ACS EARTH AND SPACE CHEMISTRY

Article

Cite This: ACS Earth Space Chem. 2019, 3, 1749−1755

http://pubs.acs.org/journal/aesccq

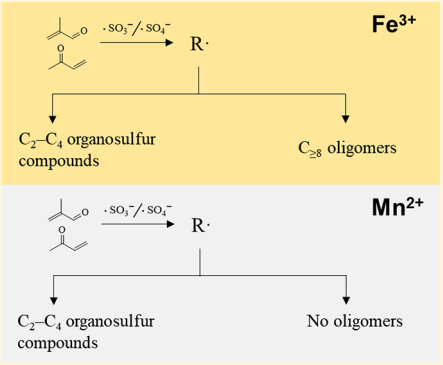
Formation of Organosulfur Compounds from Aqueous Phase Reactions of S(IV) with Methacrolein and Methyl Vinyl Ketone in the Presence of Transition Metal Ions

Liubin Huang,[†] Ellen M. Coddens,[†] and Vicki H. Grassian*[,†,‡]

[†]Department of Chemistry and Biochemistry, and [‡]Departments of Nanoengineering and Scripps Institution of Oceanography, University of California San Diego, La Jolla, California 92093, United States

Supporting Information

ABSTRACT: The catalytic oxidation of S(IV) species by transition metal ions (TMIs) is a significant pathway for aqueous sulfate formation. Sulfoxy radicals, such as SO_3^-, SO_4^-, and SO_5^- radicals, are major intermediates in this catalytic reaction. These radicals can also react with organic compounds to produce organosulfur compounds, which are important tracers of secondary organic aerosol (SOA) formation. However, the mechanism for the formation of organosulfur compounds via this pathway is not well understood. Here, we investigate the formation of organosulfur compounds from the aqueous reaction of isoprene oxidation products, in this case, methacrolein (MACR) and methyl vinyl ketone (MVK), with sulfite/bisulfite in the presence of different TMIs. In particular, we show here how this chemistry is influenced by the presence of Fe^{3+} and Mn^{2+} both separately and together. Fe^{3+} and Mn^{2+} have distinctly different effects on the mechanism for organosulfur formation. Both C_2-C_4 organosulfur compounds and their oligomers are formed in the presence of Fe^{3+}, whereas only C_2-C_4 organosulfur compounds are observed in the presence of Mn^{2+}. Fe^{3+} dominates the formation of organosulfur compounds when both Fe^{3+} and Mn^{2+} are present, as indicated by the significant increase of oligomers observed even at low ratios of Fe^{3+} to Mn^{2+} (1:25). Furthermore, the quantification of organosulfur compounds shows that organosulfur compound formation through TMI-catalyzed reactions makes a significant contribution to the fate of S(IV) in the aqueous phase. The importance of these reactions in the atmosphere is discussed.



KEYWORDS: *transition metal ions, aqueous reactions, organosulfur compounds, organosulfates, S(IV) oxidation, sulfoxy radicals*

INTRODUCTION

Organosulfates are a ubiquitous component of atmospheric aerosols with mass concentrations up to 5−10% of organic aerosols.[1−8] Organosulfates can also potentially alter the physicochemical properties of atmospheric aerosols, such as surface activity and hygroscopicity, due to their polar and hydrophilic nature, further affecting air quality and climate chage.[9,10] The pathways and mechanisms for organosulfate formation in the atmosphere such as the uptake of epoxides on acidic sulfate particles,[11,12] nucleophilic substitution of nitrate by sulfate,[13,14] heterogeneous reaction of SO_2 with long chain alkenes,[15] and sulfate radicals addition reactions[16−21] have been investigated in several laboratory studies.

The major sources of sulfate radicals in the atmospheric aqueous phase are the reaction of OH radicals with sulfate and the catalytic oxidation of S(IV) species with transition metal ions (TMIs),[22−25] of which the latter is known to be important in inorganic sulfate formation in the atmosphere.[26,27] Besides sulfate radicals, other sulfoxy radicals, that is, SO_3^- and SO_5^- radicals can also be generated in the presence of TMIs.[22] Rudziński et al.[16] reported the formation of organosulfites, which are elucidated to be produced from the reaction of isoprene with SO_3^- radicals, as well as organosulfates in the aqueous solution of isoprene mixed with sulfite and Mn^{2+}. Additionally, our previous work also observed the formation of both orgnaosulfate and organosulfite compounds (called organosulfur compounds hereafter) from the reaction of methacrolein (MACR) and methyl vinyl ketone (MVK) with bisulfite in the presence of Fe^{3+} under acidic conditions.[20] Although previous studies revealed that organosulfur compounds, particularly organosulfite that is heretofore unrecognized, can be formed from TMI-catalyzed reactions, quantitative studies about the formation of organosulfur compounds via these reactions are greatly needed.

