Kinetics of the Recombination Reaction $\text{SH} + \text{O}_2 + \text{Ar}$: Implications for the Formation and Loss of HSOO and SOO in the Atmosphere

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Unimolecular pathways for the dissociation of thiylperoxyl have been investigated computationally. Gaussian-2 (G2) theory was employed to calculate the thermochemistry, and the kinetics of $\text{SH} + \text{O}_2 \rightarrow \text{HSOO}$ are analyzed by RRKM theory. Under atmospheric conditions the rate constant is close to the low-pressure limit of $k_0 \approx 9.2 \times 10^{-34}(T/298 \text{ K})^{-1.69} \text{ molecule}^{-2} \text{ cm}^6 \text{ s}^{-1}$ for $T = 200\text{--}400 \text{ K}$. By comparison to other tropospheric oxidation reactions of thiyl radicals, addition to oxygen yields the shortest lifetime, although the low G2 S–O bond dissociation enthalpy implies a small equilibrium constant and means that HSOO formation is likely to be important only below 298 K. Singlet and triplet SOO have been characterized, and $\Delta H_{f,298}({}^1\text{SOO})$ is predicted to be $185.5 \text{ kJ mol}^{-1}$. The results are discussed in the context of atmospheric chemistry.

I. Introduction

Possible roles for thiylperoxyl radicals (HSOO) in the atmospheric oxidation of sulfur species¹ include action as a sink for SH, through the addition reaction²

while HSOO is also a possible product of HSO oxidation by O_3 .^{3,4} HSOO has never been detected, and the only available data have been obtained from *ab initio* calculations. In our earlier study Gaussian-2 (G2) theory yielded the heat of formation $\Delta H_{f,298} = 111.5 \text{ kJ mol}^{-1}$.⁵ The G2 methodology leads to approximate QCISD(T)/6-311+G(3df,2p) energies and has a target accuracy of $\pm 8 \text{ kJ mol}^{-1}$ for atomization enthalpies and an average absolute deviation of 5 kJ mol^{-1} for a set of 55 test molecules.^{6–8} As shown elsewhere,^{5,9,10} this level of computation combined, for example, with consideration of hydrogenation reactions yields good accord with the heats of formation of well-established sulfur species. The procedure overcomes deficiencies in lower levels of calculation applied, for instance, to HSO and HOS that, as noted by Xantheas and Dunning,¹¹ failed to account for nondynamical correlation and lacked high angular momentum basis functions. The G2 bond dissociation enthalpy $\text{DH}_{298}(\text{HS}–\text{OO})$ was estimated to be 31.5 kJ mol^{-1} , low enough to suggest that adduct formation between SH and O_2 may be unfavorable at room temperature but becomes favorable at lower temperatures.⁵

Here we apply the G2 method to potential breakdown products of HSOO, and RRKM theory is employed to analyze the rate constant for $\text{SH} + \text{O}_2$ addition as a function of temperature and pressure. Pathways from HSOO to SOO are considered, and the results are discussed in the context of atmospheric chemistry.

II. Ab Initio Methodology

The general principles of quantitative molecular orbital theory are given elsewhere,^{12,13} and the *ab initio* calculations were carried out with the GAUSSIAN90 and -92 programs.^{14,15} Specific application to HSOO and similar species has been described previously;⁵ here we note that geometries and frequencies were obtained at the MP2=FULL/6-31G(d) level of theory, and the stability of the wave function with respect to relaxation of internal constraints¹⁶ was verified for each stationary point. Then approximate QCISD(T)/6-311+G(3df,2p) energies were calculated at these geometries by means of the

Figure 1. MP2=FULL/6-31G(d) geometries for (A) singlet SOO and (B) triplet SOO. Distances are in angstroms and angles in degrees.

G2 methodology of additive corrections to the MP4/6-311G-(d,p) energy.⁸

III. Results and Discussion

1. Properties of SOO. Figure 1 shows MP2=FULL/6-31G(d) geometries for singlet and triplet states of SOO. We find that the spin-restricted (RHF) wave function for singlet SOO is unstable with respect to relaxation to an unrestricted (UHF) wave function. Similar behavior has been discussed for other S and O singlet diradicals,⁹ and it appears that the G2 method gives more accurate energies when based on RHF wave functions, which accordingly are employed here for SOO. We note also that Curtiss *et al.*⁸ used RHF for ozone, which shows a similar instability, and obtained good agreement with the experimental thermochemistry. Previous studies of singlet SOO have been summarized by Dunning and Raffanetti¹⁷ and Murrell *et al.*,¹⁸ and the geometries they obtained are similar to that shown in Figure 1. The bonds are long, with an S–O distance greater than the observed¹⁹ 1.57 Å for single S–O bonds in H_2SO_4 and an O–O distance midway between that for O_2 and H_2O_2 ,²⁰ and typical of superoxides. We found that with the 6-31G(d) basis set a triplet state was more stable, although this order is reversed with the larger basis sets employed in the G2 methodology.

