

Reaction kinetics and multi-sulfur products formation of sulfur-containing volatile organic compounds with OH radicals

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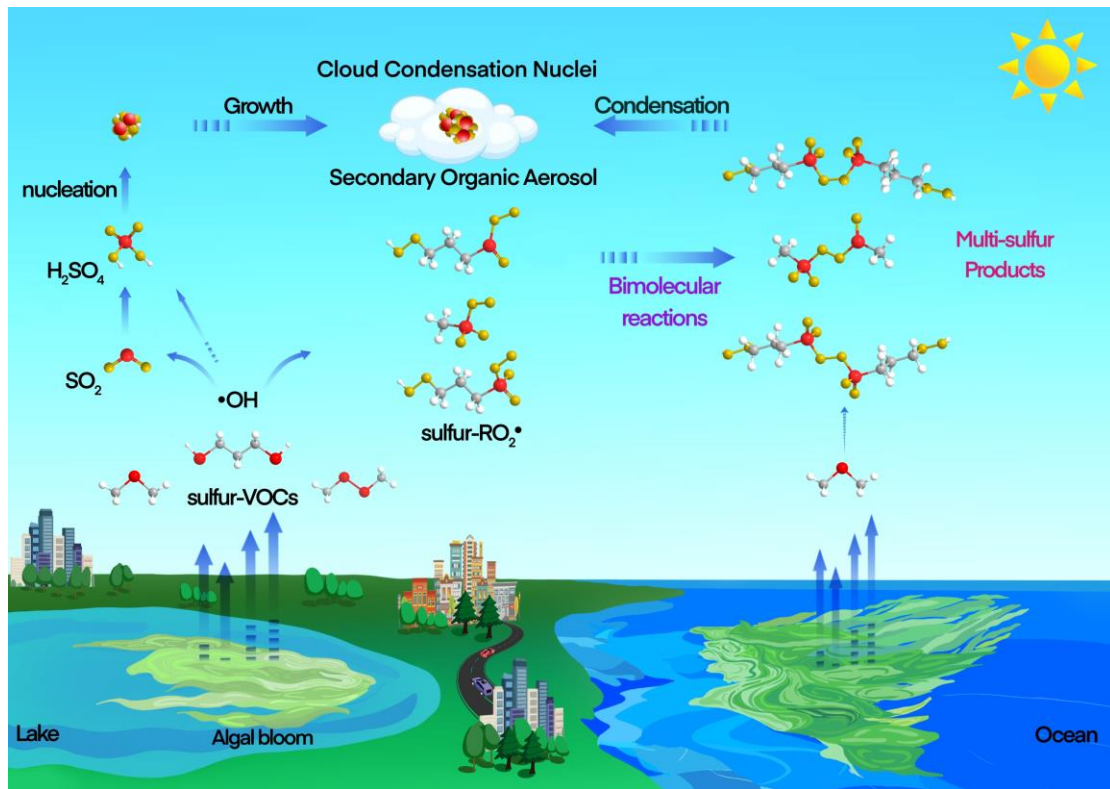
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Abstract. Atmospheric sulfur-containing volatile organic compounds (sulfur-VOCs) have been recognized as crucial precursors for gaseous sulfuric acid (H₂SO₄), particulate sulfate and secondary organic aerosol (SOA) formation. However, their reaction kinetics and multi-sulfur product formation remain poorly understood. This study presents a systematic kinetic investigation into •OH-initiated oxidation of a series of sulfur-VOCs including thiols and sulfides. The reaction rate constants vary with molecular structure, with high reactivity observed for trimethylene sulfide and dimethyl disulfide. It was further demonstrated that under ~~low-low~~-NO_x conditions, sulfur-containing RO₂ radicals can undergo bimolecular reactions forming low-volatility multi-sulfur products that enhance their SOA formation potential. Additionally, many sulfur-VOCs investigated in our chamber experiments are also identified from the emissions of algae samples collected from a major freshwater lake in China, and similar multi-sulfur oxidation products were observed after •OH oxidation. These findings advance the kinetic and mechanistic understanding of atmospheric sulfur-VOCs oxidation and suggest that the formation of low-volatility multi-sulfur products and inorganic sulfur-containing species may contribute to SOA production and new particle formation in marine and freshwater environments influenced by algal emissions.

Keywords: sulfur-VOCs, reaction rate constants, multi-sulfur products, freshwater algae emissions, secondary organic aerosol



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1 Introduction

Atmospheric sulfur-containing volatile organic compounds (sulfur-VOCs) (e.g., dimethyl sulfide (CH_3SCH_3 , DMS), methanethiol (CH_3SH), dimethyl disulfide ($\text{CH}_3\text{S}_2\text{CH}_3$, DMDS), and carbonyl sulfide (OCS)) are important biogenic VOCs and mainly produced by degradation of sulfur-containing amino acids and methylation of sulfides (Kietäväinen et al., 2025; Kilgour et al., 2021; Li et al., 2022; Wang et al., 2023b). These compounds play a key role in the global atmospheric sulfur cycle, and their atmospheric oxidation products such as sulfuric acid (H_2SO_4) and methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) are able to combine with basic species (e.g., NH_3 and amines) to form new particles and particulate sulfate, which can contribute to the formation of cloud condensation nuclei (CCN) and then have an effect on regional and global climate (Bates et al., 1992; Charlson et al., 1987; Fiddes et al., 2021; Jokinen et al., 2022; Revell et al., 2024; Wang et al., 2023a).

At present, it is widely recognized that marine ecosystems (e.g., phytoplankton) are the dominant natural sources of atmospheric sulfur-VOCs, among which DMS is the dominant one and mainly produced via the dimethylsulfoniopropionate (DMSP) metabolic pathway of phytoplankton (Andreae and Raemdonck, 1983; Novak et al., 2022; Rocco et al., 2025). Foundational studies by Kiene and co-workers demonstrated that DMSP can be transformed in marine systems through microbial cleavage and demethylation pathways, leading to the formation of reduced sulfur compounds such as DMS and methanethiol (Kiene, 1996; Kiene et al., 2000; Kiene and Taylor, 1988; Kiene and Service, 1991; Visscher et al., 1994; Yoch, 2002). The importance of this source is further underscored by recent satellite-based observations showing that, between 2003 and 2020, the global spatial extent of coastal phytoplankton blooms expanded by 13.2% (+ 3.97 million km^2) and their frequency increased by 59.2%, indicating an overall intensification of marine algae activity (Dai et al., 2023). Measurements in marine boundary layer have reported DMS mixing ratios ranging from tens to a few hundred pptv with pronounced seasonal maxima in biologically productive waters (Zhao et al., 2021). Co-emitted methanethiol has also been detected, generally ranging from ~10 to 250 pptv (Mynard et al., 2025; Novak et al., 2022; Rocco et al., 2025).

In addition to marine phytoplankton, freshwater algae are also recognized as important sources of atmospheric sulfur-VOCs, including DMS, DMDS, and dimethyl trisulfide ($\text{CH}_3\text{S}_3\text{CH}_3$, DMTS), which are released through amino acid degradation and methylation processes (Bao et al., 2024; Huang et al., 2018; Li et al., 2022). This source is becoming particularly relevant in eutrophic freshwater lakes experiencing frequent algal blooms. In China, around 85.4% of the 138 major freshwater lakes with their areas larger than 10 km^2 suffer from varying degrees of eutrophication (Wang et al., 2022). In such systems, concentrations of DMS, DMDS, and DMTS in the water column commonly reach the microgram per liter level (Bao et al., 2024; Huang et al., 2018; Lu et

al., 2012; Yu et al., 2019a). Supporting the potential for atmospheric release, previous laboratory and field studies have quantified sulfur-VOCs emission fluxes from freshwater lakes, showing that DMS can be emitted at rates of several $\mu\text{mol m}^{-2} \text{d}^{-1}$, with emission intensity strongly modulated by seasonality and trophic status of lakes (Li et al., 2022; Steinke et al., 2018). Many sulfur-VOCs have been directly observed in the atmosphere near an inland freshwater lake (Dianshan Lake, Shanghai) during winter-spring campaigns, with mixing ratios of DMS, methanethiol and DMDS can be up to 331.4 pptv, 183.8 pptv, and 153.6 pptv, respectively (Deng et al., 2025).