Furthermore, it was shown that large molar mass, oligomeric organosulfur compounds can be formed through TMI-catalyzed reactions in the aqueous phase.[20] However, the formation of these larger molar mass species was not reported

Special Issue: New Advances in Organic Aerosol Chemistry

Received: June 14, 2019
Revised: July 28, 2019
Accepted: August 12, 2019
Published: August 12, 2019

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

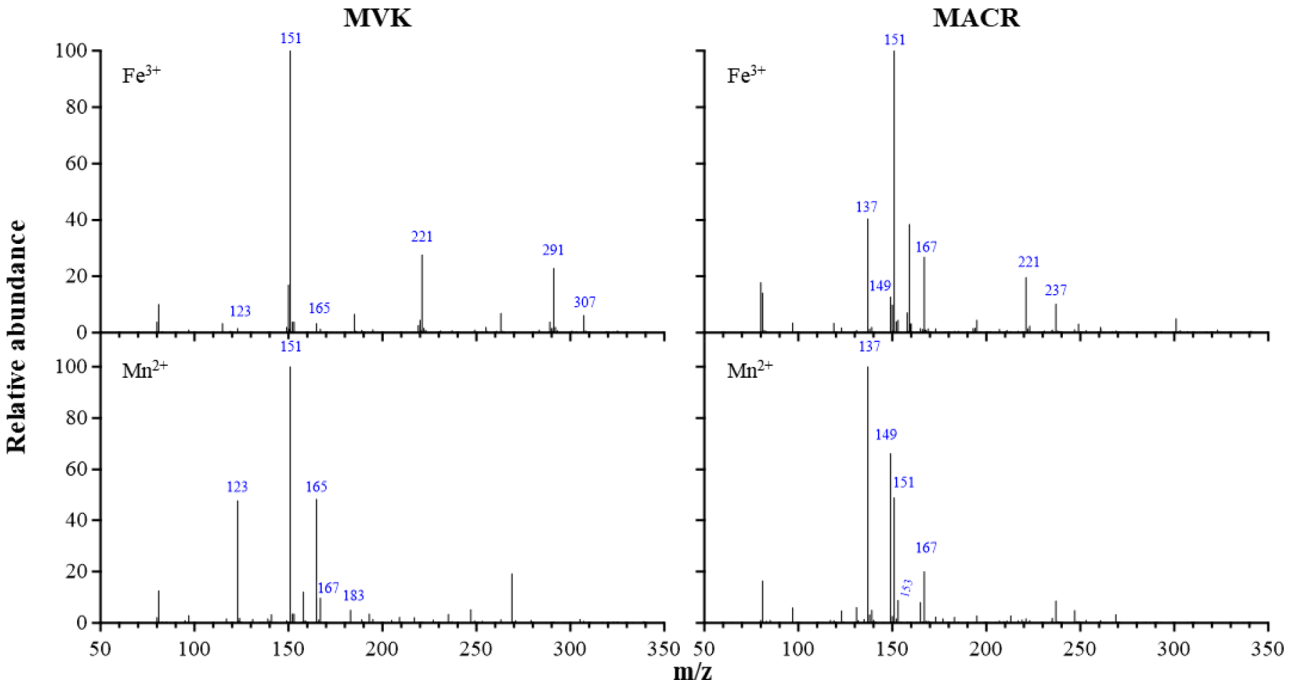


Figure 1. Mass spectra of MVK/MACR reacted with Na_2SO_3 in the presence of Fe^{3+} and Mn^{2+} at pH 5. Labeled peaks represent the major organosulfur compounds observed.

by others, for example, by Rudzinski et al.[16] in their study. This suggests there may be differences in the reaction, depending on the exact reaction conditions including the nature of the transition metal ion and the organic compounds of interest. Therefore, in order to better understand some of these differences observed in the literature, we have investigated the aqueous reaction of MVK and MACR, as model compounds for unsaturated atmospheric organic compounds, with Na_2SO_3 in the presence of Fe^{3+} and Mn^{2+}, and have measured the amount of organosulfur compounds formed in these reactions. The purpose of this study is to explore the effects of different TMIs on the formation of organosulfur compounds and to evaluate on a quantitative basis the importance of organosulfur compounds formed through TMI-catalyzed reactions in the atmosphere.

MATERIALS AND METHODS

Reactor and Experimental Conditions. A 20 mL glass reactor was used to study the aqueous reaction of organosulfur compound formation. Each experiment was conducted by filling the reactor with a desired pH value mixture (pH 5 and 3) containing MVK/MACR, Na_2SO_3, dissolved O_2, and TMI catalyst, and then sealing the reactor. All experiments were performed at 277 K in the dark for ∼12 h of reaction time. All of MVK, MACR, and Na_2SO_3 concentrations were controlled at 2 mM. The solutions containing TMI catalyst were prepared from the transition metal ion sulfate salts, $MnSO_4$, and $Fe_2(SO_4)_3$. These were used in different proportions to obtain the different molar ratios of Mn^{2+} to Fe^{3+} for a total concentration of 0.5 mM. The details of the solution preparation were described in our previous study.[20] The information on chemicals used in this study is provided in the Supporting Information.

Mass Spectrometry Analyses. Samples collected following the reaction were analyzed by a high-resolution hybrid linear ion trap mass spectrometer equipped with a heated electrospray ionization source (HESI-HRMS, Thermo Orbitrap Elite) under negative ionization mode with following settings: mass range, −50 to 2000 Da; spray voltage, −2.60 kV; capillary temperature, −325 °C; S-lens, −60%. The samples were diluted by a factor of 20 with acetonitrile and directly infused into the HESI source at the rate of 5 μL min^{-1}. For some experiments, complementary analyses were performed using ultrahigh-performance liquid chromatography (UPLC, Thermo Ultimate 3000) coupled to the HESI-HRMS system. Further details of the method are described in the Supporting Information.

