SO₂ formation and peroxy radical isomerization in the atmospheric reaction of OH radicals with dimethyl disulfide

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1 Experimental approach and product analysis

1.1 Experimental approach

Experiments on the reaction of OH radicals with dimethyl disulfide (DMDS) and CH₃SH have been conducted in a free-jet flow system at $T = 295 \pm 2$ K, a pressure of 1 bar with a total flow of 100 L min⁻¹ (STP) of purified air and a reaction time of 7.9 s. More detailed information on the experimental set-up are given elsewhere.^{1, 2}

OH radicals were produced from the ozonolysis of tetramethylethylene (TME)³ and for comparison via photolysis of isopropyl nitrite⁴ using 8 NARVA 36W Blacklight Blue lamps emitting in the range 350 - 400 nm. Isopropyl nitrite photolysis first generates i-C₃H₇O radicals and NO. The subsequent reaction of i-C₃H₇O with O₂ forms HO₂ radicals and acetone. Finally, NO reacts with HO₂ producing the desired OH radicals and NO^{2.4}

Ozone was produced by passing 2 L min⁻¹ (STP) air through an ozone generator (UVP OG-2). All gas flows were set by means of calibrated gas flow controllers (MKS 1259/1179). Ozone concentrations were measured at the outflow of the reactor by a gas monitor (Thermo Environmental Instruments 49C).

The reactant gases had the following purities: DMDS (dimethyl disulfide, Sigma, $\geq 99\%$) and CH₃SH (Sigma, 98%). Air was taken from a PSA (Pressure Swing Adsorption) unit with further purification by activated charcoal as well as by 4 Å and 10 Å molecular sieves.

Reactant concentrations were $[DMDS] = (1 - 50) \times 10^{11}$, $[CH_3SH] = 5.3 \times 10^{12}$, $[TME] = (1.0 - 3300) \times 10^9$, $[O_3] = (1.6 - 130) \times 10^{10}$ molecules cm⁻³ and [isopropyl nitrite] = 9.2×10^{11} molecules cm⁻³.

1.2 Product analysis by CI-APi-TOF

Detection of reaction products was carried out by means of CI-APi-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometry (Airmodus, Tofwerk) sampling from the centre flow of the free-jet flow system with a rate of 10 L min⁻¹ (STP). The ion-molecule reaction (IMR) proceeded at atmospheric pressure using a Boulder-type inlet.⁵

We have used the following reagent ions: I⁻ (iodide) for detection of the CH₃SSCH₂O₂ isomerization products, methane sulfinic acid (CH₃S(O)OH) and methane sulfonic acid (CH₃SO₃H, MSA), C₂H₅NH₃⁺ (ethylaminium) for the accretion product CH₃C(O)CH₂OOCH₃ and the RO₂ radical CH₃C(O)CH₂O₂, NO₃⁻ (nitrate) for MSA and SF₆⁻ and CO₃⁻ or the detection of SO₂.^{2, 6-8}

For reagent ion generation, a 35 L min⁻¹ (STP) sheath gas flow of purified nitrogen containing (5 - 200) × 10¹⁰ molecules cm⁻³ of tert-butyliodide, ethylamine, HNO₃, SF₆ or O₃ was used to form I⁻, C₂H₅NH₃⁺, NO₃⁻, SF₆⁻ and CO₃⁻, respectively, after ionization with a ²⁴¹Am source. In the case of CO₃⁻ production starting from O₃, the initially formed O₃⁻ rapidly reacts with background CO₂ forming finally CO₃⁻ and O₂. The ions from the sheath gas flow are guided into the sample flow by an electric field without mixing of both gas streams.

Measured product signal intensities were normalized with respect to the corresponding reagent ion signal intensities.⁹ Absolute signal calibration has been carried out in the case of SO₂ detection by means of SF₆⁻ and CO₃⁻ ionization. For MSA measurements using NO₃⁻ ionization, the experimentally observed calibration factor for the structurally similar sulfuric acid¹⁰ has been used. In the case of methane sulfinic acid (CH₃S(O)OH) and methane sulfonic acid (MSA) followed by means of I⁻ ionization, the stated lower limit concentrations have been obtained using a calibration factor f = 1.85×10^9 molecules cm⁻³.², ¹⁰ The "lower limit" approach assumes collision limit for the ion-molecule reaction and no ion losses within the mass spectrometer.²

2 Reaction mechanism

The reaction mechanism below has been used to calculate the DMDS (and CH₃SH) conversion in the absence and presence of NO additions as well as for the description of the SO₂ production. Rate coefficients were taken from the literature¹¹⁻¹³ at 295 K and from the present work. The low RO₂ radical concentrations in the experiments justified neglecting RO₂ radical self- and cross-reactions. To simplify matters, only the alkoxy channel: RO₂ + NO \rightarrow RO + NO₂, has been considered. The OH radical for O₃ + TME was taken from our previous experimental work.¹⁴ A HO₂ yield of 0.08 from O₃ + TME is assumed formed via a pathway other than CI decomposition that results in an OH radical yield of 0.92.

