO}_2)\) are 162.6 and 62.6 kJ mol\(^{-1}\), respectively. These
values are 50-90 kJ mol\(^{-1}\) greater than predicted previously with MP4/6-31G* theory [15], and demonstrate the importance of large basis sets in the description of bonding in the sulfur species considered here. Both species, especially HOSO, are sufficiently stable to participate as intermediates in sulfur-containing flames, although the predicted H + SO\(_2\) binding energies are significantly lower than the values between 200 and 264 kJ mol\(^{-1}\) suggested from flame models [34][35][36].

\(\Delta H_{298}(\text{HS-OO})\) is predicted to be 31.5 kJ mol\(^{-1}\), somewhat less than the measured \(\Delta H_{298}(\text{CH}_3\text{S-OO}) = 49.0 \pm 3.8\) kJ mol\(^{-1}\) [7], with a corresponding \(K_p\) for reaction (1) of 0.23 at 298 K. Thus at this temperature in 1 atm of air only about 5% of SH will be complexed with O\(_2\) at equilibrium, which explains the failure to date to observe reaction (1) in the laboratory. We estimate that the temperature would have to be lowered to about 240 K, with \(p(\text{O}_2) \approx 0.2\) atm, before half the SH can be removed by adduct formation. The extent of SH complexation is highly sensitive to \(\Delta H_{298}(\text{HS-OO})\) and temperature and, therefore, considerably larger values of \(K_p\) are possible in the troposphere. Possible roles of the analogous CH\(_3\)SOO adduct in atmospheric chemistry have been discussed by Turnipseed \textit{et al.} [7]. In particular, it should be noted that our analysis does not rule out participation of HSOO as a transient intermediate in further reactions, and these might lead to different products from the reactions of SH itself. Such further reactions of HSOO could be the dominant pathway for SH oxidation if a large fraction is complexed with O\(_2\), and therefore cannot be removed by the SH + O\(_3\) reaction.

One of the products of the reactions of HSO with O\(_3\) and NO\(_2\) is thought to be "HSO\(_2\)" of indeterminate structure [9][10][37]. Use of a recent value for \(\Delta H_{4,0}(\text{HSO})\) of -3.8 ± 2.9 kJ mol\(^{-1}\) [38] leads to \(\Delta H_0(\text{O-O})\) in HSOO of 127.2 kJ mol\(^{-1}\) at 0 K, so that the long O-O
bond is seen to be weak. $\Delta H_0(S-O)$ is predicted to be 378.1 kJ mol$^{-1}$ in HSOO. $\Delta H_0(O-O_2) = 101.5$ kJ mol$^{-1}$ and $\Delta H_0(O-NO) = 300.7$ kJ mol$^{-1}$ [28], so that in the ozone reaction both HSOO and HSO$_2$ are thermochemically plausible products, but in the nitrogen dioxide experiments only HSO$_2$ could be generated. $\Delta H_0(O-N_2) = 161.3$ kJ mol$^{-1}$ [28] and thus formation of HSO$_2$ from HSO + N$_2$O is also exothermic. Nitrous oxide might therefore provide a fast pathway to HSO$_2$ because SH + N$_2$O → HSO + N$_2$ and the subsequent consumption of HSO by N$_2$O are both rapid [39].

It should be noted that the atmospheric and combustion chemistry of e.g. SH + O$_2$ and H + SO$_2$ will be determined not only by the thermochemistry of the adducts reported here but also the presence of barriers to recombination and isomerization. Transition states for these processes are currently being investigated.

Next we analyze the thermochemistry of the methyl analogues of the three most stable sulfur radicals, which may play roles in atmospheric chemistry [1]. For

$$\text{H + CH}_3\text{SOO} \rightarrow \text{CH}_3 + \text{HSOO} \quad (7)$$

the $\Delta H_0$, based on MP4/6-311G** energies and scaled MP2/6-31G* frequencies [6], is -89.9 kJ mol$^{-1}$. This energy difference should be fairly reliable because the bonding around S and O is similar for reactants and products, and so errors arising from inadequate basis sets or treatments of correlation will largely cancel. Combination of this $\Delta H_0$ with $\Delta H_{f,0}$ for HSOO (Table 4), H and CH$_3$ [28] leads to $\Delta H_{f,0}(\text{CH}_3\text{SOO}) = 91.8$ kJ mol$^{-1}$, in excellent accord with the experimental value of 87.9 ± 4.6 kJ mol$^{-1}$ [7]. The $\Delta H_{f,0}(\text{CH}_3\text{S})$ of 131.5 ± 2.3 kJ mol$^{-1}$ [29] implies $\Delta H_0(S-O) = 39.7$ kJ mol$^{-1}$, in close agreement with the measured value of 43.5 ± 3.8 kJ mol$^{-1}$ [7]. Thus reactions like (7), combined with G2 values for the parent HSOO radical,
seem promising for estimating the thermochemistry of larger species at much less computational expense than a complete G2 calculation.