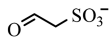
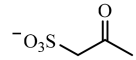
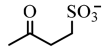
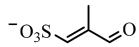
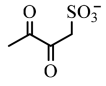
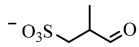
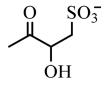
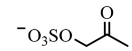
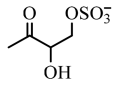
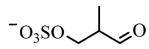
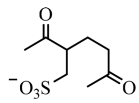
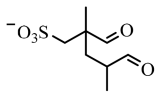
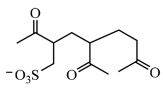
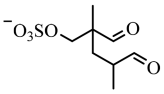
Ion Chromatography Analyses. Selected samples were analyzed by ion chromatography (IC) to determine the concentration of inorganic sulfate and residual inorganic sulfite (inorganic sulfur). The parameters of the IC program are detailed in a previous work as described in Coddens et al.[28] The difference between the measured concentration of inorganic sulfur and total sulfur is taken as the corresponding amount of organosulfur compounds formed.[4,29] In this study, the total sulfur concentration was obtained from the solution containing Na_2SO_3 and TMI catalyst under the same experimental conditions. The related discussion on the calculation of organosulfur compounds using this method can be found in the Supporting Information.

RESULTS AND DISCUSSION

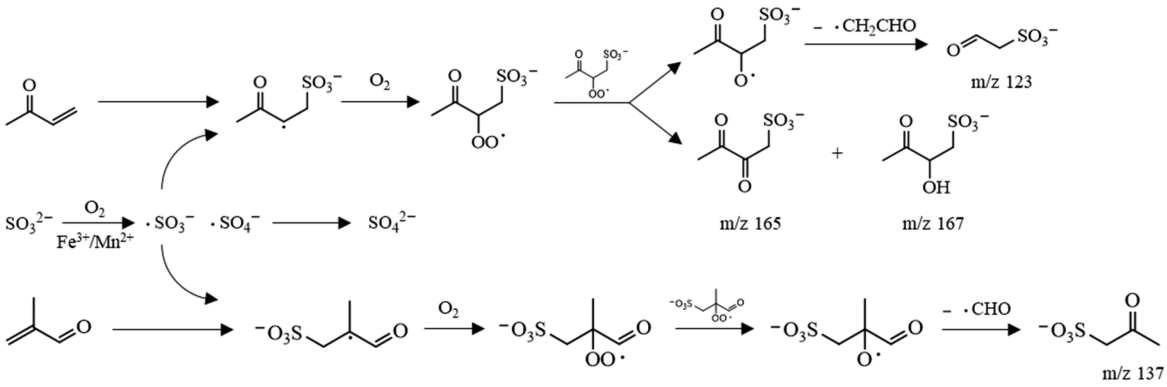
Reactions of MVK/MACR with S(IV) in the Presence of Mn^{2+} or Fe^{3+}. Figure 1 shows the mass spectra of both MVK and MACR following the reaction of each with Na_2SO_3 in the presence of TMIs, Mn^{2+} and Fe^{3+}, respectively, at pH 5. The analysis of product formation of this reaction with Fe^{3+} was discussed in detail in our previous study.[20] It was shown that organosulfur compounds can be formed in the reaction of MVK/MACR with Na_2SO_3 in the presence of Fe^{3+}. The formula, retention time, and structure of some of the organosulfur compounds observed in this previous study are

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

Table 1. Formula, Retention Time and Structure of Major Organosulfur Compounds Formed from the Reaction of MVK/MACR with Na_2SO_3 in the Presence of Transition Metal Ions

MVK				MACR			
m/z [M-H]	Retention time (min)	Formula	Structure	m/z [M-H]	Retention time (min)	Formula	Structure
122.97585	1.67	$C_2H_3SO_4$		136.99146	1.71	$C_3H_5SO_4$	
151.00703	1.76	$C_4H_7SO_4$		148.99139	1.60	$C_4H_5SO_4$	
164.98621	1.67	$C_4H_5SO_5$		151.00700	1.72	$C_4H_7SO_4$	
167.00183	1.60	$C_4H_7SO_5$		152.98624	1.69	$C_3H_5SO_5$	
182.99664	1.69	$C_4H_7SO_6$		167.00182	1.60	$C_4H_7SO_5$	
221.04865	1.85	$C_8H_{13}SO_5$		221.04861	1.78	$C_8H_{13}SO_5$	
291.09023	1.88	$C_{12}H_{19}SO_6$		237.04346	1.73	$C_8H_{13}SO_6$	

Scheme 1. Proposed Mechanism for the Formation of *m/z* 123, 165, and 167 for MVK and *m/z* 137 for MACR[a]