Once released into the atmosphere, sulfur-VOCs can undergo oxidation by multiple atmospheric oxidants, including hydroxyl radicals ($\bullet\text{OH}$), nitrate radicals ($\text{NO}_3\bullet$), and ozone (O_3), with $\bullet\text{OH}$ typically acting as the dominant daytime oxidant and $\text{NO}_3\bullet$ becoming important during nighttime conditions (Atkinson and Arey, 2003; Barnes et al., 2006; Du et al., 2007; Stark et al., 2007). The reaction rate constants between a few sulfur-VOCs (e.g., methanethiol, DMS, and DMDS) with $\bullet\text{OH}$ have been well-established, with k_{OH} values of $\sim 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methanethiol, $\sim 7.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for DMS, and $\sim 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for DMDS, at 298 K, respectively (Abbatt et al., 1992; Barnes et al., 1986; Cruz-Torres and Galano, 2007; Hashemi et al., 2019; Atkinson et al., 2004). These reactions play a critical role in determining the atmospheric lifetimes and transformation pathways of these sulfur VOCs. There are significant differences in the reactivity of sulfur-VOCs with different functional groups towards $\bullet\text{OH}$, with thiols and disulfides generally exhibiting higher reactivity than that of mono-sulfides (Abbatt et al., 1992; Cruz-Torres and Galano, 2007; Hashemi et al., 2019; Tahan and Shiroudi, 2020). However, systematic understanding of reaction kinetics of sulfur-VOCs with different functional groups towards $\bullet\text{OH}$ remains limited, particularly for sulfur-VOCs with complex molecular structures which are increasingly detected in field measurements. For instance, 1-propanethiol ($\text{CH}_3(\text{CH}_2)_2\text{SH}$), 2-propanethiol ($(\text{CH}_3)_2\text{CHSH}$), methyl propyl disulfide ($\text{CH}_3\text{S}_2(\text{CH}_2)_2\text{CH}_3$), diethyl disulfide ($\text{CH}_3\text{CH}_2\text{S}_2\text{CH}_2\text{CH}_3$), and isopropyl disulfide ($(\text{CH}_3)_2\text{CHS}_2\text{CH}(\text{CH}_3)_2$) have been detected from freshwater algae emissions, yet data on their reaction kinetics with $\bullet\text{OH}$ remain scarce (Liu et al., 2021; Yu et al., 2019b; Zhou et al., 2024). Therefore, it hinders accurate assessments of the chemical behavior and environmental impact of these biogenic sulfur-VOCs in the atmosphere, particularly in aquatic environments (e.g., huge freshwater lakes) where algae blooms frequently occur.

Previous studies on the reaction mechanisms between some sulfur-VOCs and $\bullet\text{OH}$ have established a relatively comprehensive framework, evolving from early kinetic and product studies to more recent investigations of detailed radical chemistry and autoxidation processes (Berndt et al., 2024; Goss and Kroll, 2023; Shen et al., 2022; Ye et al., 2022). The initial steps typically involve the formation of sulfur-containing radicals (sulfur- $\text{R}\bullet$) via H-extraction or $\bullet\text{OH}$ -addition, which then combine with O_2 to generate various sulfur-containing RO_2 radicals (sulfur- $\text{RO}_2\bullet$) (Berndt et al.,

2023; Goss and Kroll, 2023; Shen et al., 2022). Among these, sulfides primarily form α -carbon peroxy radicals (e.g., $\text{CH}_3\text{SCH}_2\text{OO}\cdot$), while thiols and disulfides tend to generate sulfur-centered peroxy radicals (e.g., $\text{RSOO}\cdot$) (Berndt et al., 2023; Goss and Kroll, 2023; Lily et al., 2023). Although the unimolecular reactions (e.g., H-migration) and bimolecular reaction pathways involving NO_x and $\text{HO}_2\cdot$ of these sulfur- $\text{RO}_2\cdot$ species have been investigated, the bimolecular reactions between sulfur- $\text{RO}_2\cdot$ and sulfur- $\text{R}'\text{O}_2\cdot$ remain poorly characterized (Berndt et al., 2023; Jernigan et al., 2022; Shen et al., 2022).

This study systematically investigated the reaction kinetics and multi-sulfur products formation of 11 sulfur-VOCs with $\cdot\text{OH}$ using a Teflon chamber together with a Vocus proton transfer reaction long-time-of-flight mass spectrometry (Vocus-PTR-LToF-MS, ToFwerk AG) and a nitrate-based chemical ionization long-time-of-flight mass spectrometry (nitrate-CI-LToF-MS, Aerodyne Research) (Ehn et al., 2014; Krechmer et al., 2018). To investigate the relationship between products formation and their molecular structures, these 11 sulfur-VOCs were divided into 5 classes, which are monothiols (i.e., ethanethiol ($\text{C}_2\text{H}_6\text{S}$), 1-propanethiol ($\text{C}_3\text{H}_8\text{S}$), and 2-propanethiol ($\text{C}_3\text{H}_8\text{S}$)), dithiols (i.e., 1,2-ethanedithiol ($\text{C}_2\text{H}_6\text{S}_2$), and 1,3-propanedithiol ($\text{C}_3\text{H}_8\text{S}_2$)), acyclic sulfides (i.e., dimethyl sulfide ($\text{C}_2\text{H}_6\text{S}$), methyl ethyl sulfide ($\text{C}_3\text{H}_8\text{S}$), and bis(methylthio)methane ($\text{C}_3\text{H}_8\text{S}_2$)), cyclic sulfides (i.e., trimethylene sulfide ($\text{C}_3\text{H}_6\text{S}$), and 1,3-dithiolane ($\text{C}_3\text{H}_6\text{S}_2$)) and disulfides (dimethyl disulfide ($\text{C}_2\text{H}_6\text{S}_2$)) (Table 1). Moreover, the emitted VOCs from freshwater algae samples taken from a huge freshwater lake (i.e., Taihu lake, China) and their oxidation products by $\cdot\text{OH}$ were also investigated. Similar sulfur-VOCs and multi-sulfur products were also observed from VOCs emitted from freshwater algae samples and their oxidation products, which demonstrates the atmospheric relevance of our selected sulfur-VOCs and their atmospheric transformation mechanisms in our study.

2 Materials and methods

2.1 Chamber experiments of 11 sulfur-VOCs with $\cdot\text{OH}$

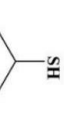
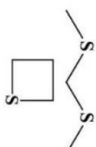
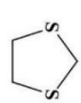
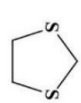
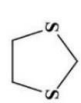
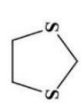
The selected 11 high-purity ($\geq 96\%$) sulfur-VOCs liquid standards (Sigma-Aldrich and Macklin) were listed in Table S1. These liquid standards were then used to generate individual sulfur-VOC standard gases with our laboratory partial-pressure gas mixing system (Li et al., 2025; Wang et al., 2020). The experimental setup is shown in Figure S1. A 0.53 m^3 polytetrafluoroethylene (FEP) chamber was employed to conduct atmospheric oxidation experiments of sulfur-VOCs with $\cdot\text{OH}$. The experimental conditions including the initial mixing ratios of sulfur-VOCs, O_3 concentration, and relative humidity (RH), are summarized in Table 1. These experiments were used for product identification and yield estimations for multi-sulfur products. The OH radicals were generated by photolysis of O_3 under humid condition using a 253 nm ultraviolet lamp (Philips TUV 16W).

During these experiments, the evolution of 11 sulfur-VOCs was monitored by a Vocus-PTR-

LToF-MS, and their oxidation intermediates and products (e.g., sulfur-containing peroxy radicals, gaseous H_2SO_4 and multi-sulfur products) were detected using a nitrate-CI-LToF-MS (Ehn et al., 2014; Krechmer et al., 2018). The Vocus-PTR-LToF-MS detects sulfur-VOCs mainly through proton-transfer reactions between reagent ions (i.e., hydronium ions (H_3O^+) and their water-cluster ions ($(\text{H}_2\text{O})_{2-3}\cdot\text{H}^+$) and sulfur-VOCs with proton affinities higher than that of water. The nitrate-CI-LToF-MS employs nitrate reagent ions, including NO_3^- , $\text{HNO}_3\cdot\text{NO}_3^-$, and $(\text{HNO}_3)_2\cdot\text{NO}_3^-$, to detect sulfuric acid and highly oxygenated organic oxidation products mainly through nitrate-adduct cluster formation. Additionally, a more detailed description of instrument operation, mass calibration, and calibration procedures is provided in Text S1. The estimation of wall and dilution loss of sulfur-VOCs in our chamber was described in Text S3. The procedure used to quantify sulfur-containing oxygenated organic molecules (sulfur-OOMs) was described in Text S5. In addition, an ozone monitor (Thermo, 49i) and a temperature and humidity sensor (Vaisala HMP110) were used to record O_3 concentration and monitor environmental conditions in the chamber. Because the chamber is not collapsible, a make-up flow of 15 L/min high-purity zero air generated from a zero air generator (AADCO 737 series) was continuously introduced to the chamber and a RH of 20-25% was maintained.

Relative-rate experiments were conducted for selected representative sulfur-VOCs to obtain their $\bullet\text{OH}$ reaction rate constants. Isoprene was used as the reference compound because its $\bullet\text{OH}$ reaction rate constant at room temperature is well established and k (isoprene + $\bullet\text{OH}$) was taken as $10.00 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Iida et al., 2002; Medeiros et al., 2018). In these experiments, each selected sulfur-VOC was introduced simultaneously with isoprene into the chamber at $298 \pm 2 \text{ K}$ and 1 atm and their temporal decays were monitored by Vocus-PTR-LToF-MS. The concentrations of sulfur-VOCs and isoprene were corrected for dilution and wall loss before relative-rate analysis. Each relative-rate experiment was conducted in triplicate. Details of the relative-rate calculation, wall/dilution loss correction, and uncertainty estimation are provided in Text S2.

169 **Table 1.** Experimental conditions for •OH-initiated oxidation experiments of 11 sulfur-VOCs used for product identification and yield estimations for multi-sulfur products
170 at 291±1 K and 1 atm.