Reaction	Rate coefficient at 295 K (cm ³ molecule ⁻¹ s ⁻¹ or s ⁻¹)
O_3 + TME (+ O_2) $\rightarrow 0.92 \times OH + 0.92 \times CH_3C(O)CH_2O_2 + 0.08 \times HO_2 + products$	1.0 × 10 ⁻¹⁵
$OH + TME (+ O_2) \rightarrow HO-TME-O_2$	$1.1 imes 10^{-10}$
$NO + HO_2 \rightarrow OH + NO_2$	$8.9 imes 10^{-12}$
$OH + HO_2 \rightarrow H_2O + O_2$	$1.1 imes 10^{-10}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.65 imes 10^{-12}$
$OH + NO \rightarrow HNO_2$	$3.3 imes 10^{-11}$
$OH + NO_2 \rightarrow HNO_3$	$6.0 imes 10^{-11}$
OH + DMDS (+ O_2) \rightarrow 0.98×CH ₃ S + 0.98×CH ₃ SOH + 0.02×CH ₃ SSCH ₂ O ₂	$2.3 imes 10^{-10}$
$CH_3SSCH_2O_2 + NO \rightarrow products + NO_2$	$1.0 imes 10^{-11}$
$CH_3C(O)CH_2O_2 + NO \rightarrow products + NO_2$	$1.0 imes 10^{-11}$
$HO-TME-O_2 + NO \rightarrow products + NO_2$	$1.0 imes 10^{-11}$
$CH_3O_2 + NO (+O_2) \rightarrow CH_2O + HO_2 + NO_2$	$7.7 imes 10^{-12}$
$CH_3SSCH_2O_2 (+ O_2) \rightarrow O_2CH_2SSCH_2OOH$	0.032
$O_2CH_2SSCH_2OOH \rightarrow HOOCH_2SSCHO + OH$	0.033
$CH_3S + O_2 \rightarrow CH_3SO_2$	$2.4 imes 10^{-14}$
$CH_3SO_2 \rightarrow CH_3S + O_2$	$2.0 imes 10^5$
$CH_3SO_2 (+ O_2) \rightarrow SO_2 + CH_3O_2$	5.0
$CH_3S + O_3 \rightarrow CH_3SO + O_2$	$4.9 imes 10^{-12}$
$CH_3SO + O_3 (+ O_2) \rightarrow SO_2 + CH_3O_2 + O_2$	$6.0 imes 10^{-13}$
O_3 + CH_3SOH (+ O_2) \rightarrow CH_3O_2 + HO_2 + SO_2	2 × 10 ⁻¹²
$O_3 + NO \rightarrow NO_2 + O_2$	$1.8 imes10^{-14}$
$O_3 + NO_2 \rightarrow NO_3 + O_2$	$3.5 imes 10^{-17}$
$O_3 + HO_2 \rightarrow OH + 2 \times O_2$	$2.0 imes 10^{-15}$
$OH + CH_3SH \rightarrow CH_3S + H_2O$	$3.4 imes 10^{-11}$

The estimated rate coefficient $k(O_3 + CH_3SOH) = 2 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ results from a fitting procedure of the measured SO₂ yields from O₃-dependent experiments on OH + DMDS as given in Fig.1 and Fig.S4, see Table S1.

Table S1: SO_2 formation yields from OH + DMDS (OH + CH₃SH) measured in air and the comparison of measured and modelled SO_2 yields from OH + DMDS for experimental conditions of the present study.

