

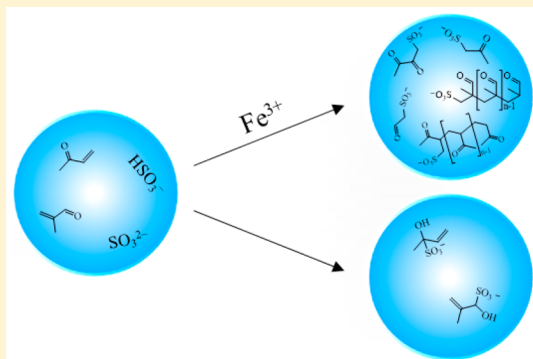
Formation of Organosulfur Compounds through Transition Metal Ion-Catalyzed Aqueous Phase Reactions

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 Supporting Information

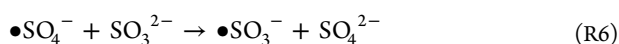
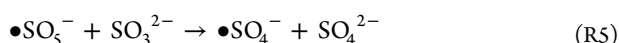
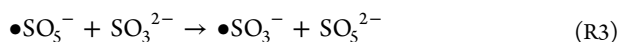
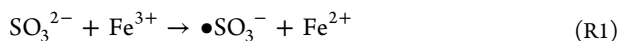
ABSTRACT: Organosulfur compounds, particularly organosulfates, are considered as important tracers of secondary organic aerosol formation. However, the mechanistic pathways for the formation of these compounds in the atmosphere are still not well understood. In this study, we show for the first time that C₂–C₄ organosulfur compounds, as well as their oligomers, can form in the aqueous phase from reactions of unsaturated carbonyl compounds, i.e., methacrolein (MACR) and methyl vinyl ketone (MVK), with the bisulfite anion (HSO₃[–]) in the presence of Fe³⁺. The mechanism for product formation in the presence of Fe³⁺ involves sulfite and sulfate ion radicals. As shown here, the formation of specific organosulfur compounds depends on the concentrations of MVK and MACR and the solution pH. Our findings provide new insights into pathways for forming organosulfur compounds in the atmosphere and the role that transition metal ions, such as Fe³⁺, play in catalyzing these reactions.



INTRODUCTION

Aqueous phase oxidation of sulfur dioxide (SO₂) by oxidants, e.g., hydrogen peroxide, ozone, and O₂, can serve as the major sink of atmospheric SO₂ and comprise ≤80% of global sulfate production.^{1,2} The first step in this process is the hydrolysis of SO₂ to yield sulfite H₂SO₃, which is deprotonated at most atmospherically relevant pHs. Sulfite is then oxidized to sulfate, and it is well-known that transition metal ions (TMI, e.g., Fe³⁺ and Mn²⁺) can catalyze the oxidation of sulfite to sulfate in the presence of dissolved O₂ via a radical mechanism.

Reactions to form radical species are as follows (similar reactions can also be written for HSO₃[–]):^{3–5}



This reaction sequence is a known important in-cloud sulfate formation pathway.^{6–8}

Furthermore, previous studies have suggested that organic compounds can inhibit the rate of these processes through competing radicals, thereby affecting the conversion of organic compounds.^{9–12} Rudzinski et al.¹¹ observed the formation of isoprene derivatives in aqueous solutions of isoprene mixed

with SO₃^{2–}/HSO₃[–] and Mn²⁺ and proposed possible product formation pathways. However, to the best of our knowledge, the mechanism for other organic compounds, which have higher Henry's law constants than that of isoprene, has yet to be explored.

As first-generation oxidation products of isoprene in the gas phase,¹³ the unsaturated organic compounds methacrolein (MACR) and methyl vinyl ketone (MVK) can also be present in the aqueous phase.¹⁴ Previous studies revealed that in the aqueous phase, MACR and MVK can interact with OH radicals to undergo decomposition, producing low-molecular weight compounds (LMWCs),^{15–17} as well as oligomerization, potentially forming aqueous secondary organic aerosols (SOA).^{18–22} In addition to OH radicals, Nozière et al.²³ and Schindelka et al.²⁴ reported that MACR and MVK can react with sulfate ion radicals to produce organosulfates, which are ubiquitous components of ambient aerosol and important tracers of SOA formation.^{25–33} Given that the sulfate ion radical is one of the radical intermediates in the oxidation of sulfites by TMI, organosulfur compound formation may be potentially important for MACR and MVK aqueous chemistry in the presence of TMI; however, little is known about these processes.