Exp.	Species	sulfur-VOCs	Formulae	Molecular structure	Precursor conc. (ppbv)	[O ₃] (ppbv)	Relative humidity (%)
1	Monothiols	ethanethiol	C ₂ H ₆ S		0.90	33.5	25.1
2		1-propanethiol	C ₃ H ₈ S		1.50	31.7	24.3
3		2-propanethiol	C ₃ H ₈ S		45.39	32.4	17.4
4	Dithiols	1,2-ethanedithiol	C ₂ H ₆ S ₂		1.10	31.8	24.0
5		1,3-propanedithiol	C ₃ H ₈ S ₂		1.77	31.5	24.0
6		1,3-propanedithiol	C ₃ H ₈ S ₂		0.65	30.0	23.9
7	Acyclic sulfides	dimethyl sulfide	C ₃ H ₈ S		1.67	30.5	24.3
8		1,2-ethanedithiol	C ₂ H ₆ S ₂		2.84	30.0	22.8
9		1,3-propanedithiol	C ₃ H ₈ S ₂		2.33	31.1	24.0
10	Cyclic sulfides	bis(methylthio)methane	C ₃ H ₈ S ₂		0.83	30.9	24.0
11		trimethylene sulfide	C ₃ H ₆ S		0.94	31.7	22.0
12		1,3-dithiolane	C ₃ H ₆ S ₂		0.28	29.5	24.2
13	Disulfides	dimethyl disulfide	C ₂ H ₆ S ₂		0.29	31.7	24.3
14		1,3-dithiolane	C ₃ H ₆ S ₂		0.79	28.6	24.3
15		1,3-dithiolane	C ₃ H ₆ S ₂		0.62	29.7	25.3
16	Disulfides	dimethyl disulfide	C ₂ H ₆ S ₂		1.40	35.0	22.8
17		1,3-dithiolane	C ₃ H ₆ S ₂		1.23	31.7	24.3
18		dimethyl disulfide	C ₂ H ₆ S ₂		0.74	33.0	25.5
19	Disulfides	dimethyl disulfide	C ₂ H ₆ S ₂		0.75	29.0	24.7
20		dimethyl disulfide	C ₂ H ₆ S ₂		0.75	29.0	24.7

2.2 Characteristic of VOC emission from freshwater algae

Fresh-water samples with algae were collected from Taihu Lake (approximately 2338.1 km²), China, which is the third largest freshwater lake in China (Qin et al., 2019; Wang et al., 2023c), at the Taihu Lake Ecosystem Research Station (Figure S2a). In the past years, frequent large-scale algal blooms have occurred in Taihu Lake due to anthropogenic nutrient inputs and endogenous pollutant releases in summer (Wang et al., 2019; Xu et al., 2021). Therefore, the water samples with algae taken from Taihu Lake were treated as representative samples of freshwater algae. Approximately 10 L of algae-containing lake water was collected using a clean 12 L polyethylene terephthalate (PET) drinking-water bottle. The sample was promptly transported to the laboratory and kept in the laboratory at approximately 21 °C for approximately 2 d before the chamber experiment. No filtration or other turbidity-removal treatment was applied before use.

During the emission characterization process, water samples were divided into 12 petri dishes (with a total exposed liquid surface area of 0.213 m²) and placed in the chamber. The chamber containing the water samples was then flushed with zero air at a flow rate of 15 L min⁻¹ for 2 h. After the flushing was completed, no additional gas was introduced, and the water samples were kept under static conditions in the chamber for 18 hours at ~~the temperature of~~ approximately 21°C to allow the release of VOCs (Figure S2b). After this static period, the VOCs released from the water samples were measured by Vocus-PTR-LToF-MS for approximately 30 min before O₃ was introduced into the chamber. After that, approximately 90 ppb of O₃ was injected into the chamber and two 253 nm UV lamps were turned on to generate •OH by photolysis of O₃ under humid conditions (Figure S3). A Vocus-PTR-LToF-MS, which was calibrated using selected sulfur-VOC standards (Text S4), was employed to measure and identify sulfur-VOCs and other VOC species released from freshwater algae, as well as their low-oxygenated oxidation products, while a nitrate-CI-LToF-MS was used to identify the mono-sulfur and multi-sulfur products derived from the reactions of sulfur-VOCs from the algal source with •OH. A filtration control experiment was also performed to examine whether the detected sulfur-VOCs were associated with algae. The sample was filtered using three stacked layers of ordinary qualitative laboratory filter paper, and the filtration procedure was repeated three times to enhance the removal of visible algal particles. Further details of the filtration control experiment are provided in Text S7.

3 Results and discussion

3.1 Rate constants of sulfur-VOCs with •OH

The •OH reaction rate constants were reported in Table 2 and determined from relative-rate experiments. The selected sulfur-VOCs covered representative functional groups, including monothiol, dithiol, acyclic sulfide, cyclic sulfide, and disulfide. Representative relative-rate plots

are shown in Figure 1. The linear relationships between the loss-corrected logarithmic depletion of sulfur-VOCs and that of isoprene indicate that the relative-rate method provides stable constraints on the $\bullet\text{OH}$ reaction rate constants under the present experimental conditions. The rate constants obtained in this work span more than one order of magnitude, ranging from $(0.83 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for DMS to $(26.99 \pm 1.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for trimethylene sulfide at $298 \pm 2 \text{ K}$.

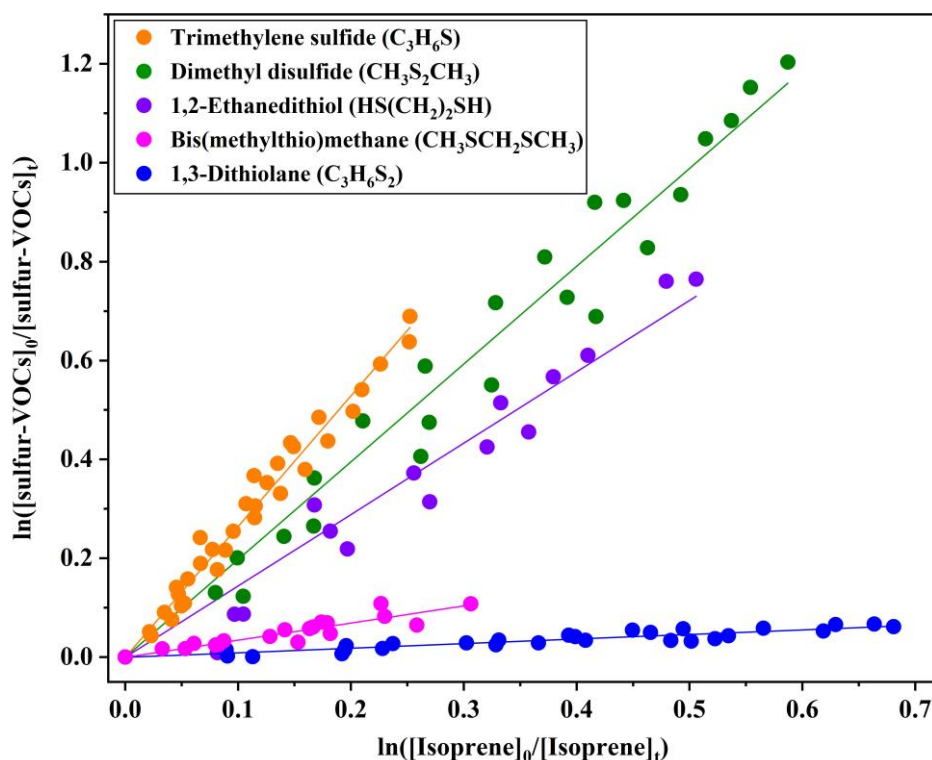


Figure 1. Relative-rate plots for selected sulfur-VOCs using isoprene as the reference compound. The loss-corrected logarithmic depletion of each sulfur-VOC is plotted against that of isoprene. Different colors indicate different sulfur-VOCs, and solid lines denote linear regressions used to derive the $\bullet\text{OH}$ reaction rate constants.

218 **Table 2.** The •OH reaction rate constants of selected sulfur-VOCs determined by the relative-rate method using isoprene as a reference species at 298 ± 2 K.