	O_3 (molecules cm ⁻³)	SO ₂ yield ^a	SO ₂ yield modelled
OH + DMDS	1.6×10^{10}	$0.92 \pm 0.19^{\mathrm{b}} \ 0.89 \pm 0.18^{\mathrm{c}}$	1.03
	3.2×10^{10}	$1.14 \pm 0.23^{\circ}$	1.11
	1.9×10^{11}	$1.61 \pm 0.35^{\circ}$	1.49
	6.1×10^{11}	$1.97 \pm 0.48^{\circ}$	1.71
	1.3×10^{12}	2.18 ± 0.45°	1.82
$OH + CH_3SH$	1.6×10^{10}	0.86 ± 0.18^{b}	-

 a includes 20% uncertainty from SO_2 calibration. b SF_6 $^{\rm -}$ ionization; c CO_3 $^{\rm -}$ ionization

3 Additional figures



Fig.S1: Formation of O₂CH₂SSCH₂OOH and HOOCH₂SSCHO from the OH + DMDS reaction in air using I-CI-APi-TOF for detection. OH radical are formed from TME ozonolysis. [DMDS] = 5.0×10^{12} , [TME] = 1.0×10^{12} and [O₃] = $(6.0 - 56) \times 10^{10}$ molecules cm⁻³.



Fig.S2: Product mass spectrum observed from the OH radical initiated oxidation of DMDS in air. OH radicals were produced via isopropyl nitrite photolysis. Products are measured as iodide clusters, I⁻-CI-APi-TOF. [DMDS] = 5.0×10^{11} and [IPN] = 9.2×10^{11} molecules cm⁻³.



Fig.S3: SO₂ signals measured at 111.95 Th (${}^{32}SO_{5}{}^{-}$) and 113.94 Th (${}^{34}SO_{5}{}^{-}$) based on the CO₃⁻ ionization scheme. The signal at 113.94 Th was multiplied by 18.17 according to the natural isotope abundance ${}^{32}SO_{5}{}^{-}/{}^{34}SO_{5}{}^{-}$. Signal intensities very close to background level for OH radical scavenging by propane further supports the absence of interferences for SO₂ detection. [DMDS] = 1.0×10^{11} , [TME] = 2.1 or 4.2×10^{9} , [O₃] = 1.3×10^{12} and [C₃H₈] = 2.5×10^{15} molecules cm⁻³.



Fig.S4: SO₂ formation from the OH + DMDS reaction for low O₃ concentration measured with SF₆⁻ and CO₃⁻ ionization. OH radicals have been produced from TME ozonolysis. Molar SO₂ formation yields are 0.92 ± 0.19 (SF₆⁻) and 0.89 ± 0.18 (CO₃⁻). The error bars represent 20 % uncertainty arising from SO₂ signal calibration. [DMDS] = 5.0×10^{11} , [TME] = $(1.3 - 33) \times 10^{11}$ and [O₃] = 1.6×10^{10} molecules cm⁻³.



Fig.S5: SO₂ formation from the OH + CH₃SH reaction for low O₃ concentration measured with SF₆⁻ ionization. OH radicals have been produced from TME ozonolysis. The molar SO₂ formation yield is 0.86 ± 0.18 . The error bars represent 20 % uncertainty arising from SO₂ signal calibration. [CH₃SH] = 5.3×10^{12} , [TME] = $(1.2 - 25) \times 10^{11}$ and [O₃] = 1.6×10^{10} molecules cm⁻³.



Fig.S6: SO₂ formation yield from the OH + DMDS reaction as a function of added NO to the reaction system. SO₂ has been measured by means of CO₃⁻ ionization and the amount of converted DMDS was calculated from a detail reaction mechanism. OH radicals have been produced via TME ozonolysis. [DMDS] = 1.0×10^{11} , [TME] = 1.1×10^{10} , [O₃] = 6.1×10^{11} and added [NO] = $(1.7 - 17) \times 10^9$ molecules cm⁻³.



Fig.S7: Lower limit concentrations of the signal at nominal 207 Th as a function of reacted DMDS using iodide ionization. The signal was tentatively attributed to methane sulfinic acid (CH₃S(O)OH). The lower limit formation yield is 0.0091 \pm 0.0003. OH radicals have been produced via TME ozonolysis. [DMDS] = 1.0×10^{11} , [TME] = $(5.0 - 90) \times 10^9$ and [O₃] = 6.1×10^{11} molecules cm⁻³.