In this study, we investigate for the first time the aqueous reactions of sulfite with MACR and MVK, as representatives of

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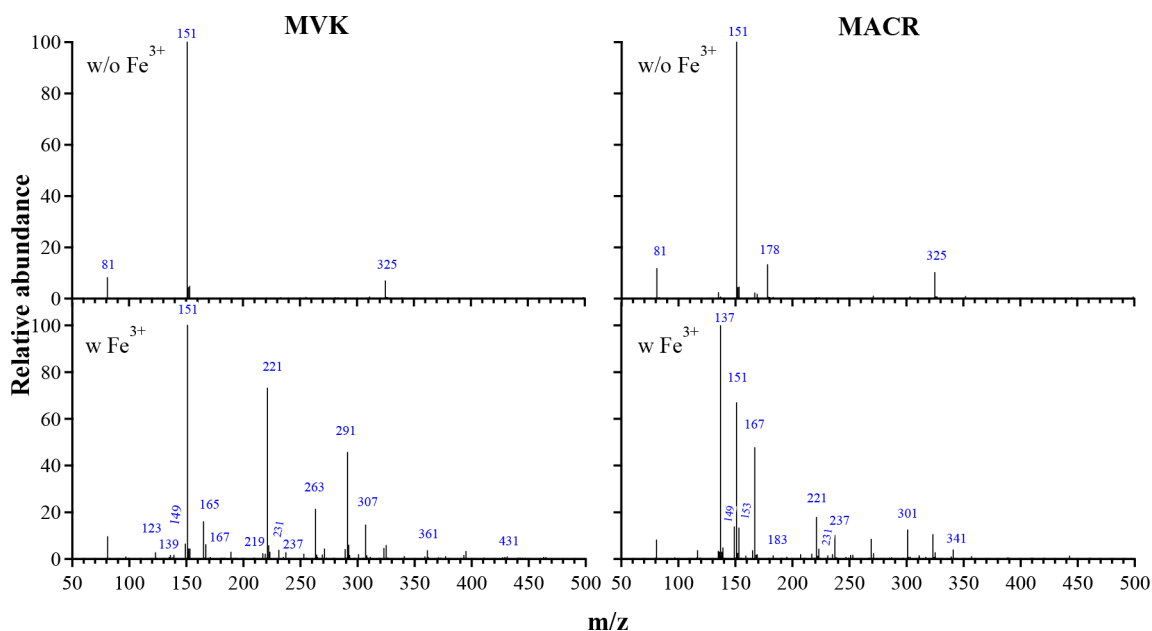


Figure 1. Mass spectra of MVK and MACR reacted with Na_2SO_3 in the absence (without, w/o) and presence (with, w) of Fe^{3+} at pH 5 after 12 h.

unsaturated organic compounds, in the absence and presence of TMI, in this case, Fe^{3+} . Soluble iron from mineral dust and other anthropogenic sources of iron, such as fly ash,^{34–36} is a known component of aqueous particles. Our study aims to show the mechanism of organosulfur compound formation and the role that Fe^{3+} plays in these reactions.

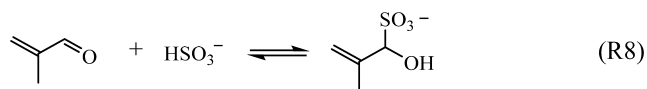
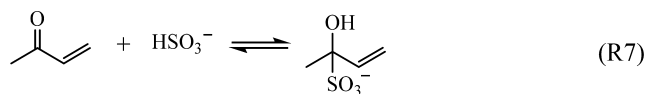
MATERIALS AND METHODS

Reactor Design and Reaction Conditions. The aqueous phase reactions were conducted in a 20 mL glass reactor. The solution of 2 mM MVK (99%, Sigma-Aldrich) or MACR (96%, Alfa Aesar), in the absence or presence of 0.25 mM $\text{Fe}_2(\text{SO}_4)_3$ (Sigma-Aldrich), was introduced into the reactor of 2 mM Na_2SO_3 (LabChem) with an adjusted pH, and then the reactor was covered. All experiments were performed at 277 K in the dark for ~12 h of reaction time. Additional details about the preparation of these solutions can be found in the [Supporting Information](#), including the varied experimental conditions used in this study ([Table S1](#)).