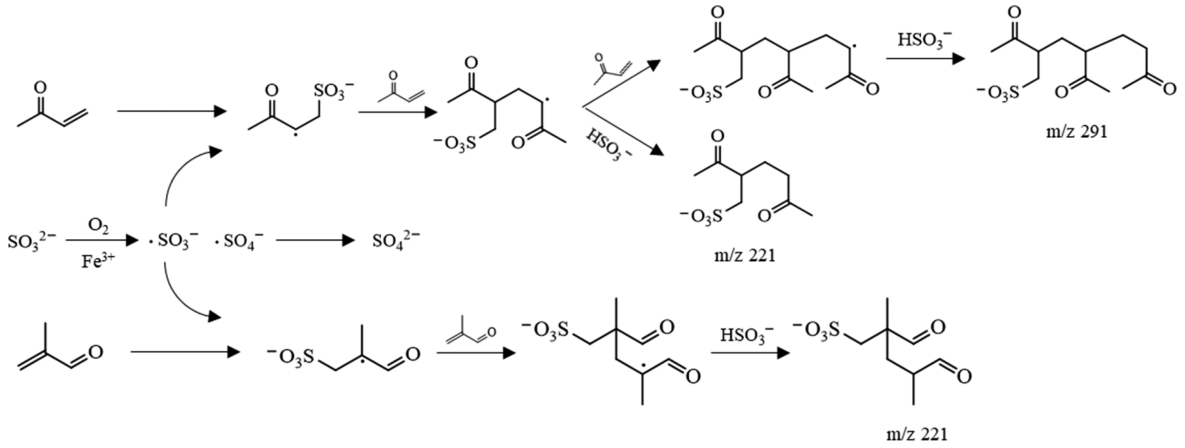


[a]The reaction of MVK/MACR with sulfate radicals is similar to that with sulfite radicals.

summarized in Table 1. These organosulfur compounds are formed via the reaction of sulfoxy radicals SO_3^- and SO_4^- with MVK/MACR. The addition of the sulfoxy radical on the C=C double bonds of MVK/MACR leads to the formation of MVK-sulfoxy/MACR-sulfoxy radicals (called R radicals hereafter). R radicals can react with O_2 to form RO_2 radicals and then undergo further decomposition to produce C_2-C_4 organosulfur compounds. Scheme 1 shows the reaction pathways for the formation of *m/z* 123, 165, and 167 for MVK and *m/z* 137 for MACR to elucidate the mechanism for the formation of C_2-C_4 organosulfur compounds from the decomposition of RO_2 radicals via unimolecular and bimolecular reactions. Alternatively, R radicals react with MVK/MACR resulting in oligomers formation, for example, *m/z* 221, 237, 291, and 307 (see Scheme 2). As shown in Figure 1, organosulfur compounds can also be observed when Mn^{2+} is present. However, when the spectra of the MVK/MACR reaction in the presence of Mn^{2+} are compared with that of MVK/MACR reaction in the presence of Fe^{3+}, distinct differences in the product distribution are observed. For the MVK reaction with Mn^{2+}, the compound with *m/z* 123 is preferentially formed, whereas oligomers are hardly apparent in the mass spectrum. Similarly, for the MACR reaction with Mn^{2+}, the oligomer organosulfur peaks are not present. These observations are also found at pH 3. Additionally, Figure 2 shows that a decrease in pH value seems to accentuate this discrepancy. Acidity favors the oligomerization of MVK in the reaction with Fe^{3+}, but the *m/z* 123 peak from MVK becomes the most pronounced peak in the spectrum of the reaction with Mn^{2+} at pH 3. The results of the MS^2 analysis show that the structures of C_2-C_4 organosulfur compounds observed in the presence of Mn^{2+} is the same to that observed in the presence

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

Scheme 2. Proposed Mechanism for the Formation of *m/z* 221 and 291 for MVK and *m/z* 221 for MACR from Oligomerization[a]



[a]The reaction of MVK/MACR with sulfate radicals is similar to that with sulfite radicals.

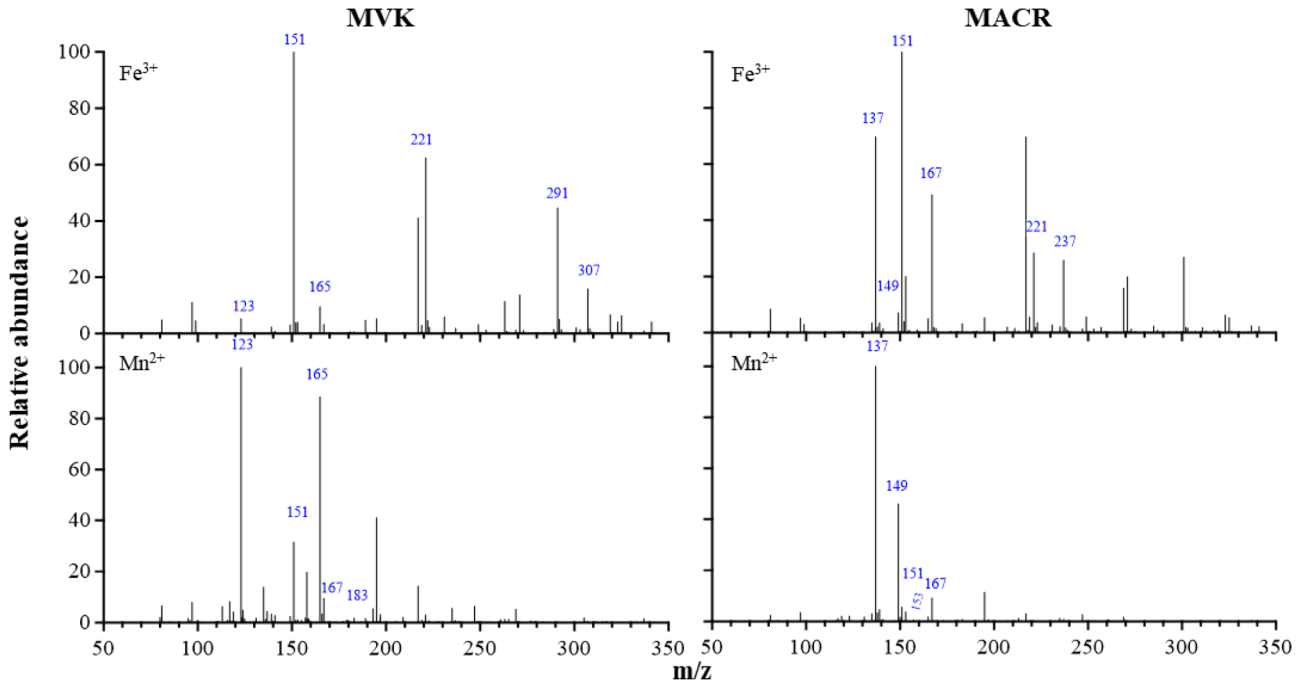


Figure 2. Mass spectra of MVK/MACR reacted with Na_2SO_3 in the presence of Fe^{3+} and Mn^{2+} at pH 3.