Fig.S8: Signals of CH₃C(O)CH₂O₂ (from O₃ + TME) and the accretion product CH₃C(O)CH₂OOCH₃ (from CH₃O₂ + CH₃C(O)CH₂O₂) for different reaction conditions. OH radical are formed via TME ozonolysis and the product analysis was carried out by means of C₂H₅NH₃⁺-CI-APi-TOF. Increasing of the O₃ concentration by a factor of 2.2 at measurement cycle 90 leads to an increase of the CH₃C(O)CH₂O₂ radical concentration by a factor of about 2.2 because CH₃C(O)CH₂O₂ is a direct product of O₃ + TME formed along with the OH radicals. At this point, the signal of the accretion product CH₃C(O)CH₂OOCH₃, however, increases by a factor of about 4.5 reflecting the square-dependence according to its formation kinetics. I.e. [CH₃O₂] approximately increases in an almost similar way as [CH₃C(O)CH₂O₂] because rising [CH₃C(O)CH₂O₂] also means rising [OH] and subsequently rising [CH₃O₂]. DMDS was substituted by CH₄ at measurement cycle 150 while maintaining the OH reactivity, i.e. k(OH+DMDS) × [DMDS] = k(OH+CH₄) × [CH₄]. The CH₃C(O)CH₂OOCH₃ signal intensity from OH + DMDS is about a factor of 1.4 higher than that of OH + CH₄. Thus, a CH₃O₂ yield from OH + DMDS of at least 1.4 follows taking into account a CH₃O₂ production via OH + DMDS compared to that of OH + CH₄.



Fig.S9: Lower limit concentrations of methane sulfonic acid (MSA) as a function of reacted DMDS measuring either the deprotonation product (MSA-H)⁻ by means of nitrate ionization or the adduct (MSA)I⁻ using iodide ionization. OH radicals have been produced via TME ozonolysis. [DMDS] = 1.0×10^{11} , [TME] = $(5.0 - 90) \times 10^9$ and $[O_3] = 6.1 \times 10^{11}$ molecules cm⁻³.

4 Quantum chemical calculations

4.1 Computational details on ion-molecule cluster calculations

The ion-molecule cluster stabilities are modelled in terms of the formation enthalpies of the clusters: $\Delta H = H_{cluster} - H_{ion} - H_{molecule}$

The enthalpies of individual molecules, ions and clusters were calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level of theory.¹⁵⁻¹⁷ For iodine, we used the corresponding aug-cc-pVTZ-PP basis set with pseudo-potentials.¹⁸⁻²⁰ The geometries were optimized and harmonic frequencies were calculated using the Gaussian program with the ultrafine integration grid.²¹ The coupled cluster single point energies were calculated using ORCA versions 4.0.0.2 and 4.2.1²² and tight PNO settings. Additional conformer sampling for molecules and clusters of the larger compounds (HOOCH₂SSCHO and O₂CH₂SSCH₂OOH) was performed using the systematic conformer search and MMFF force fields in Spartan'14.²³ The same computational approach has been used in our previous studies to model cluster stabilities in chemical ionization.^{2, 24, 25}

A comparison with previously published formation enthalpies^{21, 25} shows that the iodide clusters of the OH + DMS reaction products are slightly more stable than the corresponding clusters of the OH + DMDS reaction products (Table S2). The formation enthalpies of the (MSA)I⁻ and (MSIA)I⁻ clusters are -25.8 and -20.3 kcal/mol, respectively, indicating that MSA and MSIA can be detected at high sensitivities using iodide ionization.

Table S2.	Formation	enthalpies ((kcal/mol)	of OH +	DMDS (n	=2) and	OH + I	DMS (n=1) pr	oducts v	with I-
calculated	at the DLPI	NO-CCSD(Γ)/def2-QZ	ZVPP//ωB	97X-D/aug	g-cc-pVT	Z(-PP)	level o	of theory	v at 298.	15K.

