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 $\Delta H_{f,298}$ 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 $\Delta H_{f,0}$ 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_2S oxidation, but their fate in flames or in the atmosphere is unclear [1]. One reaction pathway that has been considered is formation of thiylperoxyl radicals:

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 $< 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ 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_3S to form methanethiylperoxyl

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 $\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$ and $\text{HSO} + \text{O}_3 \rightarrow \text{HS} + 2 \text{O}_2$ has been suggested as a potential route for removal of odd

oxygen [11]. HSO_2 has been identified by ESR spectroscopy [12], while HOSO and HSO_2 have been the subject of earlier *ab initio* studies [13][14][15], carried out with limited basis sets. Here the thermochemistry of HOSO , HSO_2 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 $\Delta\text{E(ZPE)}$ 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 $\text{QCISD(T)/6-311+G(3df,2p)}$ 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: $\Delta\text{E}(+) = \text{E}(\text{MP4/6-311+G}^{**}) - \text{E}(\text{MP4/6-311G}^{**})$, $\Delta\text{E}(2\text{df}) = \text{E}(\text{MP4/6-311G}^{**}(2\text{df})) - \text{E}(\text{MP4/6-311G}^{**})$, $\Delta\text{E(QCI)} = \text{E}(\text{QCISD(T)/6-311G}^{**}) - \text{E}(\text{MP4/6-311G}^{**})$ and $\Delta\text{E(HLC)} = (-0.00019 n_{\text{unpair}} -$

^{#1} This is a modification to the original G2 method based instead on HF/6-31G^* frequencies.

0.00614 n_{pair} au ($1 \text{ au} \approx 2625 \text{ kJ mol}^{-1}$), where n_{unpair} and n_{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 $\Delta = E(\text{MP2/6-311+G}(3\text{df},2\text{p})) - E(\text{MP2/6-311G}^{**}(2\text{df}) - E(\text{MP2/6-311+G}^{**}) + E(\text{MP2/6-311G}^{**})$ leads to the G2 energy as $E(\text{G2}) = E(\text{G1}) + \Delta + 0.00114 n_{\text{pair}} \text{ au}$. 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 CH₃SOO, with a similar overlap of half-occupied p orbitals on S and O to form a σ 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 σ bonds, 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 H₂SO₄ [25], while the O-O distance of 1.31 Å indicates some multiple bond character and falls

between those measured for O_2 (1.21 Å) and H_2O_2 (1.48 Å) [26]. The barrier E_0 to rotation about the S-O bond was investigated by optimizing the geometry at the rotational transition state (TS) and calculating E_0 as the increase in $E(\text{G2})$, excluding the $\Delta E(\text{ZPE})$ 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 $\Delta E(\text{ZPE})$ 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 HSO_2 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 SO_2 [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 HSO_2 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 ΔH_a with a target accuracy of ± 8 kJ mol⁻¹ and an average absolute deviation of 5 kJ mol⁻¹ [24]. These ΔH_a can be combined with experimental enthalpies of formation ΔH_f for atoms to obtain molecular ΔH_f . However, because the G2 ΔH_a for SO₂ is in significant error, by 21 kJ mol⁻¹ [24], we instead analyze the following gas-phase processes:

All internal modes are treated as vibrations to obtain the changes in G2 energy ^{#2}, which correspond to the enthalpy change at 0 K, ΔH_0 . For each process $\Delta H_{f,0}(\text{radical})$ is obtained from ΔH_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 $\langle S^2 \rangle = 0.76 - 0.78$, 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