of Fe^{3+}, suggesting that the mechanism for the formation of organosulfur compounds in the presence of Mn^{2+} also involves the reaction of sulfoxy radicals with MVK/MACR. Therefore, on the basis of these data and the mechanism proposed previously, the rare production of oligomers in the presence of Mn^{2+} indicates that the pathway for oligomerization (Scheme 2) is inhibited when Mn^{2+} is present.

To the best of our knowledge, the formation of organosulfur compounds via a TMI-catalyzed reaction affected by different TMIs has not been reported previously. Employing the oxidation of sulfite by Mn^{2+} as the source of sulfoxy radicals, Rudzinski et al.[16] found that four types of organosulfur compounds, *m/z* 163 ($C_5H_7SO_4$), 165 ($C_5H_9SO_4$), 179 ($C_5H_7SO_5$), and 181 ($C_5H_9SO_5$), were produced from the reaction of isoprene with these sulfoxy radicals, but found no evidence for the formation of oligomers. However, since only manganese was used as the catalyst, the formation of organosulfur compounds via this reaction using Fe^{3+} as the initiator of sulfoxy radicals remained unclear. In the current study, we also examined the different products formed from the reaction of isoprene with sulfite in the presence of Fe^{3+} and Mn^{2+}. Figure S1(a) illustrates the formation of these four organosulfur compounds when Mn^{2+} is present. However, in addition to these four peaks, new peaks at *m/z* 217 and 291 appear in the spectrum of isoprene reacted with sulfite in the presence Fe^{3+} (Figure S1(b)). Peaks at *m/z* 217 and 297 correspond to $C_{10}H_{17}SO_3$ and $C_{10}H_{17}S_2O_6$, respectively, indicating the existence of dimers. Thus, besides that for MVK and MACR, there is also a difference in organosulfur compounds formation between Mn^{2+} and Fe^{3+} for isoprene. This result shows that these differences may persist for the different organic compounds present in the atmosphere.

It is noted that R radicals undergo a competition between a reaction toward O_2 and a reaction toward MVK/MACR for

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

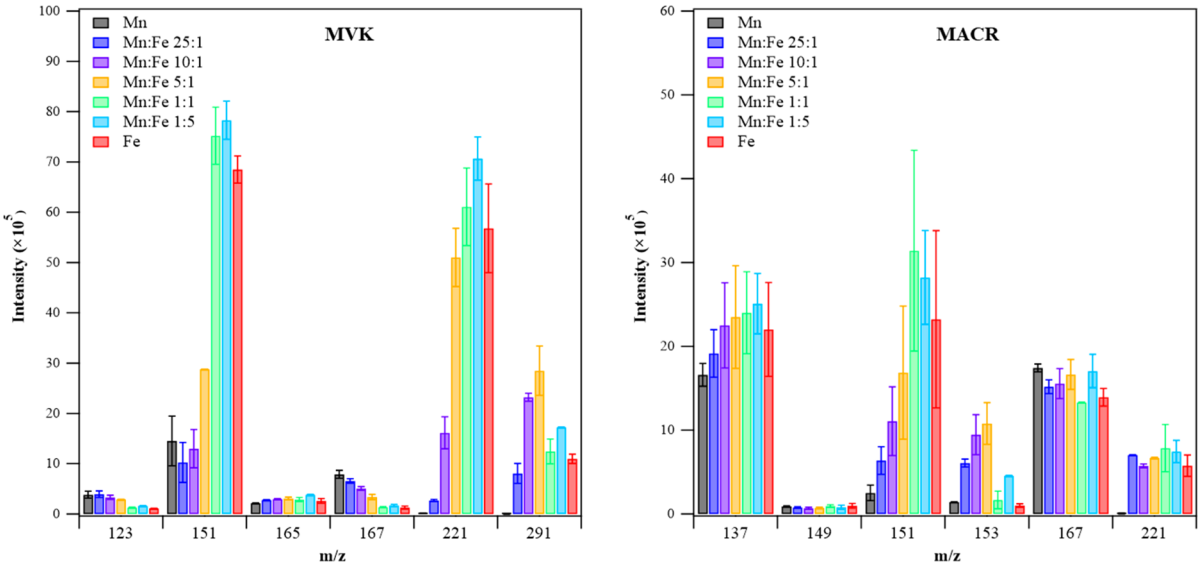


Figure 3. Organosulfur compounds detected by UPLC−MS following the reaction of MVK/MACR with Na_2SO_3 in the presence of Mn^{2+}/Fe^{3+} mixtures at pH 5.