Detection of Products. Samples obtained from these experiments were analyzed by a high-resolution hybrid linear ion trap mass spectrometer equipped with a heated electrospray ionization (HESI) source (HESI-HRMS, Thermo Orbitrap Elite). Before infusion into the HESI source, samples were diluted by a factor of 20 with acetonitrile (ACN, Fluka). This process aided in the desolvation process in the HESI source. Data were collected in negative ionization mode over the mass range of 50–2000 Da, with the spray voltage set at 2.60 kV, the capillary temperature at 325 °C, and the S-lens at 60%. For MS^2 and MS^3 experiments, a normalized collision energy level of 10–35 V was applied. To distinguish product isomers with similar masses, selected samples were analyzed by ultra-performance liquid chromatography (UPLC, Thermo Ultimate 3000) via an instrument coupled to the HESI-HRMS system. The details of the method are described in the [Supporting Information](#).

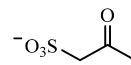
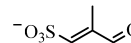
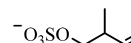
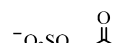
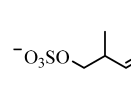
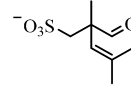
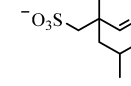
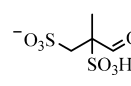
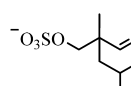
RESULTS AND DISCUSSION

Product Analysis. [Figure 1](#) shows the negative ion mass spectra of MACR and MVK reacted with Na_2SO_3 at pH 5. In the absence of Fe^{3+} , a diagnostic peak at m/z 151 dominates the spectrum. The structure of the peak could be assigned to $\text{C}_4\text{H}_7\text{SO}_4^-$, which is produced from the reversible reaction of HSO_3^- with the carbonyl group of MVK^{37–39} (R7) given that the most abundant anion present at pH 5 is HSO_3^- ([Figure S1](#)).¹ Additionally, [Figure 1](#) also shows a peak at m/z 325 with a formula of $\text{C}_8\text{H}_{14}\text{NaS}_2\text{O}_8^-$; however, this product appears to be a cluster of $[\text{2C}_4\text{H}_7\text{SO}_4 + \text{Na}]^-$ rather than a $[\text{C}_8\text{H}_{14}\text{NaS}_2\text{O}_8]^-$ dimer. The detailed explanation for this assignment is provided in [Figures S2 and S3](#). The m/z 151 peak is also the most pronounced peak in the mass spectrum of MACR reacted with bisulfite ([Figure 1](#)), indicating that the mechanism for MACR–bisulfite adduct formation is similar for MVK (R8).



The m/z 151 peak can also be observed in the presence of Fe^{3+} ([Figure 1](#)), but it contains several additional isomers compared with that in the absence of Fe^{3+} ([Figure S4](#)). Furthermore, most importantly, a number of different organosulfur compounds are observed when Fe^{3+} is present. These additional products cannot be generated from solutions of MACR and MVK mixed with Na_2SO_3 alone, Na_2SO_4 , or $\text{Fe}_2(\text{SO}_4)_3$. This suggests that the presence of Fe^{3+} can alter the mechanism of MVK and MACR reacted with sulfite and provides a TMI-catalyzed route for the formation of these organosulfur compounds. The m/z value, suggested formula, and structures are all summarized in [Table 1](#). The m/z 139, 153, 167, 183, and 237 peaks shown in [Table 1](#) are identified as organosulfates because of the observation of the HSO_4^- fragment ion at m/z 97 from these products.^{27,40} Additionally, some observed organosulfates, e.g., m/z 153, 167, 183, and 237,

Table 1. Exact Masses, Formulas, and Structures of Measured Organosulfur Compounds^a

