Hydroxysulfinyl Radical and Sulfinic Acid Are Stable Species in the Gas Phase

Aaron J. Frank, Martin Sadílek, Jordan G. Ferrier, and
František Tureček*

Department of Chemistry, Bagley Hall, Box 351700
University of Washington, Seattle, Washington 98195-1700

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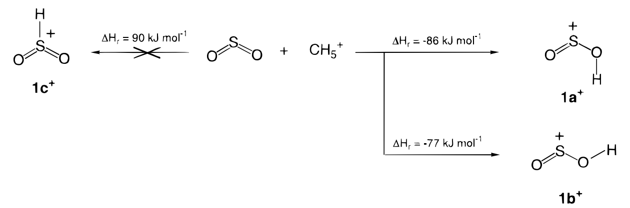
Hydrogen sulfide generated by volcanos, biomass decay, and human activity is oxidized in the troposphere to eventually produce sulfuric acid.[1] The initial step in the H_2S oxidation cascade to form $HSO^\bullet$ and the final step in converting SO_2 to sulfuric acid have been studied extensively by theory[2] and experiment[3] and appear to be well understood.[1] In contrast, very little is known about oxygenated sulfur species in which sulfur is in the intermediate +1 to +4 oxidation states. Such intermediates may be important, inter alia, for the kinetics of the H_2S-SO_2 metathesis reaction, which is used on a large scale in oil desulfurization processes. Marshall and co-workers reported ab initio calculations in which the relative stabilities of several $[H,S,O_2]$ and $[H_2,S,O_2]$ isomers were assessed.[4] We now report the first preparation of hydroxysulfinyl radical (**1a**$^\bullet$) and sulfinic acid (**2a**) in the gas phase.

We use neutralization−reionization mass spectrometry (NRMS)[5] to generate neutral intermediates **1a**$^\bullet$ and **2a** by femtosecond electron transfer from a polarizable organic molecule (dimethyl disulfide, di-*n*-butylamine, or *N*,*N*-dimethylaniline) to the corresponding gas phase cation. The neutral intermediates are allowed to drift for 4 μs, during which time a fraction may dissociate unimolecularly. Stable neutral species and their dissociation products are reionized to cations by collisions with dioxygen and analyzed by mass spectrometry.[6] Neutral collisional activation[7] and variable time measurements[8] are some other techniques used to monitor neutral dissociations.

Radical **1a**$^\bullet$ is a reduced form of the hydroxysulfinyl cation **1a**$^+$. The latter was prepared by mildly exothermic protonation of sulfur dioxide with CH_5^+, which was produced in methane chemical ionization plasma at 0.1−0.2 Torr.[9] Protonation of SO_2 can, in principle, take place at one of the oxygen atoms to form hydroxysulfinyl cations **1a**,**b**$^+$ or at sulfur to form the hydrogensulfonyl ion **1c**$^+$ (Scheme 1). Isomerization to sulfur peroxide ion, ^+SOOH (**1d**$^+$), also cannot be a priori excluded. To assess these processes we used the Gaussian 2 scheme[10] that was augmented in the geometry optimization procedure to calculate the relative stabilities of the $[H,S,O_2]^+$ isomers (Table 1).[10−12] Rotamers **1a**$^+$ and **1b**$^+$ are clearly the most stable isomers accessible from SO_2. The calculated proton affinity for $SO_2 + H^+ \rightarrow$ **1a**$^+$ (PA = 634 kJ mol^{-1}) is in an excellent agreement with the experimental values (631−636 kJ mol^{-1}).[13,14] Moreover, protonations with CH_5^+ to give **1c**$^+$ and **1d**$^+$ are 90 and 319 kJ mol^{-1} *endothermic*, respectively, and cannot occur under thermal equilibrium conditions. Hence, rotamers **1a**,**b**$^+$ must be formed exclusively.

Scheme 1



Collisional neutralization of **1a**,**b**$^+$ with organic molecules produced stable radicals that gave rise to ~40% of survivor ions following reionization (Figure 1a). The stability of **1a**,**b**$^\bullet$ was therefore clearly established. Experiment and theory also indicated that **1a**,**b**$^\bullet$ did not isomerize to other valence bond isomers. Table 1 shows that **1a**$^\bullet$ is the most stable isomer, which is consistent with the results of Marshall et al.[4b] At the present higher level of theory, the *trans*-rotamer **1b**$^\bullet$ is also found as a local potential energy minimum in contrast to previous results.[4b] Collisional activation of neutral **1a**,**b**$^\bullet$ decreased the survivor ion relative abundance (Figure 1). However, the ratios of fragment relative intensities for loss of H, O, and OH did not change appreciably, suggesting that no new dissociation channels were opened at higher internal energies that would indicate the presence of another isomer.