decomposition and oligomerization, respectively. Given that the rate constants of sulfite oxidized by Fe^{3+} is higher than that of sulfite oxidized by Mn^{2+},[30,31] control experiments were performed under the same experimental conditions with the exception of TMI concentrations. The concentration of Mn^{2+} is increased to 2 mM in order to enhance the production of sulfoxy radicals and then produce more R radicals. Figure S2(a) shows that oligomers are not formed. Alternatively, when the concentration of Fe^{3+} was decreased to 20 μM, the peaks corresponding to oligomers are still pronounced (not shown here). Previous studies revealed that the formation of oligomers is closely related to the initial concentration of organic compounds.[32,33] Our previous study also found that higher concentrations of MVK/MACR in the presence of Fe^{3+} promotes oligomer formation;[20] thus, the experiment was also carried out at 10 mM MVK in the presence of Mn^{2+}. However, as shown in Figure S2(b), the intensities of oligomers peaks are still negligible. The results of the control experiments show that the discrepancy between Fe^{3+} and Mn^{2+} in organosulfur compounds formation is not caused by the specific organic compounds used, the rate of sulfoxy radical production, or the concentration of MVK/MACR. Thus, one of the possible explanations is that this discrepancy is ascribed to the nature of the TMIs themselves. The inhibition of the oligomerization pathway in the presence of Mn^{2+} is unclear but one potential cause could be due to complexes formed between Mn^{2+} and R radicals which inhibited chain propagation.

Reaction of MVK/MACR with S(IV) in the Presence of Mn^{2+} and Fe^{3+} Mixtures. Both iron and manganese are found in catalytically significant concentrations in atmospheric aqueous phases.[34] Since the mechanism for organosulfur compounds formation in the presence of Fe^{3+} and Mn^{2+} are quite different, we also investigated the additivity of these two reactions when both Mn^{2+} and Fe^{3+} are present. It is noted that there exists a synergistic interaction between Fe^{3+} and Mn^{2+} for inorganic S(IV) oxidation,[24,35] but the mechanism for the formation of organosulfur compounds may be not significantly affected given that this interaction may only impact the production of sulfoxy radicals. The intensity of major organosulfur compounds measured by UPLC−MS at different ratios of Mn^{2+} to Fe^{3+} at pH 5 are shown in Figure 3. For MVK, as the Mn^{2+}/Fe^{3+} ratio decreases, the intensities of peaks at m/z 123 and 167 decrease, but the intensities of peaks at 221 and 291 increase. As mentioned above, there are no oligomers formed in the presence of Mn^{2+} alone, however, although a low concentration of Fe^{3+} was added (Mn^{2+}/Fe^{3+} of 25:1), the intensities of the two oligomers peaks, m/z 221 and 291, are significantly increased to $(2.7 \pm 0.2) \times 10^5$ and $(8 \pm 2) \times 10^5$, respectively. Compared to MVK, MACR is more prone to undergo decomposition, thus it seems that the intensities of both C_2-C_4 organosulfur compounds and oligomers increase with the decreasing ratio of Mn^{2+}/Fe^{3+}. Analogous to that of MVK, the peak at m/z 221, which is not observed in the spectra of the reaction with Mn^{2+}, is also pronounced even at the high Mn^{2+}/Fe^{3+} ratio. These results suggest that the formation of organosulfur compounds may be dominated by Fe^{3+} when they are in coexistence.

A previous study reported that the concentration of iron is generally 10−100 times higher than manganese in rain, fog, and cloud droplets.[34] We also employed mineral dust and fly ash to mimic the concentration of soluble iron and manganese on wet aerosols under acidic conditions (pH 5 and 3). The results of the dissolution experiments show that the concentration of iron is also much higher (>20 times) than manganese. Although the reactions were not performed at lower Mn^{2+}/Fe^{3+}, as shown in Figure S3, the spectra of the MVK/MACR reacted with sulfite in the presence of Mn^{2+}/Fe^{3+} ratio of 1:5 are similar to that of the reaction in the presence of Fe^{3+} alone, illustrating that the formation of organosulfur compounds via a TMI-catalyzed reaction is dominated by Fe^{3+} in the atmospheric aqueous phase.

In this study, the amount of specific organosulfur compounds was not measured due to the lack of any standards for quantitative analysis. However, the percentage of organosulfur compounds accounting for the total sulfur at pH 5 in the presence of TMI are displayed in Table 2. In the presence of Mn^{2+}, 18% and 26% of sulfite were converted to organosulfur compounds for MVK and MACR, respectively. It is expected that the percentage of sulfite converted in the presence of Fe^{3+} is ∼2 times higher than that in the presence of Mn^{2+} for both

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

Table 2. Percentage of Organosulfur Compounds Formed Relative to the Total Sulfur (pH 5)

	percentage (%)		
reactant	Mn^{2+}	Mn^{2+}/Fe^{3+} (1:1)	Fe^{3+}
MVK	18 ± 2	40 ± 1	39 ± 1
MACR	26 ± 3	43 ± 1	44 ± 4

MVK and MACR, as Fe^{3+} is a more efficient catalyst than Mn^{2+} for oxidation of S(IV). The high yield observed indicates that TMI-catalyzed reactions may be in fact a significant pathway for organosulfur compounds formation in the atmosphere.