Species	sulfur-VOCs	Formulae	$k \times 10^{11}$ (cm ³ molecule ⁻¹ s ⁻¹)	T (K)	p (Pa)	Buffer gas	Technique ^a	Reference
Monothiol	ethanethiol	CH ₃ CH ₂ SH	3.89 ± 0.57	298	1.01 × 10 ⁵	air	CP-GC	(Wang et al., 2008)
			4.50 ± 0.50	300	1.01 × 10 ⁵	N ₂	CP-GC	(Barnes et al., 1986)
			4.21 ± 0.32	298	1.0 × 10 ⁴	Ar	FP-RF	(Wine et al., 1984)
			4.51 ± 0.32	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
Dithiol	1,2-ethanedithiol	HS(CH ₂) ₂ SH	14.36 ± 0.26	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
Acyclic sulfide	dimethyl sulfide	CH ₃ SCH ₃	0.87 ± 0.03	298	1.01 × 10 ⁵	air	CP-GC	(Wang et al., 2008)
			0.78 ± 0.18	299	1.01 × 10 ⁵	air	CP-FTIR	(Albu et al., 2005)
			0.80 ± 0.05	298 ± 3	1.01 × 10 ⁵	air	CP-GC	(Barnes et al., 1988)
			0.83 ± 0.08	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
	bis(methylthio)methane	CH ₃ SCH ₂ SCH ₃	3.50 ± 0.09	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
Cyclic sulfide	trimethylene sulfide	C ₃ H ₆ S	26.99 ± 1.04	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
	1,3-dithiolane	C ₃ H ₆ S ₂	0.95 ± 0.05	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work
Disulfide	dimethyl disulfide	CH ₃ S ₂ CH ₃	23.90 ± 3.00	297	1466	N ₂	HPF-LIF	(Abbatt et al., 1992)
			19.80 ± 1.80	298	6666-26664	Ar	FP-RF	(Wine et al., 1981)
			22.30 ± 8.00	298	1.01 × 10 ⁵	air	CP-GC	(Cox and Sheppard, 1980)
			20.18 ± 1.53	298 ± 2	1.01 × 10 ⁵	air	Vocus-PTIR	This work

220 Note: The rate constants reported in this work were obtained from additional relative-rate experiments using isoprene as the reference compound. The •OH reaction rate constant
 221 of isoprene was taken as 10.00 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at 298 K (Iida et al., 2002; Medeiros et al., 2018). The uncertainties of this work represent the standard deviations
 222 of triplicate measurements.

223 ^a CP: continuous photolysis; GC: gas chromatography; FTIR: Fourier transform infrared spectroscopy; FP: flash photolysis; RF: resonance fluorescence; HPF: high-pressure
 224 fast flow; LIF: laser-induced fluorescence

For species with available literature data, the relative-rate-derived values agree well with previous values. For ethanethiol, the rate constant obtained in this work is $(4.51 \pm 0.32) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is consistent with previously reported values of (3.89 ± 0.57) to $(4.50 \pm 0.50) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ near room temperature (Barnes et al., 1986; Wang et al., 2008; Wine et al., 1984). For DMS, the rate constant obtained in this work is $(0.83 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, also consistent with that from previous studies. For DMDS ($\text{CH}_3\text{S}_2\text{CH}_3$), the relative-rate-derived value obtained in this work is $(20.18 \pm 1.53) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which agrees well with previously reported values of (19.80 ± 1.80) to $(23.90 \pm 3.00) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297-298 K (Abbatt et al., 1992; Cox and Sheppard, 1980; Wine et al., 1981). These agreements support the reliability of our relative-rate method and the obtained kinetic dataset.

The relative-rate results further show that $\bullet\text{OH}$ reactivity depends strongly on molecular structures of sulfur-VOCs, but not in a simple monotonic way with either sulfur atom number or cyclic structure. The dithiol 1,2-ethanedithiol ($\text{HS}(\text{CH}_2)_2\text{SH}$) exhibits a relatively high rate constant of $(14.36 \pm 0.26) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, consistent with the high reactivity of S-H functional groups toward $\bullet\text{OH}$. For thiols, previous kinetic and theoretical studies have shown that H-abstraction from the S-H group is an important and efficient initiation reaction pathway with $\bullet\text{OH}$, leading to the formation of sulfur-centered radicals (Atkinson and Arey, 2003; Cruz-Torres and Galano, 2007; Douroudgari et al., 2020; Mai et al., 2020). The presence of S-H groups therefore provides reactive H-abstraction sites and can enhance overall $\bullet\text{OH}$ reactivity, which is also consistent with previous experimental rate-constant measurements for aliphatic thiols (Barnes et al., 1986; Wang et al., 2008; Wine et al., 1984). However, the comparison among sulfur-VOCs also indicates that the number of sulfur atoms alone does not determine the rate constants. For example, bis(methylthio)methane ($\text{CH}_3\text{SCH}_2\text{SCH}_3$) contains two sulfur atoms but shows a moderate rate constant of $(3.50 \pm 0.09) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, behaving kinetically more like an acyclic sulfide than a highly reactive dithiol or disulfide.

The two cyclic sulfides investigated show contrasting reactivities. Trimethylene sulfide ($\text{C}_3\text{H}_6\text{S}$) exhibits the highest rate constant $((26.99 \pm 1.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ among the selected sulfur-VOCs. This high reactivity is likely associated with its strained three-membered ring structure, which may facilitate $\bullet\text{OH}$ -initiated reaction pathways. In contrast, 1,3-dithiolane ($\text{C}_3\text{H}_6\text{S}_2$) shows a lower rate constant of $(0.95 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This contrast indicates that cyclic structure alone does not necessarily lead to enhanced $\bullet\text{OH}$ reactivity, and ring strain, sulfur functionality, and specific molecular configuration need to be considered together.

Acyclic and cyclic sulfides can react with $\bullet\text{OH}$ through both H-abstraction from $\alpha\text{-C-H}$ bonds and $\bullet\text{OH}$ -addition to the sulfur atom. Previous studies have shown that the $\bullet\text{OH}$ -addition pathway can become more competitive under lower-temperature conditions (Barnes et al., 2006; Ye et al., 2022).

Because the rate constants reported here are derived from overall precursor decay, the observed values represent the combined contribution of possible initiation pathways, and the relative branching between H-abstraction and $\bullet\text{OH}$ -addition cannot be directly separated in the present experiments. Overall, the kinetic results demonstrate that the $\bullet\text{OH}$ reaction rate constants of sulfur-VOCs depend on molecular features, such as reactive S-H groups, sulfur functionality, α -C-H sites and ring strain.

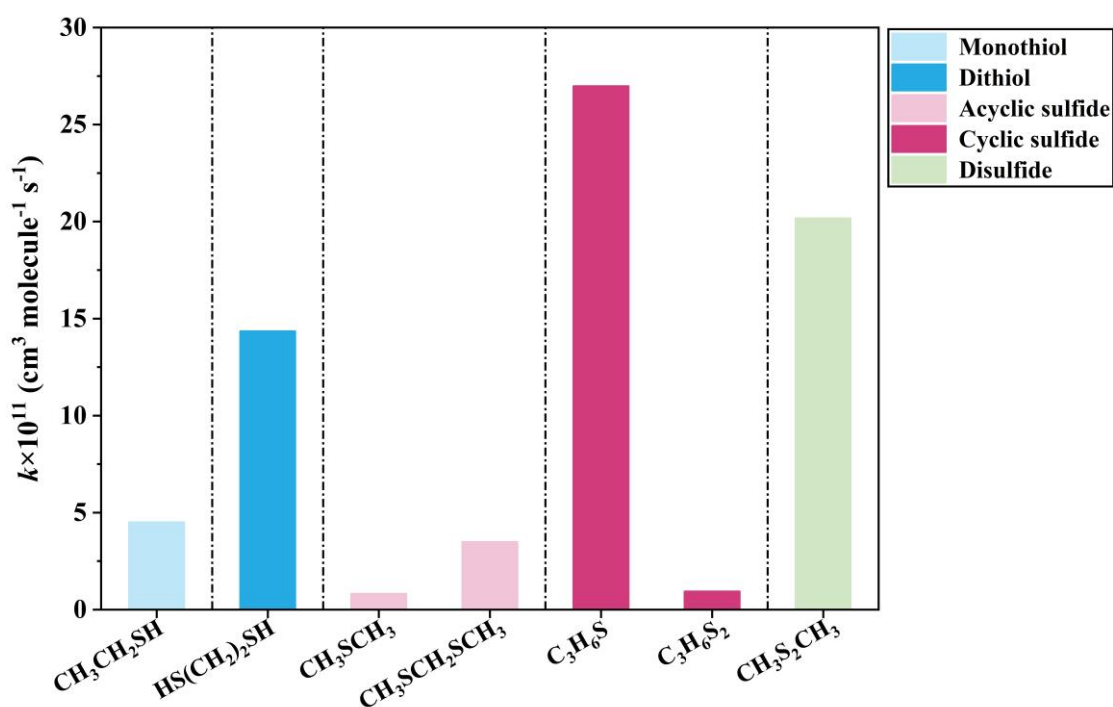


Figure 2. Reaction rate constants of 7 sulfur-VOCs with $\bullet\text{OH}$, divided by their functional groups.

3.2 Formation of multi-sulfur products

During our chamber experiments, many multi-sulfur products which contain 2 sulfur atoms in their chemical formulas were detected by nitrate-CI-LToF-MS (Table S3). The formation pathways of multi-sulfur products from $\bullet\text{OH}$ -initiated oxidation of 11 selected sulfur-VOCs under NO_x -free conditions were investigated. The 11 sulfur-VOCs examined here comprise 5 thiols ($\text{CH}_3\text{CH}_2\text{SH}$, $\text{CH}_3(\text{CH}_2)_2\text{SH}$, $(\text{CH}_3)_2\text{CHSH}$, $\text{HS}(\text{CH}_2)_2\text{SH}$, $\text{HS}(\text{CH}_2)_3\text{SH}$), 3 acyclic sulfides (CH_3SCH_3 , $\text{CH}_3\text{CH}_2\text{SCH}_3$, $\text{CH}_3\text{SCH}_2\text{SCH}_3$), 2 cyclic sulfides ($\text{C}_3\text{H}_6\text{S}$, $\text{C}_3\text{H}_6\text{S}_2$) and 1 disulfide ($\text{CH}_3\text{S}_2\text{CH}_3$). Among them, to exhibit the formation pathways of multi-sulfur products, DMS and $\text{HS}(\text{CH}_2)_3\text{SH}$ are adopted as representative compounds for acyclic sulfides and thiols, respectively, whereas DMDS is treated as a representative compound for disulfide.