The normal modes of both states of SOO are all of A' symmetry, and the MP2/6-31G(d) vibrational frequencies, scaled by a standard factor of 0.95,¹² are $480, 781, \text{ and } 1979 \text{ cm}^{-1}$ for ${}^1\text{SOO}$ and $409, 672, \text{ and } 1021 \text{ cm}^{-1}$ for ${}^3\text{SOO}$. These values are employed to derive the zero-point vibrational energy and various thermochemical quantities shown below.

The enthalpy of formation of ${}^1\text{SOO}$ is assessed by means of working reactions similar to those we employed earlier for species of HSO_2 stoichiometry:⁵

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TABLE 1: Absolute G2 Energies of Singlet and Triplet SOO

species	state	MP4/6-311G(d,p) ^a	$\langle S^2 \rangle^b$	$\Delta E(+)^c$	$\Delta E(2df)^c$	$\Delta E(\text{QCI})^c$	$\Delta E(\text{ZPE})^c$	Δ^c	$E(\text{G2})^a$
¹ SOO	¹ A'	-547.649 84	0.000	-14.63	-134.82	9.76	7.38	-8.46	-547.835 61
³ SOO	³ A'	-547.616 99	2.022	-12.62	-131.93	-2.73	4.79	-7.88	-547.807 74

^a In au (1 au ≈ 2625 kJ mol⁻¹). ^b For the HF/6-311G(d,p) wave function. ^c Component of G2 energy in 10⁻³ au (see ref 8).

For each process the change in G2 energy (Table 1) equals the enthalpy change at 0 K, ΔH_0 . Errors arising from inadequate basis sets, incomplete accounting for electron correlation, and basis set superposition largely cancel.²¹ $\Delta H_{f,0}(\text{SOO})$ is obtained from ΔH_0 and the measured $\Delta H_{f,0}$ of SO₂, H, SO, OH, H₂O, H₂S,²⁰ and SH.^{22,23} Reactions of 2–5 yield a mean $\Delta H_{f,0}$ of 187.8 kJ mol⁻¹ with a standard deviation of 4.0 kJ mol⁻¹. We quote data to one decimal place to avoid accumulation of round-off errors, without implication of this degree of accuracy. This value corresponds to an enthalpy 482.1 kJ mol⁻¹ above SO₂ at 0 K, which is somewhat larger than the purely electronic energy changes for reaction 2 derived by Dunning and Raffanetti¹⁷ and Murrell *et al.*¹⁸ of 417.4 and 421.5 kJ mol⁻¹, respectively, with configuration interaction calculations. The ³A' state has not been investigated previously; the G2 energies imply an adiabatic excitation of 72.8 kJ mol⁻¹ above the ¹A' state. We use our $\Delta H_{f,0}(\text{SOO})$ plus statistical mechanics²⁴ to derive $C_{p,298} = 41.6$ J K⁻¹ mol⁻¹, $S_{298} = 257.2$ kJ mol⁻¹, and $\Delta H_{f,298} = 185.5$ kJ mol⁻¹. These data, combined with information for S, O, SO, and O₂,²⁰ yield the following bond dissociation enthalpies: $\text{DH}_{298}(\text{S}-\text{O}_2) = 91.5$ kJ mol⁻¹ and $\text{DH}_{298}(\text{SO}-\text{O}) = 68.7$ kJ mol⁻¹.