We extend this method to CH$_3$OSO and CH$_3$SO$_2$ via the processes

\[
\begin{align*}
\text{H} + \text{CH}_3\text{OSO} & \rightarrow \text{CH}_3 + \text{HOSO} \\
\text{H} + \text{CH}_3\text{SO}_2 & \rightarrow \text{CH}_3 + \text{HSO}_2
\end{align*}
\]  

(8) (9)

for which, based on PMP4/6-311G** energies and MP2/6-31G* frequencies [16], $\Delta H_0$ is -89.9 and -2.7 kJ mol$^{-1}$, respectively. Our $\Delta H_{f,0}$ values for HOSO and HSO$_2$ thus imply $\Delta H_{f,0}(\text{CH}_3\text{OSO}) = -222.6$ kJ mol$^{-1}$ and $\Delta H_{f,0}(\text{CH}_3\text{SO}_2) = -199.4$ kJ mol$^{-1}$. The corresponding bond dissociation enthalpies are $D_0$(C-O) = 77.3 kJ mol$^{-1}$ and $D_0$(C-S) = 54.1 kJ mol$^{-1}$. Studies of CH$_3$ + SO$_2$ adduct [40][41] lead to bond strengths of 72 and 84 ± 8 kJ mol$^{-1}$ at 298 K [42]. The nature of the adduct was not determined: there is good accord with experiment if the thermodynamic product CH$_3$OSO was formed. The sulfinyl CH$_3$ + SO$_2$ adduct bonded through S shows a similar dissociation enthalpy to HSO$_2$, whereas the sulfonyl adduct bonded through O is less tightly bound than its H-atom analogue.

4. Conclusions

Geometries, vibrational frequencies and internal rotations for HSOO, HOSO, HSO$_2$ and HOOS have been characterized, and enthalpies of formation for the four isomers have been derived by means of G2 theory. Combination with other thermochemical data shows that the adduct formed between HS and O$_2$ is too weakly bound to observe easily at room temperature, although adduct formation may be important at lower temperatures in the troposphere where HSOO could be an intermediate in further reactions. HOSO and HSO$_2$ may bind atomic H
strongly enough to be important in SO₂-containing flames. The thermochemistry of HSO reactions with O₃, NO₂ and N₂O indicates that only the first could form HSOO exothermically, while all three could produce HSO₂. The enthalpies of formation of CH₃SOO, CH₃OSO and CH₃SO₂ have also been derived; the agreement with experiment for the first species is excellent.

Acknowledgments

We thank the R. A. Welch Foundation (Grant B-1174), the NSF Pittsburgh Supercomputing Center (Grant CHE900059P) and the UNT Faculty Research Fund for their support.
REFERENCES


19. M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, GAUSSIAN90 (Gaussian, Pittsburgh, 1990).


27. M. Scheutz, S. Perego and S. Leutwyler, University of Berne, personal communication.


Table 1
Barriers to Internal Rotation*

<table>
<thead>
<tr>
<th>Minimum energy conformation</th>
<th>Barrier(s), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staggered HSOO</td>
<td>2.4 (cis) and 2.6 (trans)</td>
</tr>
<tr>
<td>cis-HOSO</td>
<td>7.9 (trans)</td>
</tr>
<tr>
<td>trans-HOOS</td>
<td>2.4 (cis)</td>
</tr>
</tbody>
</table>

*Calculated with G2 theory, excluding zero-point vibrational energies.
Table 2: Vibrational Frequencies

<table>
<thead>
<tr>
<th>Species</th>
<th>Mode</th>
<th>Sym.</th>
<th>HF/6-31G**</th>
<th>MP2=FULL/3-21G**b</th>
<th>MP2=FULL/6-31G**b</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSOO</td>
<td>torsion</td>
<td>A</td>
<td>242</td>
<td>263</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>SOO bend</td>
<td>A</td>
<td>427</td>
<td>398</td>
<td>397</td>
</tr>
<tr>
<td></td>
<td>SO stretch</td>
<td>A</td>
<td>726</td>
<td>639</td>
<td>631</td>
</tr>
<tr>
<td></td>
<td>HSO bend</td>
<td>A</td>
<td>981</td>
<td>937</td>
<td>909</td>
</tr>
<tr>
<td></td>
<td>OO stretch</td>
<td>A</td>
<td>1062</td>
<td>1514</td>
<td>1099</td>
</tr>
<tr>
<td></td>
<td>SH stretch</td>
<td>A</td>
<td>2606</td>
<td>2617</td>
<td>2635</td>
</tr>
<tr>
<td>HOSO</td>
<td>torsion</td>
<td>A'</td>
<td>142i*</td>
<td>102</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>OSO bend</td>
<td>A'</td>
<td>382</td>
<td>337</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td>SO stretch</td>
<td>A'</td>
<td>789</td>
<td>745</td>
<td>764</td>
</tr>
<tr>
<td></td>
<td>HOS bend</td>
<td>A'</td>
<td>1079</td>
<td>1047</td>
<td>1073</td>
</tr>
<tr>
<td></td>
<td>SO stretch</td>
<td>A'</td>
<td>1137</td>
<td>1409</td>
<td>1351</td>
</tr>
<tr>
<td></td>
<td>OH stretch</td>
<td>A'</td>
<td>3600</td>
<td>3285</td>
<td>3476</td>
</tr>
<tr>
<td>HSO₂</td>
<td>OSO scissor</td>
<td>A'</td>
<td>458</td>
<td>430</td>
<td>431</td>
</tr>
<tr>
<td></td>
<td>deformation</td>
<td>A'</td>
<td>845</td>
<td>814</td>
<td>810</td>
</tr>
<tr>
<td></td>
<td>OSO sym str</td>
<td>A'</td>
<td>1026</td>
<td>1074</td>
<td>1065</td>
</tr>
<tr>
<td></td>
<td>HSO bend</td>
<td>A''</td>
<td>1056</td>
<td>1187</td>
<td>1128</td>
</tr>
<tr>
<td></td>
<td>OSO asym str</td>
<td>A''</td>
<td>1248</td>
<td>2193</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>SH stretch</td>
<td>A'</td>
<td>2446</td>
<td>3231</td>
<td>2269</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>HOOS</td>
<td>torsion</td>
<td>A&quot;</td>
<td>63i</td>
<td>113</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>SO stretch</td>
<td>A'</td>
<td>396</td>
<td>390</td>
<td>392</td>
</tr>
<tr>
<td></td>
<td>SOO bend</td>
<td>A'</td>
<td>780</td>
<td>776</td>
<td>796</td>
</tr>
<tr>
<td></td>
<td>OO stretch</td>
<td>A'</td>
<td>989</td>
<td>1346</td>
<td>1353</td>
</tr>
<tr>
<td></td>
<td>HOO bend</td>
<td>A'</td>
<td>1413</td>
<td>2727</td>
<td>1727</td>
</tr>
<tr>
<td></td>
<td>OH stretch</td>
<td>A'</td>
<td>3635</td>
<td>3259</td>
<td>3508</td>
</tr>
</tbody>
</table>