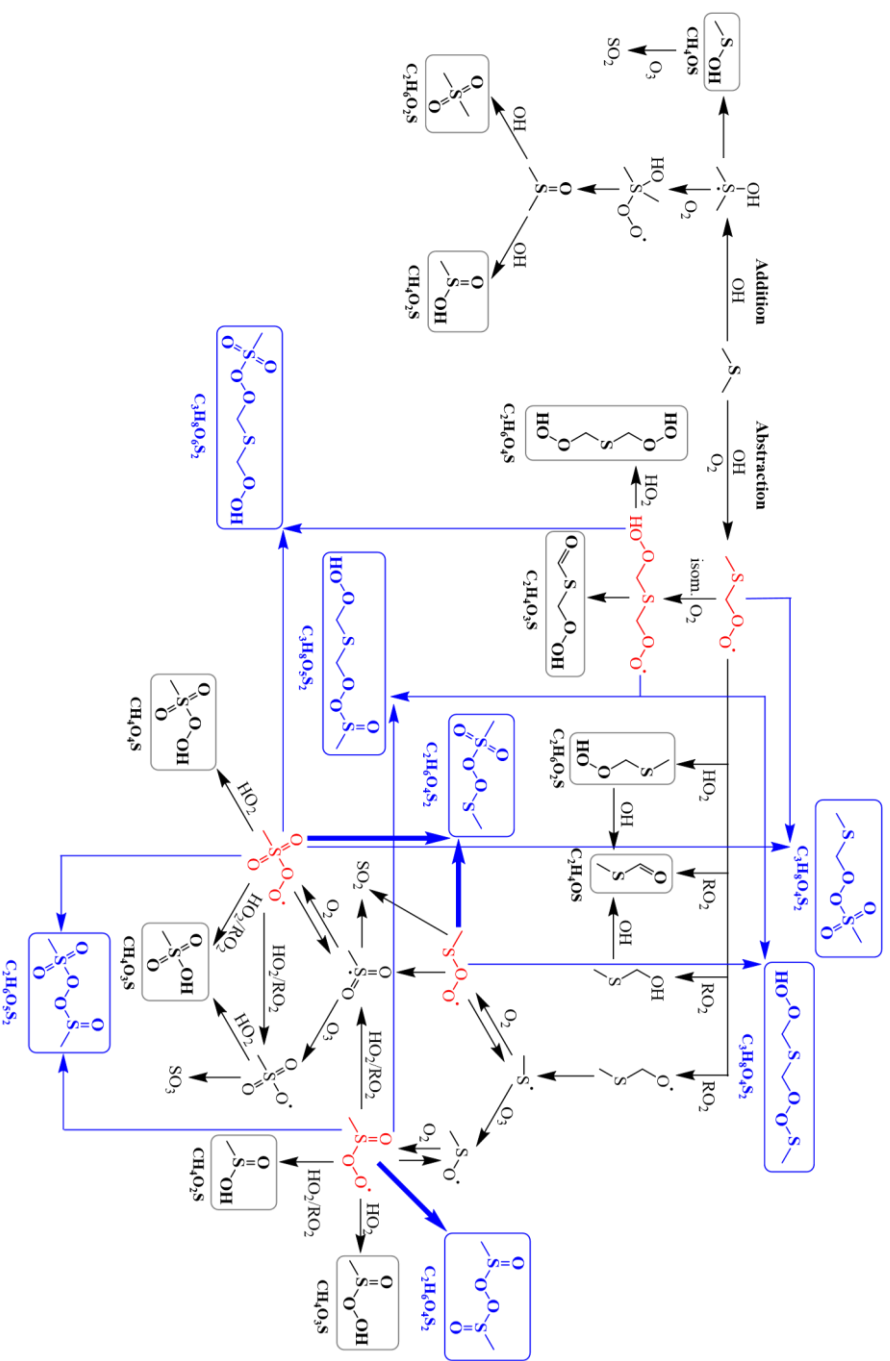
The reactions between DMS and $\bullet\text{OH}$ primarily proceed via two competing pathways (Scheme 1). One is that $\bullet\text{OH}$ adds to sulfur atom to form $\text{CH}_3\text{S}\bullet(\text{OH})\text{CH}_3$. Another is that $\bullet\text{OH}$ abstracts H-atom from the methyl group to generate the $\text{CH}_3\text{SCH}_2\bullet$. These primary radicals subsequently react with O_2 to form a series of sulfur-containing $\text{RO}_2\bullet$, including the initially formed DMS-derived $\text{RO}_2\bullet$.

(e.g., $\text{CH}_3\text{SCH}_2\text{OO}\cdot$), as well as other sulfur-containing $\text{RO}_2\cdot$ intermediates (Berndt et al., 2023; Goss and Kroll, 2023; Shen et al., 2022). Notably, under NO_x -free conditions, sulfur-containing $\text{RO}_2\cdot$ are not efficiently removed by NO, and their subsequent fate is expected to involve competition among unimolecular isomerization via H-migration, and bimolecular reactions of $\text{RO}_2\cdot + \text{HO}_2\cdot$ and $\text{RO}_2\cdot + \text{R}'\text{O}_2\cdot$ (Jenkin et al., 2003; Orlando and Tyndall, 2012). Recent studies of DMS oxidation have shown that H-shift isomerization of $\text{CH}_3\text{SCH}_2\text{OO}\cdot$ can be an important pathway associated with hydroperoxymethyl thioformate (HPMTF) formation (Berndt et al., 2019; Jernigan et al., 2022; Ye et al., 2022). In the box-model analysis of DMS oxidation by $\cdot\text{OH}$, this H-shift process was included to evaluate its competition with bimolecular reactions of $\text{RO}_2\cdot$ (Text S6; Figure S7). The model results indicate that H-shift dominates the initial fate of $\text{CH}_3\text{SCH}_2\text{OO}\cdot$ under the present chamber conditions. However, based on the detection by nitrate-CI-LToF-MS, various multi-sulfur bimolecular products (e.g., $\text{C}_2\text{H}_6\text{O}_4\text{S}_2$ and $\text{C}_2\text{H}_6\text{O}_5\text{S}_2$) resulting from $\text{RO}_2\cdot\text{-R}'\text{O}_2\cdot$ reactions were still identified (Figure S5). Among these, $\text{C}_2\text{H}_6\text{O}_4\text{S}_2$ may originate from the bimolecular reaction of $\text{CH}_3\text{SOO}\cdot$ with $\text{CH}_3\text{S}(\text{O})_2\text{OO}\cdot$ or the self-polymerization of $\text{CH}_3\text{S}(\text{O})\text{OO}\cdot$, while $\text{C}_2\text{H}_6\text{O}_5\text{S}_2$ may be formed by the bimolecular reaction between $\text{CH}_3\text{S}(\text{O})_2\text{OO}\cdot$ and $\text{CH}_3\text{S}(\text{O})\text{OO}\cdot$ (Scheme 1).

Previous studies on the $\cdot\text{OH}$ -initiated oxidation of DMS have extensively investigated the formation and fate of sulfur- $\text{RO}_2\cdot$, and have highlighted the potential importance of $\text{RO}_2\cdot\text{-R}'\text{O}_2\cdot$ reactions, particularly under low- NO_x or NO_x -free conditions (Barnes et al., 2006; Ye et al., 2022). However, direct molecular-level identification of multi-sulfur products has been very limited in earlier studies. Most previous investigations mainly focused on major oxidation products such as $\text{C}_2\text{H}_6\text{OS}$ (dimethyl sulfoxide), $\text{C}_2\text{H}_6\text{O}_2\text{S}$ (dimethyl sulfone), CH_4SO_3 , and SO_2 , rather than explicit characterization of individual bimolecular products from $\text{RO}_2\cdot\text{-R}'\text{O}_2\cdot$ chemistry (Chen et al., 2023; Hatakeyama et al., 1982). Self- and cross-reactions of $\text{RO}_2\cdot$ are known to produce organic peroxides (ROOR') and multimeric products, and such pathways have been experimentally confirmed for a variety of alkyl peroxy radicals (Cho et al., 2023; Nozière, 2025; Orlando and Tyndall, 2012). In addition, studies on highly oxygenated organic molecules (HOMs) formation from biogenic VOC oxidation have demonstrated that $\text{RO}_2\cdot\text{-R}'\text{O}_2\cdot$ reactions can lead to complex, multifunctional products that are efficiently detected using nitrate-CIMS (Bianchi et al., 2019; Ehn et al., 2014; Gao et al., 2023). Nevertheless, there have been no previous reports explicitly identifying molecular formulas such as $\text{C}_2\text{H}_6\text{O}_4\text{S}_2$ and $\text{C}_2\text{H}_6\text{O}_5\text{S}_2$ as products of $\text{RO}_2\cdot\text{-R}'\text{O}_2\cdot$ reactions in the atmospheric oxidation of sulfur-VOCs. The formation of these multi-sulfur products can likely be favored by low- NO_x and NO_x -free experimental conditions, which can prolong the lifetime of sulfur-containing $\text{RO}_2\cdot$ and favor their bimolecular reactions.