2. Kinetics of $\text{HSOO} + \text{Ar} \rightleftharpoons \text{SH} + \text{O}_2 + \text{Ar}$. The unimolecular kinetics of the reverse of reaction 1 were analyzed in terms of RRKM theory as detailed by Gilbert and co-workers,^{25,26} and implemented with their UNIMOL program suite²⁶ for an Ar bath gas, on the assumption of a weak collision "exponential down" model for energy transfer between the bath gas and HSOO. The Lennard-Jones parameters $\sigma = 3.81$ Å and $\epsilon/k_B = 186$ K were chosen to describe collisions with the bath gas, based on suggested values for $\text{Ar} + \text{HSO}_2$.²⁷ G2 calculations indicate there is no barrier to dissociation beyond the endothermicity,²⁸ and the transition state (TS) was therefore treated as loose and analyzed in terms of canonical variational transition state theory. The reaction coordinate ($r(\text{S}-\text{O})$, the length of the breaking bond) was fitted to a Morse potential, and different trial $r(\text{S}-\text{O})$ values were tested, with full angular momentum conservation, to find the structure (i.e., $r^\ddagger(\text{S}-\text{O})$) that gave the smallest high-pressure rate constant k_∞ . We applied a Gorin model to the TS where the separating moieties were assumed to have the same geometries and frequencies as in the completely dissociated products. Several vibrational modes of HSOO disappear during dissociation, and these modes were represented by internal rotations in the Gorin TS. The HSO and SOO bending modes and torsion about the SO bond were converted to internal rotations of fragments within the TS, while SO stretching of course corresponds to motion along the reaction coordinate. The two bending motions were replaced in the TS by a two-dimensional internal rotor, whose moment of inertia was derived from the moments for rocking of SH and O₂ about two axes perpendicular to the central SO bond. The torsional mode of HSOO was replaced in the TS by a one-dimensional free rotor about the SO axis.

Angular momentum effects for the molecule and the TS were taken into account by allowing the energy of the external or overall rotational mode with the one-dimensional moment of inertia to be active,²⁵ i.e., to be available to help cross the potential barrier, while the external two-dimensional rotor was taken to be inactive. All the constants for internal and external rotations were calculated by means of the GEOM part of the

TABLE 2: RRKM Parameters for $\text{HSOO} \rightarrow \text{SH} + \text{O}_2$ at 298 K^a

Molecule	
ν	180, 397, 631, 909, 1099, 2635
$B_{\text{ext}}(\text{inactive})$, dim	0.203, 2
$B_{\text{ext}}(\text{active})$, dim	1.820, 1
D_e, D_0, β	37.8, 26.7 kJ mol ⁻¹ , 6.58 Å ⁻¹
$r_e(\text{S}-\text{O})$	1.753 Å
Transition State	
ν	2641 (S-H str), 1343 (O-O str)
$B_{\text{ext}}(\text{inactive})$, dim	0.116, 2
$B_{\text{ext}}(\text{active})$, dim	1.662, 1
B_{int} , dim	9.935, 2
B_{int} , dim	10.26, 1
$r^\ddagger(\text{S}-\text{O})$	≈ 2.6 Å

^a Rotational constants B and vibrational frequencies ν in cm⁻¹. The symmetry numbers for all internal and external rotations are 1.

TABLE 3: Comparison of Atmospheric Lifetimes of SH, τ , with Respect to Removal by Oxidants at 298 K and 1 atm

oxidant, X	effective bimolecular rate constant $k_{\text{SH}+\text{X}}$, molecule ⁻¹ cm ³ s ⁻¹	[X], molecules cm ⁻³	$\tau = 1/k_{\text{SH}+\text{X}}[\text{X}]$
O ₂	2.3×10^{-14} ^a	4.9×10^{18}	9.0 μs ^b
OH	$< 10^{-10}$ ^c	1×10^7 ^d	> 17 min
NO	3.4×10^{-12} ^e	1.3×10^{13} ^d	24 ms
NO ₂	6.5×10^{-11} ^e	4.9×10^{12} ^d	3.1 ms
O ₃	3.5×10^{-12} ^e	5×10^{12} ^d	57 ms

^a This work. ^b In the absence of reverse reaction. ^c Estimated upper limit. ^d Reference 31. ^e Reference 30.

UNIMOL suite, and the input parameters are summarized in Table 2. Rate constants for the reverse association reaction were obtained via microscopic reversibility, using the calculated equilibrium constant $K_p = 8.03 \times 10^{-7} \exp(3760 \text{ K}/T)$ for a standard state of 10⁵ Pa, for the temperature interval 200–400 K.