From the point of view of the **1a**,**b**$^\bullet$ stability in the troposphere, the lowest-energy unimolecular dissociation (eq 1) and reaction with triplet dioxygen (eq 2) are of interest.

$$\mathbf{1a}^\bullet \rightarrow SO_2 + H^\bullet \qquad (1)$$

$$\mathbf{1a}^\bullet + (^3\Sigma)O_2 \rightarrow SO_2 + HOO^\bullet \qquad (2)$$

Reaction 1 (eq 1) is calculated to be 170 kJ mol^{-1} endothermic at 298 K and should not proceed with measurable rate constants under tropospheric thermal equilibrium. Radical **1a**$^\bullet$ is therefore intrinsically stable. However, reaction 2 (eq 2) is 47 kJ mol^{-1} exothermic at 298 K and thus represents a viable channel for the **1a**$^\bullet \rightarrow SO_2$ conversion. From the energetics of eqs 1 and 2 and the known heats of formations of the products,[13] the $\Delta H_{f,298}$ of **1a**$^\bullet$ is bracketed at -243 ± 3 kJ mol^{-1}.

The cation radical of sulfinic acid **2a**$^{+\bullet}$ was generated by dissociative ionization of dimethyl sulfate (Scheme 2). This approach relied on the high hydrogen atom affinity of oxygen atoms in oxyacid cation radicals that made hydrogen transfer to oxygen substantially exothermic.[15] According to calculations, isomer **2a**$^{+\bullet}$ was the most stable structure on the $[H_2,S,O_2]^{+\bullet}$ potential energy surface (Table 1), while the $O{=}S\cdots OH_2^{+\bullet}$ ion−

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[11] Gaussian 2(MP2) energies were obtained from effective QCISD-(T)/6-311+G(3df,2p) calculations (ref 10) using fully optimized MP2-(FULL)/6-31+G(d,p) geometries (ref 12) and including zero-point and 298 K corrections obtained from MP2(FULL)/6-31+G(d,p) harmonic frequencies scaled by 0.93. Calculational details will be reported separately.

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Table 1. Relative Enthalpies in the $[H,S,O_2]$ and $[H_2,S,O_2]$ Systems

species	rel enthalpy[a]	species	rel enthalpy[a]
$[H,S,O_2]$		$[H_2,S,O_2]$	
cis-HO−S═O$^+$ (**1a**$^+$)	0	$S(OH)_2^{+\bullet}$ (C_{2v}, **2a**$^{+\bullet}$)	0
trans-HO−S═O$^+$ (**1b**$^+$)	9	$S(OH)_2^{+\bullet}$ (C_1, **2b**$^{+\bullet}$)	0.5
$H{-}SO_2^+$ (**1c**$^+$)	176	$O{=}S\cdots OH_2^{+\bullet}$ (**2c**$^{+\bullet}$)	20
$HOOS^+$ (**1d**$^+$)	405	$O{=}S(H)OH^{+\bullet}$ (**2d**$^{+\bullet}$)	149
		$H_2SO_2^{+\bullet}$ (**2e**$^{+\bullet}$)	349
cis-HO−S═O$^\bullet$ (**1a**$^\bullet$)	0	$S(OH)_2$ (C_2, **2a**)	0
trans-HO−S═O$^\bullet$ (**1b**$^\bullet$)	8	$S(OH)_2$ (C_s, **2b**)	5
$H{-}SO_2^\bullet$ (**1c**$^\bullet$)	100	$O{=}S(H)OH$ (**2d**)	20
$HOOS^\bullet$ (**1d**$^\bullet$)	307		

[a] In units of kilojoules per mole at 298 K.

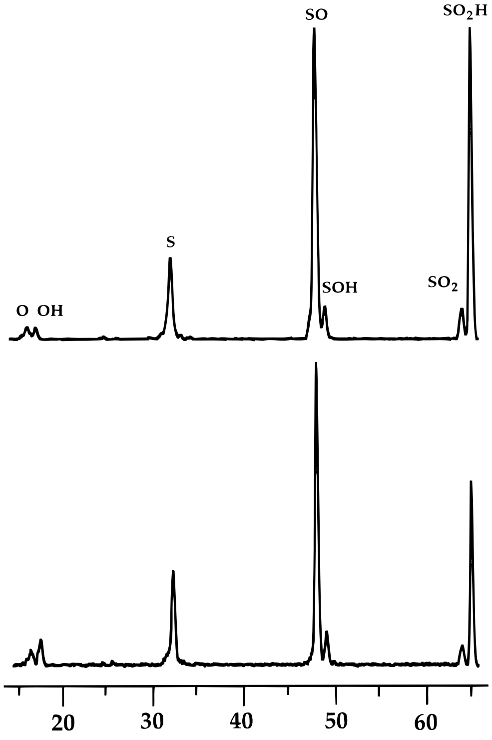
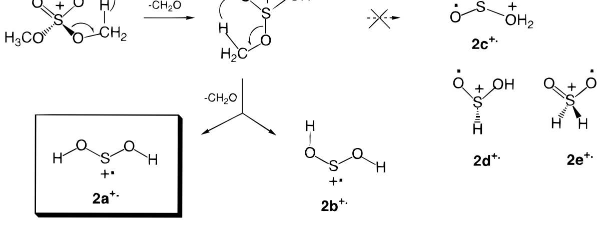


Figure 1. Neutralization−reionization (CH_3SSCH_3(70% *T*)/O_2(70% *T*), top) and neutralization−collisional activation−reionization (CH_3SSCH_3(70% *T*)/He(50% *T*)/O_2(70% *T*), bottom) mass spectra of **1a**,**b**$^+$ (where T = ion transmittance).