MVK				MACR			
m/z [M-H]	Error [ppm]	Formula	Structure	m/z [M-H]	Error [ppm]	Formula	Structure
122.97585	0.792	C ₂ H ₃ SO ₄		136.99146	0.419	C ₃ H ₅ SO ₄	
138.97069	0.164	C ₂ H ₃ SO ₅		148.99139	-0.085	C ₄ H ₅ SO ₄	
148.99142	0.116	C ₄ H ₅ SO ₄		151.00700	-0.349	C ₄ H ₇ SO ₄	
151.00703	-0.150	C ₄ H ₇ SO ₄		152.98624	-0.505	C ₃ H ₅ SO ₅	
164.98621	-0.650	C ₄ H ₅ SO ₅		167.00182	-0.882	C ₄ H ₇ SO ₅	
167.00183	-0.822	C ₄ H ₇ SO ₅		219.03300	-1.221	C ₈ H ₁₁ SO ₅	
182.99664	-1.322	C ₄ H ₇ SO ₆		221.04861	-1.391	C ₈ H ₁₃ SO ₅	
219.03300	-1.221	C ₈ H ₁₁ SO ₅		230.96347	-1.720	C ₄ H ₇ S ₂ O ₇	
221.04865	-1.210	C ₈ H ₁₃ SO ₅		237.04346	-1.570	C ₈ H ₁₃ SO ₆	
237.04350	-1.401	C ₈ H ₁₃ SO ₆		301.00519	-1.801	C ₈ H ₁₃ S ₂ O ₈	

^aProducts larger than C₈ are not shown here.

are consistent with previous laboratory and field data reported in the literature.^{23,24} They proposed that these organosulfates are formed through the addition of the sulfate ion radical to the carbon–carbon double bond (C=C) of MACR and MVK. Therefore, in this study, the formation of organosulfates can also be explained by it because of the generation of sulfate ion radicals resulting from the oxidation of sulfites by Fe³⁺ (eqs R1–R6).

In addition, Figure 1 shows the *m/z* 123 (C₂H₃SO₄) and *m/z* 137 (C₃H₅SO₄) peaks, which differ by one O atom when compared with the same number of carbon atoms in the corresponding organosulfates, e.g., *m/z* 139 (C₂H₃SO₅) and *m/z* 153 (C₃H₅SO₅); hence, these products can be assigned to organosulfites. The MS² data of several observed organosulfites are presented in Figure S5. The spectra of *m/z* 151, 167, and 221 peaks show the characteristic product ion at *m/z* 81 (HSO₃[−]), which may result from the fragmentation of a cyclic syn-elimination mechanism.^{41,42} However, the spectra of *m/z* 123, 149, and 165 peaks fail to exhibit the ion at *m/z* 81. The sulfite ion radical is the initiator radical for the formation of

other oxysulfur radicals in the reaction of sulfites with Fe³⁺. Therefore, it can be inferred that organosulfite formation arises from the reaction of MVK and MACR with sulfite ion radicals. Previous studies also found that the production of two isoprene-derived sulfonates, sulfurous acid mono-(2-methyl-4-oxo-but-2-enyl) ester and sulfurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester, occurs via the reaction of isoprene with sulfite ion radicals.^{11,43} Additionally, it is found that the relative abundance (RA) of C₂H₃SO₄ is much lower than that of C₃H₅SO₄, meaning that MACR is prone to decomposition compared to MVK because C₂H₃SO₄ and C₃H₅SO₄ are produced from degradation of MVK and MACR, respectively. We speculate that this discrepancy is attributed to the different solubilities of their precursors, CH₂(SO₃)C(OO)CH(O)CH₃ (called R1O₂ radical hereafter) and CH₂(SO₃)C(OO)(CH₃)-CHO (called R2O₂ radical hereafter). Previous studies found that RO₂ radicals can combine with water to form RO₂·H₂O complexes.^{44,45} The tertiary radical, R2O₂, seems to be more hydrophobic than the secondary radical, R1O₂, as judged by the difficulties in forming complexes with water molecules,