Atmospheric Implications. Our current study shows that organosulfur compounds can be formed through the aqueous reaction of MVK/MACR with sulfite in the presence of a TMI. However, Fe^{3+} and Mn^{2+} have distinctly different product distributions and mechanisms for the formation of these organosulfur compounds. Given the concentration of iron and manganese in the atmospheric aqueous phase, the formation of organosulfur compounds via this TMI-catalyzed reaction may be dominated by Fe^{3+}. Additionally, our findings also reveal that the formation of organosulfur compounds through these reactions contributes significantly to the conversion of S(IV). The formation of organosulfur compounds indicates a reduction in the formation of of inorganic sulfate; thus, the interaction of unsaturated organic compounds, sulfite, and TMI not only can serve as the source of organosulfur compounds, but also has a significant inhibitory effect on the formation of inorganic sulfate in the atmosphere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.9b00173.

Additional materials and methods information; mass spectra of MVK, MACR, and isoprene reacted with Na_2SO_3 in the presence of TMI under different experimental conditions (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vhgrassian@ucsd.edu.

ORCID

Vicki H. Grassian: 0000-0001-5052-0045

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant AGS1702488.

■ REFERENCES

(1) Surratt, J. D.; Gomez-Gonzalez, Y.; Chan, A. W. H.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H. Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A* **2008**, *112*, 8345−8378.

(2) Froyd, K. D.; Murphy, S. M.; Murphy, D. M.; de Gouw, J. A.; Eddingsaas, N. C.; Wennberg, P. O. Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 21360−21365.

(3) Kristensen, K.; Glasius, M. Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring. *Atmos. Environ.* **2011**, *45*, 4546−4556.

(4) Tolocka, M. P.; Turpin, B. Contribution of organosulfur compounds to organic aerosol mass. *Environ. Sci. Technol.* **2012**, *46*, 7978−7983.

(5) He, Q. F.; Ding, X.; Wang, X. M.; Yu, J. Z.; Fu, X. X.; Liu, T. Y.; Zhang, Z.; Xue, J.; Chen, D. H.; Zhong, L. J.; Donahue, N. M. Organosulfates from pinene and isoprene over the Pearl River Delta, South China: Seasonal variation and implication in formation mechanisms. *Environ. Sci. Technol.* **2014**, *48*, 9236−9245.

(6) Hansen, A. M. K.; Kristensen, K.; Nguyen, Q. T.; Zare, A.; Cozzi, F.; Nøjgaard, J. K.; Skov, H.; Brandt, J.; Christensen, J. H.; Ström, J.; Tunved, P.; Krejci, R.; Glasius, M. Organosulfates and organic acids in Arctic aerosols: Speciation, annual variation and concentration levels. *Atmos. Chem. Phys.* **2014**, *14* (15), 7807−7823.

(7) Wang, Y.; Hu, M.; Guo, S.; Wang, Y.; Zheng, J.; Yang, Y.; Zhu, W.; Tang, R.; Li, X.; Liu, Y.; Le Breton, M.; Du, Z. F.; Shang, D. J.; Wu, Y. S.; Wu, Z. J.; Song, Y.; Lou, S. R.; Hallquist, M.; Yu, J. Z. The secondary formation of organosulfates under interactions between biogenic emissions and anthropogenic pollutants in summer in Beijing. *Atmos. Chem. Phys.* **2018**, *18*, 10693−10713.

(8) Brüggemann, M.; Poulain, L.; Held, A.; Stelzer, T.; Zuth, C.; Richters, S.; Mutzel, A.; van Pinxteren, D.; Iinuma, Y.; Katkevica, S.; Rabe, R.; Herrmann, H.; Hoffmann, T. Realtime detection of highly oxidized organosulfates and BSOA marker compounds during the F−BEACh 2014 field study. *Atmos. Chem. Phys.* **2017**, *17*, 1453−1469.

(9) Hansen, A. M. K.; Hong, J.; Raatikainen, T.; Kristensen, K.; Ylisirniö, A.; Virtanen, A.; Petajä, T.; Glasius, M.; Prisle, N. L. Hygroscopic properties and cloud condensation nuclei activation of limonene-derived organosulfates and their mixtures with ammonium sulfate. *Atmos. Chem. Phys.* **2015**, *15*, 14071−14089.

(10) Estillore, A. D.; Hettiyadura, A. P. S.; Qin, Z.; Leckrone, E.; Wombacher, B.; Humphry, T.; Stone, E. A.; Grassian, V. H. Water uptake and hygroscopic growth of organosulfate aerosol. *Environ. Sci. Technol.* **2016**, *50*, 4259−4268.

(11) Surratt, J. D.; Chan, A. W.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 6640−6645.

(12) Drozd, G. T.; Woo, J. L.; McNeill, V. F. Self-limited uptake of α-pinene oxide to acidic aerosol: the effects of liquid-liquid phase separation and implications for the formation of secondary organic aerosol and organosulfates from epoxides. *Atmos. Chem. Phys.* **2013**, *13*, 8255−8263.

(13) Darer, A. I.; Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. Formation and stability of atmospherically relevant isoprene derived organosulfates and organonitrates. *Environ. Sci. Technol.* **2011**, *45*, 1895−1902.

(14) Hu, K. S.; Darer, A. I.; Elrod, M. J. Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates. *Atmos. Chem. Phys.* **2011**, *11*, 8307−8320.

(15) Passananti, M.; Kong, L.; Shang, J.; Dupart, Y.; Perrier, S.; Chen, J.; Donaldson, D. J.; George, C. Organosulfate formation through the heterogeneous reaction of sulfur dioxide with unsaturated fatty acids and longchain alkenes. *Angew. Chem., Int. Ed.* **2016**, *55*, 10336−10339.