	n=1	n=2
HOOCH ₂ S _n CHO	22.1 ^a	19.7
O ₂ CH ₂ S _n CH ₂ OOH	20.5 ^a	20.2

^a ref 25

4.2 Theoretical methods for calculation of reaction rate coefficients and RRKM-ME modelling The conformational sampling and subsequent electronic structure calculations are based on the procedure outlined in Møller et al.²⁶ Briefly, conformers are generated using MMFF in Spartan'18 with a neutral charge enforced on the radical atom and constraints on three selected bond lengths for the transition states (TSs).^{27, 28} The resulting conformers are optimized at the B3LYP/6-31+G(d) level in Gaussian 16, rev. A.03.^{21, 29-33} The transition state optimization is preceded by an optimization with the same constraints as employed for the conformational sampling. Unique conformers with electronic energies within 2 kcal/mol of the lowest-energy conformer are further optimized at the ω B97X-D/aug-cc-pVTZ level (with the aug-cc-pV(T+d)Z basis set for sulfur).³⁴⁻³⁸ This combination will be referred to as ω B97X-D/aVTZ. For the lowest-energy conformer of reactant and TS in terms of electronic energy including zero-point vibrational correction at this level, a restricted-open shell RO-CCSD(T)-F12a/VDZ-F12 single-point energy calculation (gem_beta=0.9) is done in Molpro2012.³⁹⁻⁴⁵ All energies mentioned in the results section are RO-CCSD(T)-F12a/VDZ-F12 electronic energy with ω B97X-D/aVTZ zero-point corrections for the lowest-energy conformer unless specifically stated.

Reaction rate coefficients for the unimolecular reactions, k, are calculated using multi-conformer transition state theory, MC-TST:^{26, 46-48}

$$k = \kappa \frac{k_B T \sum_{i}^{TS \ conf.} \exp\left(-\frac{\Delta E_i}{k_B T}\right) Q_{TS_i}}{\sum_{j}^{R \ conf.} \exp\left(-\frac{\Delta E_j}{k_B T}\right) Q_{R_j}} \exp\left(-\frac{E_{TS} - E_R}{k_B T}\right)$$

 κ is the Eckart tunnelling coefficient (see next paragraph), k_B is the Boltzmann constant, T is the temperature and h is Planck's constant. The two sums run over the conformers of transition state and reactant, respectively, and sum their partition functions, Q, exponentially weighted by the relative zero-point corrected electronic energy of the corresponding conformer, ΔE. The final term is the energy difference between the lowest-energy conformer of transition state and reactant, the barrier height. The barrier height is calculated based on RO-CCSD(T)-F12a/VDZ-F12 electronic energies with ω B97X-D/aVTZ zero-point correction and the relative energies between conformers (ΔE) and partition functions (Q) are calculated at the ω B97X-D/aVTZ level. All calculations are done at 298.15 K.

Tunnelling is calculated using the Eckart approach based on optimized IRC end-points from the lowest-energy TS conformers.⁴⁹ Energies are calculated at the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ level with zero-point corrections and an imaginary frequency calculated using ω B97X-D/aVTZ.

The reaction of CH₃SOH with ozone and the subsequent reactions along that pathway are modelled using Rice-Ramsperger-Kassel-Marcus Master Equation (RRKM-ME) methods in the Master Equation Solver for Multi-Energy well Reactions, MESMER.⁵⁰

The RRKM-ME simulations in MESMER are based on RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ electronic energies with ω B97X-D/aVTZ zero-point vibrational corrections for the lowest energy conformers. For testing purposes, the equivalent simulations were run also with electronic energies at the ω B97X-D/aVTZ level.

The MESMER simulations were run with the following parameters:

- $k(CH_3SOH+O_3, 298 \text{ K}) = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- $[O_3] = 1 \times 10^{12}$ molecules/cm³ (a value of 1×10^{20} molecules/cm³ was used for testing purposes, Fig.S14)
- Exponential energy decay with an average energy transfer per collision: $\Delta E_{down} = 225 \text{ cm}^{-1}$.
- Lennard-Jones parameters for O₃: $\sigma = 3.9$ Å, $\epsilon/k_B = 210$ K.⁵¹
- Lennard-Jones parameters for O_2 : $\sigma = 3.4$ Å, $\epsilon/k_B = 121$ K.⁵¹
- Lennard-Jones parameters for HO₂: $\sigma = 3.3$ Å, $\epsilon/k_B = 130$ K.⁵¹
- Lennard-Jones parameters for other species: $\sigma = 5.3$ Å, $\epsilon/k_B = 310$ K.⁵¹
- Bath gas = N_2 (σ = 3.919 Å, ϵ/k_B = 91.85 K). ⁵²
- P = 760 Torr, T = 298.15 K.
- Grain size = 100 cm^{-1} and energy grain span above highest stationary point = $50k_BT$.
- Tunnelling for the unimolecular channels is modelled using the Eckart approach.
- The products of the O₂ loss and HO₂ loss channels are modelled as "sinks" using the energies and geometries of the product complexes.

4.3 Hydrogen shift isomerizations in the H-abstraction channel of OH + DMDS

The autoxidation pathway (consecutive H-shifts and O_2 -additions) following H-abstraction from DMDS is shown in Fig.S10 with rate coefficients for the unimolecular H-shifts calculated using the approach by Møller et al.²⁶ Details of the calculated rate coefficients are given in Table S3.