^{#2} G2 energies for the 1-3 atom species from ref. 24, modified to incorporate $\Delta E(\text{ZPE})$ at the scaled MP2=FULL/6-31G* rather than HF/6-31G* level, are: -548.01664 (SO₂), -0.50000 (H), -472.82978 (³SO), -75.64394 (OH), -398.28687 (SH), -150.14922 (³O₂), -1.16600 (H₂), -398.93048 (H₂S) and -76.33216 (H₂O), 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 ΔH_0 is checked by comparison with three known enthalpy changes. The G2 ΔH_0 for $\text{SH} + \text{O}_2 \rightarrow \text{SO}_2 + \text{H}$ is $-211.4 \text{ kJ mol}^{-1}$ *cf* the experimental result $-220.8 \pm 3.0 \text{ kJ mol}^{-1}$, the G2 ΔH_0 for $\text{SH} + \text{O}_2 \rightarrow \text{SO} + \text{OH}$ is $-98.8 \text{ kJ mol}^{-1}$ *cf* the experimental value $-99.1 \pm 3.0 \text{ kJ mol}^{-1}$, and the G2 ΔH_0 for $\text{SO}_2 + 3 \text{H}_2 \rightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O}$ is $-210.4 \text{ kJ mol}^{-1}$ *cf* the experimental value $-201.1 \pm 0.8 \text{ kJ mol}^{-1}$. Based on these comparisons we suggest approximate error limits of at least $\pm 10 \text{ kJ mol}^{-1}$ 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 DH_{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 be isolable only if there is a significant barrier to this dissociation. By contrast $\text{DH}_{298}(\text{H-OSO})$ and $\text{DH}_{298}(\text{H-SO}_2)$ 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 + SO₂ binding energies are significantly lower than the values between 200 and 264 kJ mol⁻¹ suggested from flame models [34][35][36].

DH₂₉₈(HS-OO) is predicted to be 31.5 kJ mol⁻¹, somewhat less than the measured DH₂₉₈(CH₃S-OO) = 49.0 ± 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 O₂ 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(O₂) ≈ 0.2 atm, before half the SH can be removed by adduct formation. The extent of SH complexation is highly sensitive to DH₂₉₈(HS-OO) and temperature and, therefore, considerably larger values of K_p are possible in the troposphere. Possible roles of the analogous CH₃SOO adduct in atmospheric chemistry have been discussed by Turnipseed *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 O₂, and therefore cannot be removed by the SH + O₃ reaction.

One of the products of the reactions of HSO with O₃ and NO₂ is thought to be "HSO₂", of indeterminate structure [9][10][37]. Use of a recent value for ΔH_{f,0}(HSO) of -3.8 ± 2.9 kJ mol⁻¹ [38] leads to DH₀(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. $DH_0(S-O)$ is predicted to be $378.1 \text{ kJ mol}^{-1}$ in HSO_2 . $DH_0(O-O_2) = 101.5 \text{ kJ mol}^{-1}$ and $DH_0(O-NO) = 300.7 \text{ kJ mol}^{-1}$ [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. $DH_0(O-N_2) = 161.3 \text{ kJ mol}^{-1}$ [28] and thus formation of HSO_2 from $HSO + N_2O$ is also exothermic. Nitrous oxide might therefore provide a fast pathway to HSO_2 because $SH + N_2O \rightarrow HSO + N_2$ and the subsequent consumption of HSO by N_2O 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

the ΔH_0 , based on MP4/6-311G** energies and scaled MP2/6-31G* frequencies [6], is $-89.9 \text{ kJ mol}^{-1}$. 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 ΔH_0 with $\Delta H_{f,0}$ for $HSOO$ (Table 4), H and CH_3 [28] leads to $\Delta H_{f,0}(CH_3SOO) = 91.8 \text{ kJ mol}^{-1}$, in excellent accord with the experimental value of $87.9 \pm 4.6 \text{ kJ mol}^{-1}$ [7]. The $\Delta H_{f,0}(CH_3S)$ of $131.5 \pm 2.3 \text{ kJ mol}^{-1}$ [29] implies $DH_0(S-O) = 39.7 \text{ kJ mol}^{-1}$, in close agreement with the measured value of $43.5 \pm 3.8 \text{ kJ mol}^{-1}$ [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_3OSO and CH_3SO_2 via the processes

for which, based on PMP4/6-311G** energies and MP2/6-31G* frequencies [16], ΔH_0 is -89.9 and -2.7 kJ mol⁻¹, respectively. Our $\Delta H_{f,0}$ values for HOSO and HSO₂ 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 $D_0(\text{C-O}) = 77.3$ kJ mol⁻¹ and $D_0(\text{C-S}) = 54.1$ kJ mol⁻¹. Studies of $\text{CH}_3 + \text{SO}_2 \rightleftharpoons \text{adduct}$ [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_3OSO was formed. The sulfinyl $\text{CH}_3 + \text{SO}_2$ adduct bonded through S shows a similar dissociation enthalpy to HSO₂, 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, HSO₂ 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 O₂ 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 HSO₂ may bind atomic H

strongly enough to be important in SO_2 -containing flames. The thermochemistry of HSO reactions with O_3 , NO_2 and N_2O indicates that only the first could form HSOO exothermically, while all three could produce HSO_2 . The enthalpies of formation of CH_3SOO , CH_3OSO and CH_3SO_2 have also been derived; the agreement with experiment for the first species is excellent.