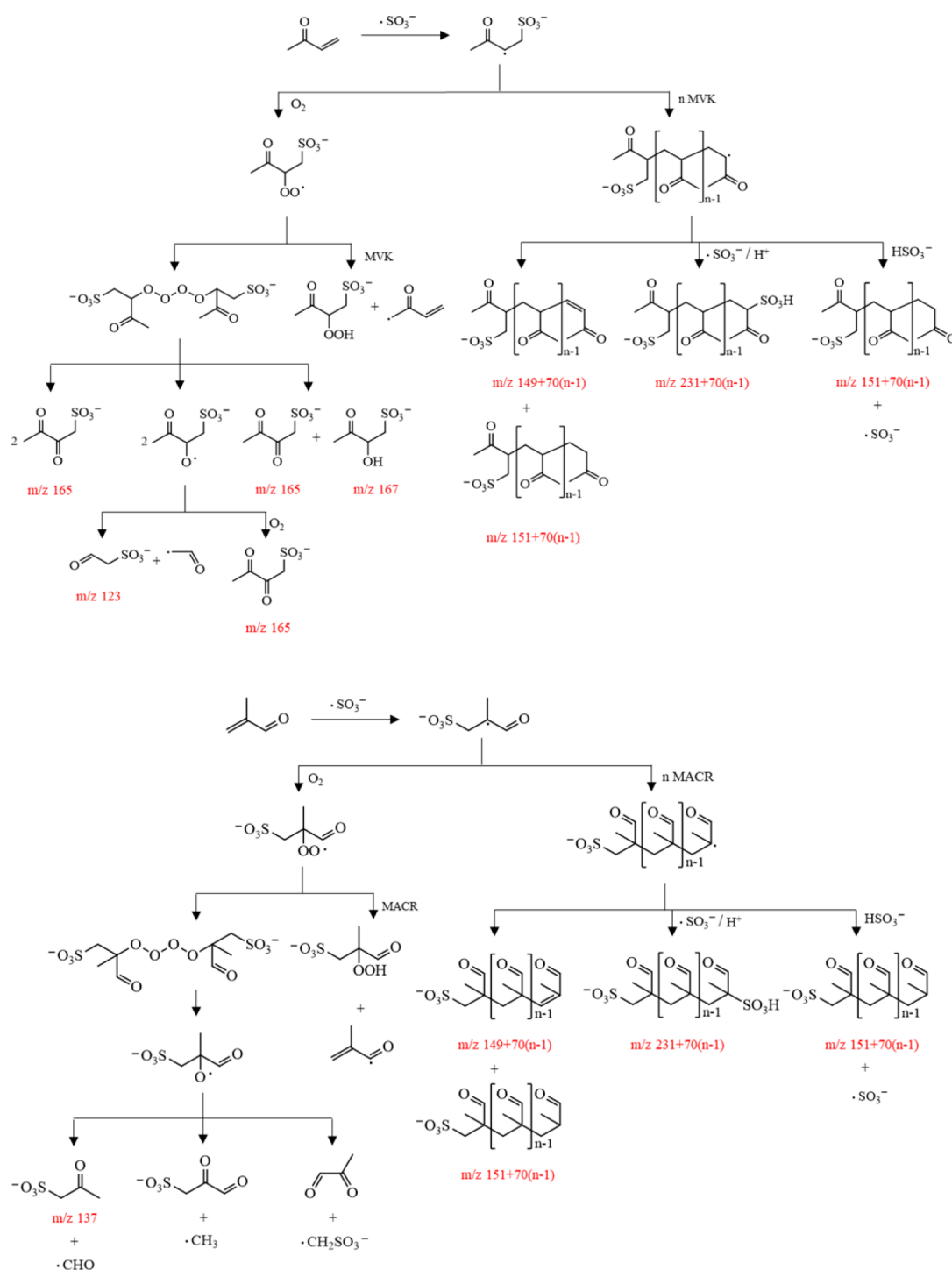


Figure 2. Proposed mechanisms for the formation of observed products from the reaction of MVK and MACR with sulfite radicals in the aqueous phase with masses of particular products detected. In the mechanism, n is the number of MVK or MACR units with a molar mass of 70.

resulting in aggregation. This aggregation may inhibit the chain transfer of RO_2 radicals (Figure 2) and instead promote self-reactions, which can generate RO radicals, thereby decomposing to LMWCs. The different solubilities of RO_2 radicals leading to the different yields of their products have also been reported by Huang et al.⁴⁶

Besides C_2 – C_4 organosulfur compounds, some other higher-molecular weight compounds (HMWCs), particularly molar masses of ≤ 431 for MVK and ≤ 341 for MACR, were found in this study. It is noted that some peaks, such as those at m/z

151, 221, 291, 361, and 431, display the mass difference of 70.04162, which is consistent with the molecular weight of MVK and MACR monomers. Control experiments were conducted to verify that these HMWCs are oligomers (Figures S3 and S4), which may result from the oligomerization of MVK and MACR. To the best of our knowledge, the formation of oligomeric organosulfites related to sulfite ion radicals has not been previously reported. Additionally, we observed other series of oligomers with the monomer of m/z 149, 167, and 231, but the intensities of these oligomers are much lower than

those of oligomers with the monomer at m/z 151. Interestingly, the observed peak at m/z 231 indicates oligomers that contain two SO_3 groups (Figures S6 and S7) can be formed via these reactions.