Fig.S10. DMDS autoxidation mechanism with H-shift rate coefficients (T = 298.15 K) calculated using the approach by Møller et al. with barrier heights at the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ level. The alkyl radical in the brackets is unstable and promptly loses OH to form the hydroperoxy aldehyde in the dashed red square.⁵³

Table S3. RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ calculated barrier heights ($E_{TS} - E_R$, in kcal/mol), ω B97X-D/aVTZ summed, weighted partition function ratio (Q_{TS}/Q_R), Eckart tunneling coefficient (κ) and MC-TST rate coefficients (k, in s⁻¹) for the two H-shift reactions in the DMDS H-abstraction pathway shown in Fig.S10.

Rate coefficient	$E_{TS} - E_R$	Q_{TS}/Q_R	κ	k
<i>k</i> ₁	21.0	2.6×10^{-2}	478	3.2×10^{-2}
<i>k</i> ₂	23.2	1.0	536	3.3×10^{-2}

4.4 Reactions in the OH-addition channel of OH + DMDS

OH addition to one of the sulfur atoms in DMDS forms the OH-adduct $CH_3S(OH)SCH_3$. This radical has a low barrier (about 3 kcal/mol, Fig.S11) for scission of the S-S bond and this reaction has an estimated rate coefficient on the order of 10^{10} s⁻¹ (Table S4). Scission of the S-S bond forms the methylthio radical (CH₃S) and CH₃SOH, which both have further oxidation pathways leading to SO₂ (Scheme 1, main manuscript). The very high rate coefficient of CH₃S(OH)SCH₃ decomposition suggests that this pathway will dominate over potential competing reactions. Reaction of the CH₃S(OH)SCH₃ radical with O₂ will happen with a pseudo first order rate coefficient of the order of 10^8 s⁻¹ and will lead to formation of CH₃SOO (identical to the product from CH₃S + O₂) and CH₃SOH. Thus CH₃S (will react with O₂ and give CH₃SOO) and CH₃SOH will dominate, or even be the sole products with an expected formation yield of close to unity.



Reaction coordinate

Fig.S11. Stationary points for DMDS+OH and the subsequent dissociation reaction calculated at the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ level.

Table S4. RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ calculated barrier heights ($E_{TS} - E_R$, in kcal/mol), ω B97X-D/aVTZ summed, weighted partition function ratio (Q_{TS}/Q_R), Eckart tunneling coefficient (κ) and MC-TST rate coefficients (k, in s⁻¹) for the DMDS-OH decomposition (Fig.S11). Note that the barrier is so low that the absolute MC-TST rate coefficient is only approximate.

Reaction	$E_{TS} - E_R$	Q_{TS}/Q_R	κ	k
DMDS-OH decomposition	3.4	2.57	1.00	5.4×10^{10}

4.5 Reaction of ozone with methane sulfenic acid

We find that methane sulfenic acid (CH₃SOH) formed by the CH₃S(OH)SCH₃ dissociation reaction may react with ozone (O₃) in a concerted reaction in which one end of the ozone molecule abstracts a hydrogen from the hydroxy group while the other end adds to the sulfur atom, forming CH₃S(O)OOOH. The reaction proceeds by formation of a pre-reactive complex lower than the free reactants by 3.6 kcal/mol at the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ level (Fig. 2, main manuscript). The TS is further lowered by 0.6 kcal/mol (Fig. 2, main manuscript).

For the formed intermediate CH₃S(O)OOOH, we find two possible unimolecular decomposition channels; one occurring by a concerted reorganization and O₂-loss (Fig. 2, main manuscript, grey) and the other by HO₂-loss (Fig. 2, main manuscript, orange). The O₂-loss channel occurs via a sixmembered cyclic TS structure, has a barrier of 12.7 kcal/mol and forms methanesulfinic acid CH₃S(O)OH and singlet molecular oxygen. The two products form a weak complex with a binding energy of about 2.5 kcal/mol. The HO₂ loss channel is simply the O-O bond cleavage with a reaction barrier of 11.7 kcal/mol leading to the formation of the CH₃S(O)O radical and HO₂. These form a strong complex with a binding energy of 9.5 kcal/mol, where the oxygen from HO₂ is closely interacting with the sulfur. Even so, the energy from the previous steps is likely sufficient to separate the two products. The CH₃S(O)O radical will then decompose to form CH₃ and SO₂ (see main manuscript).