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Table 1
Barriers to Internal Rotation^a

Minimum energy conformation	Barrier(s), kJ mol ⁻¹
Staggered HSOO	2.4 (<i>cis</i>) and 2.6 (<i>trans</i>)
<i>cis</i> -HOSO	7.9 (<i>trans</i>)
<i>trans</i> -HOOS	2.4 (<i>cis</i>)

^aCalculated with G2 theory, excluding zero-point vibrational energies.

Table 2: Vibrational Frequencies

Species	Mode	Sym.	HF/6-31G ^{*a}	MP2=FULL/ 3-21G ^{*b}	MP2=FULL/ 6-31G ^{*b}
HSOO	torsion	A	242	263	180
	SOO bend	A	427	398	397
	SO stretch	A	726	639	631
	HSO bend	A	981	937	909
	OO stretch	A	1062	1514	1099
	SH stretch	A	2606	2617	2635
HOSO	torsion	A''	142i ^c	102	200
	OSO bend	A'	382	337	343
	SO stretch	A'	789	745	764
	HOS bend	A'	1079	1047	1073
	SO stretch	A'	1137	1409	1351
	OH stretch	A'	3600	3285	3476
HSO ₂	OSO scissor	A'	458	430	431
	deformation	A'	845	814	810
	OSO sym str	A'	1026	1074	1065
	HSO bend	A''	1056	1187	1128
	OSO asym str	A''	1248	2193	1600
	SH stretch	A'	2446	3231	2269

HOOS	torsion	A''	63i ^c	113	55
	SO stretch	A'	396	390	392
	SOO bend	A'	780	776	796
	OO stretch	A'	989	1346	1353
	HOO bend	A'	1413	2727	1727
	OH stretch	A'	3635	3259	3508

^aFrequency scaled by 0.893, in cm⁻¹.

^bFrequency 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

Species	Sym.	State	MP4/6-311G** ^a	$\Delta E(+)^b$	$\Delta E(2df)^b$	$\Delta E(QCI)^b$	$\Delta E(ZPE)^b$	Δ^b	E(G2) ^a
HSOO	C ₁	² A	-548.25454	-12.11	-132.15	-4.18	+13.33	-10.68	-548.44552
<i>cis</i> -HOSO	C _s	² A''	-548.37049	-16.71	-152.41	+1.88	+16.42	-13.55	-548.58006
HSO ₂	C _s	² A'	-548.32363	-14.24	-163.08	+5.36	+16.64	-16.97	-548.54111
<i>trans</i> -HOOS	C _s	² A''	-548.27636	-14.26	-134.99	-2.12	+17.85	-10.38	-548.46546

^aIn au.

^bComponent of G2 energy in 10⁻³ au. $n_{\text{pair}} = 9$ and $n_{\text{unpair}} = 1$, so that $\Delta E(\text{HLC}) = -0.05545$ au for all isomers.

Table 4
Thermochemistry of HSO₂ isomers in the gas phase

Species	$\Delta H_{f,0},$ kJ mol ⁻¹	$H_{298}-H_0,$ kJ mol ⁻¹	$\Delta H_{f,298},$ kJ mol ⁻¹	$S_{298},$ J K ⁻¹ mol ⁻¹	$C_{p,298},$ J K ⁻¹ mol ⁻¹
HSOO	115.8	13.0	111.5	283.0	51.7
<i>cis</i> -HOSO	-237.4	13.3	-241.4	282.3	53.4
HSO ₂	-135.1	11.0	-141.4	263.7	44.4
<i>trans</i> -HOOS	63.4	12.8	58.9	284.1	47.9

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.