Over the same range the low-pressure limiting rate constant for $\text{SH} + \text{O}_2$ recombination is given by $k_0 = 9.2 \times 10^{-34} (T/298 \text{ K})^{-1.69}$ molecule⁻² cm⁶ s⁻¹. Reaction 1 is firmly at the low-pressure limit, and for example, at 200 K and 1 atm the rate constant lies more than 3 orders of magnitude below the high-pressure limit, given by $k_\infty = 2.0 \times 10^{-10} (T/298 \text{ K})^{0.31}$ molecule⁻¹ cm³ s⁻¹. Above 400 K the reverse rate constant for HSOO dissociation becomes so fast that net HSOO formation is negligible; i.e., K_p for reaction 1 becomes very small.⁵ The small value predicted for K_p may account for the failure so far to observe reaction 1 in the laboratory.²⁹

Table 3 summarizes some oxidation pathways for SH³⁰ and shows that even using oxidant concentrations appropriate to heavily polluted atmospheres,³¹ reaction 1 is the fastest route for consumption of SH. At 298 K, however, K_p is predicted to be unfavorable, which limits the fraction of SH that can be tied up as an adduct, although this conclusion is very sensitive to the theoretical S–O bond strength.⁵ It should be noted that above ground level the air temperature drops, and the fast reaction 1 is increasingly favorable thermodynamically. This may be important for tropospheric modeling because HSOO can undergo different chemistry from SH, as outlined below.

3. Reaction Pathways for Thiylperoxyl Radicals. Apart from the reverse of reaction 1, HSOO could react through dissociation of the H–S or O–O bonds:

The thermochemistry for SOO developed in section III.1, combined with G2 data for HSOO,⁵ leads to ΔH_{298} for reaction 6 of 292.0 kJ mol⁻¹, so this process will be negligibly slow under atmospheric conditions. Our G2 value of $\Delta H_{f,298}(\text{HSO})^{10} = -19.9$ kJ mol⁻¹ implies $\Delta H_{298} = 117.8$ kJ mol⁻¹ for reaction 7, which suggests this process will also be fairly slow in the atmosphere. On the assumption of a preexponential factor of 10¹⁶⁻¹⁷ s⁻¹ for reaction 7,³² at the high-pressure limit at 298 K the lifetime of HSOO would be around 1.2–12 h. If at 1 atm the dissociation is in the falloff region, then the lifetime will be greater.

Bimolecular reactions of thiylperoxyl are possible. $\text{DH}_{298}(\text{H}-\text{SOO})$ is less than $\text{DH}_{298}(\text{H}-\text{OH})$,²⁰ thus, H atom abstraction from HSOO by OH radicals is thermochemically allowed, and the O–O bond strength in HSOO is small enough to permit O atom abstraction by, for example, NO. H atom abstraction by O₂ is 76 kJ mol⁻¹ endothermic. Taking this value as a lower bound to the activation energy for this process, in combination with the assumption of a preexponential factor of 7×10^{-11} cm³ molecule⁻¹ s⁻¹ by analogy with $\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{O}_2$,³³ leads to a rate constant for formation of HO₂ + SOO of 3.3×10^{-24} cm³ molecule⁻¹ s⁻¹ at 298 K. The corresponding lower bound to the atmospheric lifetime is about 17 h, which will vary strongly with temperature, because of the large activation energy for O₂ + HSOO. Addition reactions of atmospheric species to HSOO may also be possible. The kinetics of these processes remain to be established, but if the energy barriers are small, then the tropospheric lifetime of HSOO with respect to H atom abstraction will be of the order of 1–10 h or less.

Thus, a potential product of HSOO reactions is SOO. This superoxide-like species is unstable with respect to both the SOO “ring isomer” and regular SO₂, but because isomerization of SOO to SO₂ involves “substantial rearrangements in the σ system ... a larger barrier” was expected by Dunning and Raffanetti.¹⁷ The rate of this isomerization is currently under investigation, because it completes a new atmospheric pathway for SH oxidation to SO₂ via HSOO. If SOO can exist as an independent species, then its low bond strengths may imply some interesting chemistry, which has not yet been explored.

IV. Conclusions

The rate constant for recombination of SH with O₂ has been characterized *ab initio*, and this reaction is faster in the troposphere than other oxidation pathways for thiyl radicals. The extent of HSOO formation is controlled by the thermochemistry, which is probably unfavorable at 298 K because of the weak S–O bond, but addition becomes more favorable at lower temperatures. Adduct formation may tie up SH and therefore slow its chemistry, while new pathways become accessible: abstraction of H from HSOO by atmospheric species to form SOO is thermochemically feasible, as well as dissociation to HSO + O. The thermochemistry of the superoxide SOO has been assessed, and this molecule may be reactive because of its low S–O and O–O bond dissociation enthalpies.

Note Added in Proof. A very recent study of SOO by MRCISD methods yielded an energy 472 kJ mol⁻¹ above SO₂ at the highest level of theory,³⁴ close to the value obtained here.

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