As shown in Scheme S1, the $\cdot\text{OH}$ -initiated oxidation of DMDS follows a reaction framework

317 similar to that of sulfides. Cleavage of the S-S bond leads to the formation of sulfur-centered radical
318 intermediates which are analogous to those generated from acyclic sulfides. Among the multi-sulfur
319 products detected from the $\bullet\text{OH}$ -initiated oxidation of DMDS, $\text{C}_2\text{H}_6\text{O}_4\text{S}_2$ was identified under the
320 present experimental conditions, and its formation is also derived from $\text{RO}_2\bullet\text{-R}'\text{O}_2\bullet$ bimolecular
321 reactions inferred for the DMS oxidation system.



323 **Scheme 1.** Scheme of the reaction pathways of DMS (CH_3SCH_3) with $\bullet\text{OH}$. Gray boxes denote mono-sulfur oxygenated organic products detected by Vocus-PTR-LToF-MS
324 and nitrate-Cl-LToF-MS. Blue boxes indicate multi-sulfur products detected by nitrate-Cl-LToF-MS and these multi-sulfur products are presumably generated by the red-
325 labeled sulfur-containing RO_2 radicals via bimolecular reactions. The bold blue arrows highlight the potential dominant pathways leading to the abundant multi-sulfur products.

For thiols, the reactions between $\text{HS}(\text{CH}_2)_3\text{SH}$ and $\bullet\text{OH}$ are initiated predominantly by H-abstraction from the S-H group (Scheme 2), forming the sulfur-centered radical $(\text{HS}(\text{CH}_2)_3\text{S}\bullet)$ (Berndt et al., 2023; Douroudgari et al., 2020; Mai et al., 2020). Subsequent reactions lead to the formation of a few sulfur-containing $\text{RO}_2\bullet$ intermediates, including $\text{HS}(\text{CH}_2)_3\text{OO}\bullet$, $\text{HOO}(\text{CH}_2)_3\text{SOO}\bullet$, and $\text{HOO}(\text{CH}_2)_3\text{S}(\text{O})_2\text{OO}\bullet$. Compared to $\text{RO}_2\bullet$ derived from acyclic sulfides and disulfides, thiol-derived $\text{RO}_2\bullet$ are more structurally diverse, enabling more bimolecular reaction pathways. As a result, more multi-sulfur products were identified (Figure S9), including $\text{C}_6\text{H}_{14}\text{O}_8\text{S}_2$, $\text{C}_6\text{H}_{14}\text{O}_9\text{S}_2$, $\text{C}_6\text{H}_{14}\text{O}_{10}\text{S}_2$, etc. Plausible formation pathways for these multi-sulfur products are illustrated in Scheme 2. Specifically, $\text{C}_6\text{H}_{14}\text{O}_9\text{S}_2$ can originate from the bimolecular reaction of $\text{HOO}(\text{CH}_2)_3\text{S}(\text{O})_2\text{OO}\bullet$ with $\text{HOO}(\text{CH}_2)_3\text{S}(\text{O})\text{OO}\bullet$. The formation pathways of $\text{C}_6\text{H}_{14}\text{O}_8\text{S}_2$ and $\text{C}_6\text{H}_{14}\text{O}_{10}\text{S}_2$ are similar with $\text{C}_6\text{H}_{14}\text{O}_9\text{S}_2$. In addition, multi-sulfur products were also detected for other investigated sulfur-VOCs (Figures S8 and S10-S12). Although acyclic sulfides and disulfides are structurally distinct, the reaction pathways presented above indicate that their $\bullet\text{OH}$ -initiated oxidation proceeds through similar sulfur-centered radical intermediates and subsequent reactions of sulfur- $\text{RO}_2\bullet$.

To evaluate the yields and volatility distributions of these multi-sulfur products, Figure 3 summarizes the estimated volatility distributions and formation yields from the $\bullet\text{OH}$ -initiated oxidation of 10 sulfur-VOCs except for ethanethiol. No multi-sulfur products were detected for ethanethiol, suggesting that their formation was either negligible or that the resulting concentrations were below the detection limit of the nitrate-CI-LToF-MS. The volatilities were estimated using the parameterization proposed by (Li et al., 2016). Overall, the total yields of multi-sulfur products varied substantially among the 10 sulfur-VOCs, ranging from 0.001% to 11.73% (Table S3), indicating a strong dependence on precursor structure and sulfur functionality.

Among all investigated compounds, trimethylene sulfide ($\text{C}_3\text{H}_6\text{S}$) exhibited the highest total yield (11.73%), suggesting its highly efficient formation of multi-sulfur products. In contrast, several thiol systems and certain acyclic sulfides produced only trace amounts of multi-sulfur products, with total yields below 0.1%. Acyclic sulfides and disulfide systems (e.g., DMS) predominantly generated semi-volatile organic compounds (SVOCs), with total multi-sulfur yields generally below ~4%. In comparison, cyclic sulfides displayed more diverse volatility distributions. For $\text{C}_3\text{H}_6\text{S}$, multi-sulfur products extended into the low-volatility organic compounds (LVOCs) and extremely low-volatility organic compounds (ELVOCs) regimes, with a significant fraction of the total yield residing in these low-volatility classes. By contrast, 1,3-dithiolane ($\text{C}_3\text{H}_6\text{S}_2$) mainly produced SVOCs-range multi-sulfur products, and individual species yields remained below ~0.4%, despite a moderate summed yield. Thiols (e.g., $\text{HS}(\text{CH}_2)_3\text{SH}$) exhibited a distinct pattern: although their oxidation generated products extending into the LVOCs and ELVOCs regimes, the overall formation efficiency was low, with total yields ranging from 0.001% to 0.40%. This suggests that structural factors, such as the position and number of -SH groups, may influence both $\text{RO}_2\bullet$ reactivity and multi-sulfur product formation efficiency. The presence of LVOCs and ELVOCs multi-sulfur products, particularly for cyclic sulfides, implies a potential role in secondary organic aerosol formation and particle growth.

It should be noted that the semi-quantification of these multi-sulfur products is based on the calibration factor of gaseous sulfuric acid (H_2SO_4) (Text S5), a common approach in nitrate-CIMS measurements due to the lack of authentic standards for highly oxygenated organic compounds (Ehn et al., 2014; Jokinen et al., 2012). It was assumed that the ionization efficiency of H_2SO_4 towards the reagent ions ($(\text{HNO}_3)_n\text{NO}_3^-$, $n=0, 1$ and 2) is the same as that of multi-sulfur products. As a result, the reported yields may have an additional uncertainty because of ionization efficiency difference between H_2SO_4 and multi-sulfur products towards the reagent ions, as discussed in previous studies (Ehn et al., 2014; Hyttinen et al., 2015).

Although the formation yields of many detected multi-sulfur products are relatively low, their low volatility indicates SOA forming potential. The reported yields represent only the gas-phase multi-sulfur products detected by nitrate-CI-LToF-MS and should not be interpreted as total

oxidation product yields. A substantial fraction of sulfur may be converted to inorganic sulfur products and mono-sulfur oxidation products, such as SO_2 , H_2SO_4 , sulfoxides, sulfones, methanesulfonic acid, and other mono-sulfur oxygenated compounds, which are not included in the reported multi-sulfur product yields. In addition, nitrate-CI-LToF-MS preferentially detects highly oxygenated and low-volatility compounds, while more volatile or less oxygenated sulfur-containing products may be underrepresented. Product wall loss and possible particle-phase transfer may further reduce the observed gas-phase concentrations of multi-sulfur products. Therefore, the reported yields should be treated as lower-limit gas-phase yields of multi-sulfur products.