In Fig.S12, we show the energy diagram corresponding to Fig. 2 in the main manuscript, but calculated without the final RO-CCSD(T)-F12a/VDZ-F12 single-point energy correction. At this level of theory, which also provides the geometry for the RO-CCSD(T)-F12a/VDZ-F12 calculation, the barrier for the reaction between CH_3SOH and ozone is 2.8 kcal/mol relative to the pre-reactive complex (Fig.S12).



Fig.S12. Stationary points in the ozone-initiated CH₃SOH oxidation mechanism calculated at the ω B97X-D/aVTZ level. The reaction between CH₃SOH and ozone is shown in blue. The O₂ loss channel is shown in grey, the HO₂ loss channel is shown in orange. The corresponding figure at the higher RO-CCSD(T)-F12a/VDZ-F12 level is given in Fig. 2 of the main manuscript.

The calculated MC-TST reaction rate coefficients at the RO-CCSD(T)-F12a/VDZ-F12 level for the O_2 and HO_2 loss channels are 5.9×10^3 s⁻¹ and 1.2×10^4 s⁻¹, respectively, following thermalization of the CH₃S(O)OOOH intermediate (Table S5). However, our RRKM-ME simulations (Fig.S13) show that the unimolecular reactions occur promptly via the excess energy from the preceding reaction between CH₃SOH and ozone (Fig.S14). The MESMER modelling suggests that the HO₂-loss channel is favoured by 76:24 (Table S6) using the potential energy surface calculated for the lowest-energy conformers at the RO-CCSD(T)-F12a/VDZ-F12a level (Fig.S13). Changes of ± 1 kcal/mol to the two barrier heights independently decrease/increase their relative importance by about 5-10 % (Table S6). For the potential calculated at the slightly lower ω B97X-D/aVTZ level (Fig.S12), the branching is about 50:50 (Fig.S15).

Table S5. RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ calculated barrier heights ($E_{TS} - E_R$, in kcal/mol), ω B97X-D/aVTZ summed, weighted partition function ratio (Q_{TS}/Q_R), Eckart tunneling coefficient (κ) and MC-TST rate coefficients (k, in s⁻¹) for the two unimolecular reactions of the thermalized CH₃S(O)OOOH (Fig. 3, main manuscript).

Rate coefficients	$E_{TS} - E_R$	Q_{TS}/Q_R	к	k
HO ₂ loss	11.7	0.72	1.04	1.2×10 ⁴
O ₂ loss	12.7	0.33	5.88	5.9×10 ³



Reaction coordinate

Fig.S13. Potential energy surface used for the MESMER simulations. The energies are calculated using RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ electronic energies with ω B97X-D/aVTZ zero-point correction. The potential is modified relative to Fig. 3, main manuscript, by removing the pre-reactive complex and initial TS and modelling the initial bimolecular reaction with a rate coefficient of 1×10⁻¹² cm³ molecule⁻¹ s⁻¹. The relative energies of the products refer to the post-reaction complexes.



Fig.S14. Fractional species populations as a function of time from the RRKM simulations using the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ potential energy surface (Fig.S13) with two different O₃ concentration: Left: [O₃] = 1×10¹² molecules/cm³ corresponding to the experimental conditions. Right: [O₃] = 1×10²⁰ molecules/cm³ to assess whether the two unimolecular reactions occur by excess energy.

Table S6. The O₂ and HO₂ loss branching ratio simulated by MESMER based on the potential calculated at the RO-CCSD(T)-F12a/VDZ-F12// ω B97X-D/aVTZ level (Fig.S13) and with barriers for the two unimolecular pathways decreased or increased by 1 kcal/mol.

	Barrier		Channel ratio	
	[kcal/m	ol]		
	O ₂ HO ₂		O ₂	HO ₂
	loss loss		loss	loss
Calculated barriers	12.5	11.6	24%	76%
O ₂ -loss -1 kcal/mol	11.5	11.6	32%	68%
HO ₂ -loss +1 kcal/mol	12.5	12.6	32%	68%
O ₂ -loss +1 kcal/mol	13.5	11.6	18%	82%
HO ₂ -loss -1 kcal/mol	12.5	10.6	18%	82%



Fig.S15. Fractional species populations as a function of time from the RRKM simulations using the ω B97X-D/aVTZ potential energy surface with $[O_3] = 1 \times 10^{12}$ molecules/cm³ corresponding to the experimental conditions.