*a* Frequency scaled by 0.893, in cm⁻¹.

*b* Frequency scaled by 0.95, in cm⁻¹.

*c* *cis*-HOSO and *trans*-HOOS are transition states for internal rotation at the HF/6-31G* level.
Table 3
Absolute energies of HSO₂ isomers calculated at the MP2=FULL/6-31G* optimized geometries

<table>
<thead>
<tr>
<th>Species</th>
<th>Sym.</th>
<th>State</th>
<th>MP4/6-311G**</th>
<th>ΔE(+)b</th>
<th>ΔE(2df)b</th>
<th>ΔE(QCI)b</th>
<th>ΔE(ZPE)b</th>
<th>Δb</th>
<th>E(G2)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSOO</td>
<td>C₁</td>
<td>2A</td>
<td>-548.25454</td>
<td>-12.11</td>
<td>-132.15</td>
<td>-4.18</td>
<td>+13.33</td>
<td>-10.68</td>
<td>-548.44552</td>
</tr>
<tr>
<td>cis-HOSO</td>
<td>C₃</td>
<td>2A&quot;</td>
<td>-548.37049</td>
<td>-16.71</td>
<td>-152.41</td>
<td>+1.88</td>
<td>+16.42</td>
<td>-13.55</td>
<td>-548.58006</td>
</tr>
<tr>
<td>HSO₂</td>
<td>C₃</td>
<td>2A'</td>
<td>-548.32363</td>
<td>-14.24</td>
<td>-163.08</td>
<td>+5.36</td>
<td>+16.64</td>
<td>-16.97</td>
<td>-548.54111</td>
</tr>
</tbody>
</table>

aIn au.
bComponent of G2 energy in 10⁻³ au. \( n_{pair} = 9 \) and \( n_{unpair} = 1 \), so that \( ΔE(HLC) = -0.05545 \) au for all isomers.
Table 4
Thermochemistry of HSO₂ isomers in the gas phase

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔHₚ₀,</th>
<th>H₂₉₈-H₀,</th>
<th>ΔH₂₉₈,</th>
<th>S₂₉₈,</th>
<th>Cₚ₂₉₈,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol⁻¹</td>
<td>kJ mol⁻¹</td>
<td>kJ mol⁻¹</td>
<td>J K⁻¹ mol⁻¹</td>
<td>J K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>HSOO</td>
<td>115.8</td>
<td>13.0</td>
<td>111.5</td>
<td>283.0</td>
<td>51.7</td>
</tr>
<tr>
<td>cis-HOSO</td>
<td>-237.4</td>
<td>13.3</td>
<td>-241.4</td>
<td>282.3</td>
<td>53.4</td>
</tr>
<tr>
<td>HSO₂</td>
<td>-135.1</td>
<td>11.0</td>
<td>-141.4</td>
<td>263.7</td>
<td>44.4</td>
</tr>
<tr>
<td>trans-HOOS</td>
<td>63.4</td>
<td>12.8</td>
<td>58.9</td>
<td>284.1</td>
<td>47.9</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 Geometries for HSO$_2$, HOOS, HSOO and HOSO calculated at three levels of theory: MP2=FULL/6-31G* (upper numbers), MP2=FULL/3-21G(*) (middle numbers) and HF/6-31G* (lower numbers). Distances in 10$^{-10}$ m and angles in degrees.