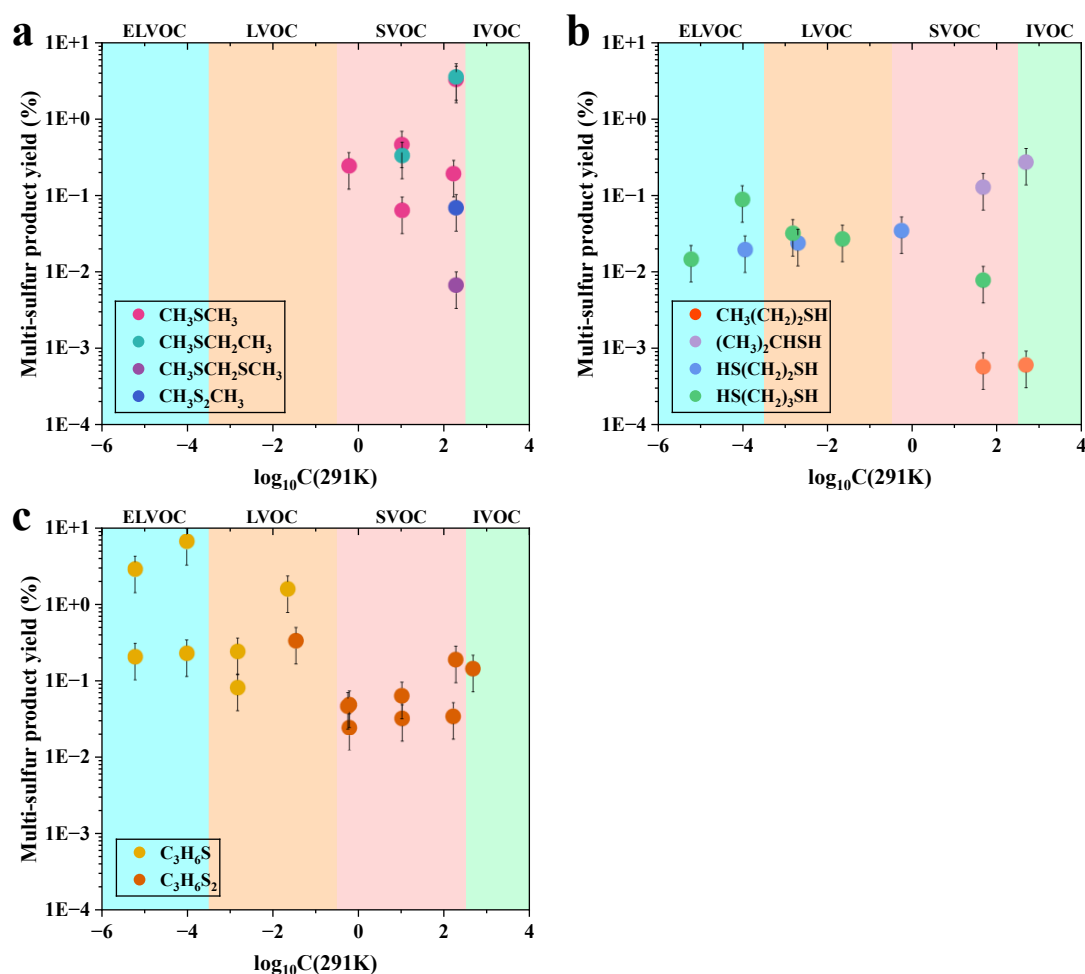


Figure 3. Volatility ($\log_{10}C^*$, at 291 K) versus the yield (%) of multi-sulfur products formed from the $\bullet\text{OH}$ -initiated oxidation of sulfur-VOCs. (a) acyclic sulfides and disulfide: CH_3SCH_3 , $\text{CH}_3\text{SCH}_2\text{CH}_3$, $\text{CH}_3\text{SCH}_2\text{SCH}_3$ and $\text{CH}_3\text{S}_2\text{CH}_3$; (b) thiols: $\text{CH}_3(\text{CH}_2)_2\text{SH}$, $(\text{CH}_3)_2\text{CHSH}$, $\text{HS}(\text{CH}_2)_2\text{SH}$, and $\text{HS}(\text{CH}_2)_3\text{SH}$; (c) cyclic sulfides: $\text{C}_3\text{H}_6\text{S}$, $\text{C}_3\text{H}_6\text{S}_2$. The volatility ranges were divided into ELVOCs, LVOCs, SVOCs and IVOCs (intermediate volatile organic compounds). Error bars represent an estimated uncertainty of approximately $\pm 50\%$, primarily arising from the use of calibration factor of gaseous H_2SO_4 .

3.3 Identification and atmospheric oxidation of sulfur-VOCs and other VOCs emitted from freshwater algae

As shown in Figure 4a, the emitted VOCs from freshwater algae were measured by Vocus-PTR-LToF-MS and 240 compounds in total were identified, including 143 CHO species, 43 CH species, 20 sulfur-VOCs, and 34 other VOCs. High-resolution peak fittings for the assigned sulfur-VOCs were shown in Figure S15. The molecular formulas and mixing ratios of 20 sulfur-VOCs are summarized in Table S5 and Figure 4b.

Under the specific treatment conditions (see Section 2.2), mixing ratios of emitted VOCs spanned over three orders of magnitude, ranging from 0.01 to 11.77 ppbv. Among the 20 identified sulfur-VOCs, 6 monosulfur species were detected and they are dominated ones. Specifically, CH₄S reached the highest level (11.77 ppbv), followed by C₂H₆S (8.60 ppbv), CH₂S (4.09 ppbv), and C₂H₄S (3.57 ppbv), while the remaining monosulfur species were present at sub-ppbv levels. 9 disulfur species were identified with generally lower abundances, spanning from 0.04 to 0.78 ppbv, with C₆H₁₄S₂ (0.78 ppbv) and C₃H₆S₂ (0.69 ppbv) representing the most abundant disulfur species. 3 trisulfur species were detected at similarly low levels, ranging from 0.06 to 0.50 ppbv, with C₄H₁₀S₃ showing the highest mixing ratio within this group. In contrast, 2 tetrasulfur species were the least abundant, with mixing ratios decreasing to ~0.01 ppbv for C₂H₆S₄ and C₃H₆S₄. Overall, a clear and systematic decrease in mixing ratios was observed with increasing sulfur number. Because Vocus-PTR-LToF-MS measurements constrain molecular formulas rather than isomer-specific structures, isomeric species (e.g., DMS and ethanethiol, C₂H₆S) cannot be distinguished solely by their exact mass and may have different sensitivities. Therefore, the reported mixing ratios should be interpreted as semi-quantitative apparent ones rather than definitive isomer-specific concentrations.

In addition, photographs taken before and after repeated filtrations show that the green algal suspension became nearly clear, indicating effective removal of most visible algal biomass (Figure S16). Consistently, removal of algal biomass by repeated filtrations through stacked qualitative filter papers led to a remarkable decrease in the abundance of sulfur-VOCs (Figure S17), suggesting that the emissions of sulfur-VOCs were closely associated with the algal biological processes. Although only molecular formulas rather than structures could be assigned, the results still provide a comprehensive inventory of freshwater algae-emitted sulfur-VOCs. However, because the freshwater lake samples contained natural microbial communities and the filtration procedure was not designed to sterilize the samples or fully remove bacteria, this experiment cannot distinguish direct algal emissions or other biological processing. Notably, the molecular formulas of sulfur-VOCs targeted in our chamber study were also present in the list of sulfur-VOCs emitted from freshwater algae. Although Vocus-PTR-LToF-MS measurements constrain molecular formulas rather than isomer-specific structures, the co-occurrence of these formula families in algal emissions supports the atmospheric relevance of the structure-resolved kinetics and oxidation mechanisms derived from our chamber experiments.

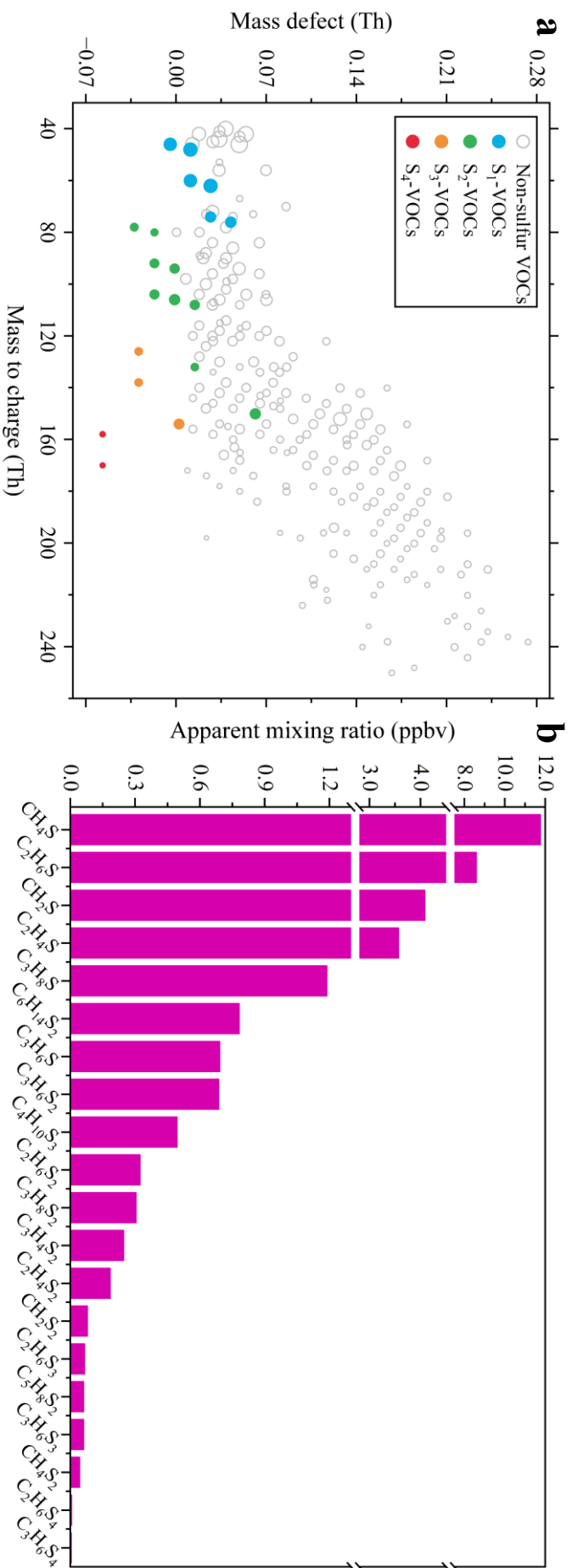


Figure 4. (a) Mass-defect plot of VOCs detected by Vocous-PTR-LToF-MS before oxidation. The 20 sulfur-VOCs are highlighted and grouped according to the number of sulfur atoms in their assigned molecular formulas, while non-sulfur VOCs are shown in gray. Marker size represents normalized PTR-MS signal intensity rather than calibrated concentration. (b) Semi-quantitative mixing ratios of the 20 sulfur-VOCs detected from the algal emissions.