5 Importance of DMDS emissions and its potential relevance for the SO₂ budget

In order to assess the potential importance of DMDS emissions from biomass burning for the overall SO₂ budget, the different emission strengths from (i) savanna and grassland fires and (ii) forest fires were compared. Global emission data of DMS and SO₂ for the two different biomass burning sources were taken from Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP).⁵⁴ To estimate realistic emissions of DMDS, a DMDS/DMS emission ratio of about 13.5 was applied in this study determined by Meinardi et al. (2003) ⁵⁵ during a savanna fire period in Northern Australia in 1999. Thus, the global emissions during the year 1999 were chosen in this study. Unfortunately, a DMDS/DMS emission ratio has not been determined for forest burning. As the ratio can strongly differ between different biomass burning sources and conditions, the ratio of 13.5 has been considered as an upper-limit estimate and the ratio of unity was applied as lower-limit estimate.

Fig.S16 shows the global emission pattern of DMS, DMDS (DMS×13.5), and SO₂ from the two different biomass burning sources: (i) savanna and grassland fires and (ii) forest fires. The global maps of the forest fires reveal quite similar DMDS and SO₂ emission patterns in distribution and size. On the other hand, the SO₂ emissions are dominant for savanna and grassland fires. Additionally, it can be seen that the emission strengths of the forest fires are substantially larger in terms of DMS and DMDS compared to savanna and grassland fire emissions.

Fig.S17 shows the calculated global monthly sulfur emission of DMS, DMDS, and SO₂ for both the upper-limit and lower-limit estimate. In Fig.S17, a clear seasonality can be seen. Forest fires show the highest emission rates during March, August, September and October, whereas the strongest emissions from savanna and grassland fires occur during the summer period at the Northern and Southern hemisphere. A comparison of the calculated values with the ones by Meinardi et al. (2003) ⁵⁵ reveals a good agreement for DMDS emissions related to savanna and grassland fires for the applied ratio of 13.5. The emission estimate by Meinardi et al. (2003) ⁵⁵ ranges between 9.5 and 41.5 Gg S yr⁻¹ and the calculations done in this study give 80.1 Gg S yr⁻¹. However, in terms of the estimated global sulfur emissions, 119 Gg S yr⁻¹, it fails when this ratio is applied for forest fire emissions that are 2360 Gg S yr⁻¹. In this case, a better agreement is obtained for the lower-limit estimate with overall 175 Gg S yr⁻¹. But still, it has to be noted that the total sulfur emissions related to DMS are 133 Gg S yr⁻¹ that is far too high compared to the estimations of 6 Gg S yr⁻¹. However, this is maybe caused by the use of DMS measurements of savanna fires as proxy, only.

Overall, it can be concluded from the applied upper-limit estimate that DMDS contributes with more than 50 % significantly to biomass burning related sulfur emissions. It is also not negligible even for the lower-limit estimate where it contributes to about 8 % globally. Consequently, global models have to consider the emission and oxidation of DMDS to predict realistic sulfate aerosol concentrations and their effect on the atmosphere.

A direct comparison of the strength of DMDS-derived SO₂ formation with the SO₂ emissions becomes possible due to the rapid DMDS conversion to two SO₂. The atmospheric lifetime of DMDS with respect to the OH radical reaction is about 35 min. based on $k(OH + DMDS) = 2.3 \times 10^{-10} \text{ cm}^3$ molecule ⁻¹ s⁻¹ at 298 K ¹² and a steady-state OH radical concentration of 2×10^6 molecules cm⁻³. In the presence of $(5 - 10) \times 10^{11}$ molecules cm⁻³ of ozone (mixing ratio: 20 - 40 ppbV), SO₂ formation is complete within the first 20 s after the OH attack towards DMDS, as experimentally shown in the main manuscript. This study implicates that the DMDS-derived SO₂ formation can be as high as the direct SO₂ emission and, thus, demonstrates its global importance.



Fig.S16. Annual emissions of sulfur from biomass burning related to DMS, DMDS and SO_2 for the year 1999 of the upper-limit estimate for forest fires (left), and savanna and grassland fires (right).



Fig.S17. Monthly emissions of sulfur from biomass burning related to DMS, DMDS and SO_2 for the year 1999 of the lower-limit (top) and upper-limit estimate (bottom) for forest fires (left) as well as for savanna and grassland fires (right).

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