(16) Rudziński, K. J.; Gmachowski, L.; Kuznietsova, I. Reactions of isoprene and sulphoxy radical-anions−a possible source of atmospheric organosulphites and organosulphates. *Atmos. Chem. Phys.* **2009**, *9*, 2129−2140.

(17) Perri, M. J.; Lim, Y. B.; Seitzinger, S. P.; Turpin, B. J. Organosulfates from Glycolaldehyde in Aqueous Aerosols and Clouds: Laboratory Studies. *Atmos. Environ.* **2010**, *44*, 2658−2664.

(18) Nozière, B.; Ekström, S.; Alsberg, T.; Holmström, S. Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols. *Geophys. Res. Lett.* **2010**, *37*, L05806.

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755

(19) Schindelka, J.; Iinuma, Y.; Hoffmann, D.; Herrmann, H. Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols. *Faraday Discuss.* **2013**, *165*, 237−259.
(20) Huang, L.; Cochran, R.; Coddens, E.; Grassian, V. H. Formation of organosulfur compounds through transition metal ion-catalyzed aqueous phase reactions. *Environ. Sci. Technol. Lett.* **2018**, *5*, 315−321.
(21) Schmidt, M.; Jansen van Beek, S. M.; Abou-Ghanem, M.; Oliynyk, A. O.; Locock, A. J.; Styler, S. A. Production of atmospheric organosulfates via mineral-mediated photochemistry. *ACS Earth Space Chem.* **2019**, *3*, 424−431.
(22) Tang, Y.; Thorn, R. P.; Mauldin, R. L., III; Wine, P. H. Kinetics and spectroscopy of the SO_4^- radical in aqueous solution. *J. Photochem. Photobiol., A* **1988**, *44*, 243−258.
(23) Jiang, P. Y.; Katsumura, Y.; Nagaishi, R.; Domae, M.; Ishikawa, K.; Ishigure, K.; Yoshida, Y. Pulse-radiolysis study of concentrated sulfuric-acid-solutions: Formation mechanism, yield and reactivity of sulfate radicals. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1653−1658.
(24) Brandt, C.; Van Eldik, R. Transition metal-catalyzed oxidation of sulfur (IV) oxides. Atmospheric-relevant processes and mechanisms. *Chem. Rev.* **1995**, *95*, 119−190.
(25) Herrmann, H.; Ervens, B.; Jacobi, H. W.; Wolke, R.; Nowacki, P.; Zellner, R. CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry. *J. Atmos. Chem.* **2000**, *36*, 231−284.
(26) Alexander, B.; Park, R. J.; Jacob, D. J.; Gong, S. Transition metal-catalyzed oxidation of atmospheric sulfur: global implications for the sulfur budget. *J. Geophys. Res.* **2009**, *114*, D02309.
(27) Harris, E.; Sinha, B.; van Pinxteren, D.; Tilgner, A.; Fomba, K. W.; Schneider, J.; Roth, A.; Gnauk, T.; Fahlbusch, B.; Mertes, S.; Lee, T.; Collett, J.; Foley, S.; Borrmann, S.; Hoppe, P.; Herrmann, H. Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO_2. *Science* **2013**, *340*, 727−730.
(28) Coddens, E. M.; Huang, L.; Wong, C.; Grassian, V. H. Influence of glyoxal on the catalytic oxidation of S (IV) in acidic aqueous media. *ACS Earth Space Chem.* **2019**, *3*, 142−149.
(29) Sorooshian, A.; Crosbie, E.; Maudlin, L. C.; Youn, J. S.; Wang, Z.; Shingler, T.; Ortega, A. M.; Hersey, S.; Woods, R. K. Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas. *J. Geophys. Res.: Atmos.* **2015**, *120*, 8535−8548.
(30) Martin, L.; Good, T. W. Catalyzed oxidation of sulfur dioxide in solution: The iron-manganese synergis. *Atmos. Environ., Part A* **1991**, *25*, 2395−2399.
(31) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: from air pollution to climate change*, 2nd ed.; Wiley: New York, 2006.
(32) Liu, Y.; Siekmann, F.; Renard, P.; El Zein, A.; Salque, G.; El Haddad, I.; Temime-Roussel, B.; Voisin, D.; Thissen, R.; Monod, A. Oligomer and SOA formation through aqueous phase photooxidation of methacrolein and methyl vinyl ketone. *Atmos. Environ.* **2012**, *49*, 123−129.
(33) Renard, P.; Siekmann, F.; Gandolfo, A.; Socorro, J.; Salque, G.; Ravier, S.; Quivet, E.; Clement, J.-L.; Traikia, M.; Delort, A.-M.; Voisin, D.; Vuitton, V.; Thissen, R.; Monod, A. Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen. *Atmos. Chem. Phys.* **2013**, *13*, 6473−6491.
(34) Deguillaume, L.; Leriche, M.; Desboeufs, K.; Mailhot, G.; George, C.; Chaumerliac, N. Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters. *Chem. Rev.* **2005**, *105*, 3388−3431.
(35) Berglund, J.; Fronaeus, S.; Elding, L. I. Kinetics and mechanism for manganese-catalyzed oxidation of sulfur(IV) by oxygen in aqueous solution. *Inorg. Chem.* **1993**, *32*, 4527−4538.

DOI: 10.1021/acsearthspacechem.9b00173
ACS Earth Space Chem. 2019, 3, 1749−1755