Scheme 2



molecule complex (**2c**$^{+\bullet}$), which was the nearest in energy, was separated by a 144 kJ mol^{-1} energy barrier.

Collisional neutralization of **2a**,**b**$^{+\bullet}$ with organic molecules yielded stable molecules of sulfinic acid rotamers **2a**,**b** which produced ~20% of survivor ions following reionization (Figure 2a). The identity of sulfinic acid thus formed was supported by experiment and theory. Collisional activation of the transient neutrals decreased the fraction of survivor **2a**,**b**$^{+\bullet}$ but did not change appreciably the ratios of product formation due to losses of H, OH and H_2O (Figure 2). This suggested that most of the dissociations occurred in the reionized **2a**,**b**$^{+\bullet}$ rather than in neutral **2a**,**b**. Ab initio calculations indicated sulfinic acid rotamers **2a** and **2b** to be the lowest-energy isomers. O═S(H)OH (**2d**), which was the next stable isomer (Table 1), was separated from **2a** by a 196 kJ mol^{-1} energy barrier. The other valence bond $[H_2,S,O_2]$ isomers were substantially less stable than **2a**,**b**.[4a]

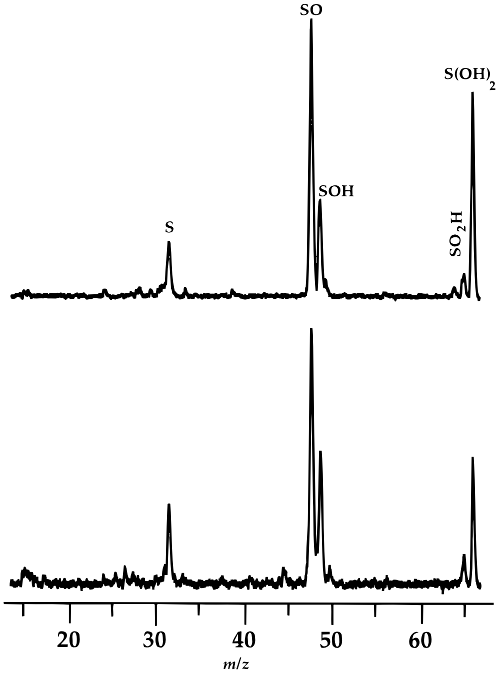


Figure 2. Neutralization−reionization (CH_3SSCH_3/O_2, top) and neutralization−collisional activation−reionization (CH_3SSCH_3/He/O_2, bottom) mass spectra of **2a**,**b**$^{+\bullet}$. Ion transmittances (T) were as in Figure 1.

Unimolecular dissociations of **2a** were all endothermic. The lowest-energy channel corresponding to a spin-allowed reaction was elimination of water to give ($^1\Delta$)SO, which required 133 kJ mol^{-1} at 298 K and very likely involved an additional activation barrier. The spin-forbidden formation of ($^3\Sigma_g$)SO and H_2O had the lowest threshold at 50 kJ mol^{-1} above **2a**. Sulfinic acid (**2a**) was therefore intrinsically stable under thermal equilibrium conditions. Interestingly, the bimolecular reaction of **2a** with ($^3\Sigma$)O_2 (eq 3) was 43 kJ mol^{-1} *endothermic* at 298 K, and it was therefore predicted to be slow. However, photochemical reactions of **2a** with singlet oxygen (eq 4) and hydroxyl radical (eq 5) were 68 and 248 kJ mol^{-1} *exothermic*, respectively, and may thus represent viable channels for efficient depletion of **2a** in the troposphere. From the energy balance

$$\mathbf{2a} + (^3\Sigma)\mathrm{O_2} \rightarrow \mathbf{1a}^\bullet + \mathrm{HOO}^\bullet \tag{3}$$

$$\mathbf{2a} + (^1\Delta)\mathrm{O_2} \rightarrow \mathbf{1a}^\bullet + \mathrm{HOO}^\bullet \tag{4}$$

$$\mathbf{2a} + \mathrm{HO}^\bullet \rightarrow \mathbf{1a}^\bullet + \mathrm{H_2O} \tag{5}$$

in eqs 3 and 5 and the product $\Delta H_{f,298}$, one can bracket the $\Delta H_{f,298}$(**2a**) at −275 ± 4 kJ mol^{-1}.

In conclusion, hydroxysulfinyl radical and sulfinic acid were found to be thermodynamically stable neutral species in the gas phase. Hydroxysulfinyl radical was predicted to undergo exothermic reaction with ($^3\Sigma$)O_2 to yield SO_2. Sulfinic acid can be depleted by photoinduced reactions with ($^1\Delta$)O_2 or hydroxyl radical.

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