Given that wide ranges of concentrations of unsaturated organic compounds²⁰ and pH values^{47–49} are found in aqueous phase environments in the atmosphere, we also investigated the effects of concentration and pH on the formation of these organosulfur compounds. The results show that the chain length of oligomers increases with increasing MVK or MACR concentration (Figure S8). This concentration dependence agrees well with previous studies focused on oligomerization.^{19,20,50,51} Additionally, organosulfur compounds formed at pH 3 and 1.6 (Figure S9) are similar to what is observed at pH 5 (as shown in Figure 1). However, the RA values of these products are different at these different pH values, suggesting that pH has an impact on the yields of specific organosulfur compounds.

Mechanism and Atmospheric Impacts. On the basis of these new observations, as well as earlier studies,^{16,20,52} a possible mechanism for these MVK- and MACR-derived organosulfite compounds is shown in Figure 2. In the initial step, MVK reacts with sulfite ion radicals to yield MVK- SO_3 radicals. In contrast to OH radicals, which can also undergo H abstraction, the sulfite ion radical adds to MVK across the $\text{C}=\text{C}$ bond, resulting in α - or β -C atom additions.²⁰ Here, we focus on the β addition. The generated MVK- SO_3 radicals can undergo chain propagation that proceeds in MVK addition or rapidly react with dissolved O_2 to form RIO_2 radicals. Chain propagation is terminated by reaction with HSO_3^- to form $(\text{MVK})_n\text{-SO}_3$ oligomers, combining with sulfite ion radicals to form oligomers containing two SO_3 groups or via the disproportionation mechanism to generate two series of oligomers.⁵³ RIO_2 radicals can undergo chain-transfer reactions, resulting in the formation of ROOH and MVK radicals, as well as self-reaction to form a tetroxide,¹⁶ followed by decomposition via three pathways. The RO radical formation channel⁵⁴ can further decompose to a smaller organosulfite, i.e., $\text{C}_2\text{H}_3\text{SO}_4$, accompanied by the CH_3CO radical. Analogously, sulfite ion radicals attack the $\text{C}=\text{C}$ bond of MACR to form tertiary radicals, MACR- SO_3 radicals, and subsequently proceed to either decompose or oligomerize. The mechanism for MACR oligomerization and the RO_2 radical reactions are similar for MVK, as well; however, the fate of the tetroxide is different. RO radical formation dominates the decomposition of the tetroxide of MACR, subsequently producing more types of smaller compounds together with radicals via the scission of the carbon–carbon bond. It is noted that new radicals produced from chain-transfer reactions and decomposition of RIO_2 or RO_2 radicals can induce the formation of other products, but these products are not a focus of this study.

The study presented here reveals a plausible mechanism for the formation of organosulfites through the aqueous phase reactions of MVK and MACR with sulfite in the presence of Fe^{3+} . The formula and m/z of some observed organosulfites are identical to those of species detected in ambient aerosol collected from two suburban sites (Table S2),⁵⁵ indicating the potential existence of these compounds in the atmosphere, although they were not identified. This suggests that the reactions uncovered here may in fact be a heretofore unrecognized source of organosulfur species and SOA in the atmosphere, particularly for nighttime aqueous chemistry when the level of OH radical formation is low. Furthermore, although

the experiments were performed in bulk solutions, the formation of organosulfur compounds under highly acidic conditions and high initial MVK and MACR concentrations implies that these reactions can happen in the aerosol phase and in fact may have been detected previously in earlier field studies. However, the scarcity of cogent evidence of the identification of organosulfites in the atmosphere warrants further investigation of the formation and fate of organosulfites and evaluation of their importance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.8b00225.

Solution preparation, masses of organosulfites observed in this work and field study, distribution of S(IV) species, verification of cluster or oligomer formation, MS^2 spectra for several organosulfites, characterization of the m/z 231 ion, mass spectra of concentration dependence, and mass spectra of pH dependence (PDF)

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Notes

The authors declare no competing financial interest.

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