In subsequent atmospheric oxidation experiments of these emitted VOCs including sulfur-VOCs, our chamber was maintained under NO_x-free conditions, hence the termination of RO₂• by NO_x was suppressed and bimolecular reactions of RO₂• were favored. Approximately 110 oxidation products were identified using nitrate-CI-LToF-MS, including dozens of mono-sulfur organic compounds, a few inorganic sulfur-containing species (e.g., H₂SO₄ and its clusters), and 11 multi-sulfur products (Figure 5 and Table S6). Among 11 multi-sulfur products, 7 of them could be inferred from our selected sulfur-VOCs chamber simulation experiments and their high-resolution peak fitting plots were also shown in Figure S18. Additionally, 4 multi-sulfur products could not be reproduced from our chamber simulation experiments (Figure S19). These experimental results not only provide evidence that multi-sulfur products can be formed from bimolecular reactions of sulfur-containing RO₂• under low-NO_x conditions, but also improve our understanding of the atmospheric oxidation chemistry of algae-emitted sulfur-VOCs in ambient air (especially in ~~low~~-low-NO_x environments). Notably, the detection of H₂SO₄ and its clusters, which are well-established precursors for atmospheric new particle formation, suggests that the oxidation of algae-emitted sulfur-VOCs may contribute to secondary particle formation (Jokinen et al., 2012; Lee et al., 2019; Yao et al., 2018). These findings expand the current understanding of the atmospheric processing of biogenic sulfur-VOCs released from freshwater algae and suggest that their chemical complexity may have broader implications for sulfur transformation and secondary aerosol formation. However, due to the complex composition of algae-derived sulfur-VOCs, specific formation pathways of these multi-sulfur products need to be further elucidated.

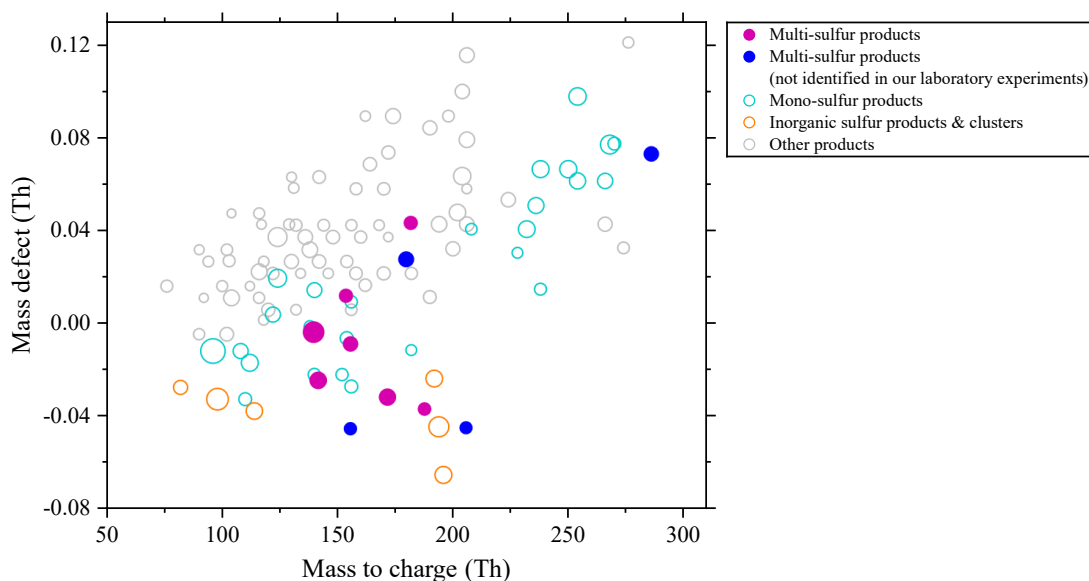


Figure 5. Mass defect plot of oxidation products detected by nitrate-CI-LToF-MS during the $\bullet\text{OH}$ -initiated oxidation of algae-emitted VOCs. Multi-sulfur products shown in deep purple represent species whose molecular formulas were also identified in our chamber simulation experiments of the selected sulfur-VOCs, whereas those shown in dark blue represent multi-sulfur products whose corresponding molecular formulas were not identified in our chamber experiments. Marker size is proportional to the corresponding signal intensity.

Although the oxidation experiments were conducted under NO_x -free conditions, such chemical regimes are still representative of atmospherically relevant environments characterized by low-low- NO_x levels conditions and strong biogenic sulfur-VOC emissions (e.g., inland eutrophic lakes, remote marine boundary layer and polar regions). In these environments, NO_x concentrations are typically very low and $\text{RO}_2\bullet$ termination by NO_x is strongly suppressed, while $\text{RO}_2\bullet + \text{HO}_2\bullet$ and $\text{RO}_2\bullet + \text{R}'\text{O}_2\bullet$ pathways may become more important (Berresheim et al., 1998; Novak et al., 2022; Read et al., 2008; Steinke et al., 2018). Field observations in these environments have reported sulfur-VOCs such as DMS and methanethiol at dozens to hundreds of pptv levels (Berresheim et al., 1998; Novak et al., 2022; Read et al., 2008). Therefore, multi-sulfur products derived from $\text{RO}_2\bullet$ - $\text{R}'\text{O}_2\bullet$ bimolecular reactions during atmospheric oxidation of sulfur-VOCs may have SOA forming potential in these environments. While the quantitative contribution of sulfur-VOCs-derived multi-sulfur products to SOA formation remains uncertain, the present results only highlight the detection and formation pathways of multi-sulfur products from atmospheric oxidation of sulfur-VOCs.

4 Conclusions

This study provides an integrated understanding of kinetics and formation pathways of multi-sulfur products of $\bullet\text{OH}$ -initiated oxidation of a series of selected sulfur-VOCs with different functional groups. The kinetic results show that $\bullet\text{OH}$ reactivity is strongly influenced by molecular

structure, including reactive S-H groups, sulfur functionality, α -C-H sites, molecular configuration, and ring strain. Under low-NO_x chamber conditions, sulfur-RO₂• can undergo bimolecular reactions ~~under low NO_x~~, leading to the formation of multi-sulfur products with distinct volatility characteristics. Acyclic sulfides and disulfides mainly produce semi-volatile multi-sulfur products with relatively higher yields, whereas thiols (particularly dithiols) favor the formation of more highly oxygenated, low-volatility products that may promote SOA formation. Furthermore, the selected sulfur-VOCs were also observed from the emission of freshwater algae and some of the multi-sulfur products derived from our chamber simulation experiments of selected sulfur-VOCs were also identified from •OH-initiated oxidation of VOCs emitted from freshwater algae. These results together further confirm the atmospheric relevance of these selected sulfur-VOCs and the sulfur-RO₂• chemistry leading to the formation of multi-sulfur products.

Biogenic sulfur-VOCs could have increased significance in the context of ongoing changes in the atmospheric sulfur budget. Anthropogenic SO₂ emissions have been declining worldwide, reducing the dominance of the traditional gaseous H₂SO₄ formation pathway from anthropogenic SO₂ in atmospheric sulfur cycling (Crippa et al., 2016; Smith et al., 2011; Zheng et al., 2018). In addition to anthropogenic SO₂, natural sulfur sources such as H₂S, DMS-derived SO₂, and naturally emitted SO₂, including passive volcanic SO₂ emissions, can also contribute to gaseous H₂SO₄ and particulate sulfate formation (Bates et al., 1992; Faloon, 2009; Yvon and Saltzman, 1996). In this evolving context, the relative contribution of biogenic sulfur-VOCs becomes increasingly important, particularly in low-NO_x environments. Our results demonstrate that, in addition to conventional oxidation pathways, sulfur-containing RO₂• bimolecular reactions can lead to the formation of low-volatility multi-sulfur products, providing an additional pathway linking sulfur-VOCs to secondary aerosol formation. Overall, this study underscores the growing role of biogenic sulfur-VOCs in the atmospheric sulfur budget and highlights the necessity of explicitly considering the atmospheric chemistry of sulfur-VOCs in atmospheric models.

Data availability. The data used to support the conclusions in this study are available at a public data repository of Zenodo via <https://doi.org/10.5281/zenodo.18923240>. Additional data related to this paper can be requested from the authors (lei_yao@fudan.edu.cn).

Author contributions. L.Y. conceived and designed this study and revised the manuscript. X.R. conducted the experiments, performed data analysis, and prepared the manuscript with contributions from all co-authors. C.L. assisted in designing the experiments. C.A. and G.Y. assisted with data collection. J.L.S, R.L.C., D. R. Worsnop, and L.W. interpreted the results and revised the manuscript.

514

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