Catalytic role of formaldehyde in particulate matter formation

Eleni Dovrou1,2, Kelvin H. Bates3, Jonathan M. Moch3, Loretta J. Mickley5, Daniel J. Jacob4,6, and Frank N. Keutsch2,3,7

1John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138; 2Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138; and 3Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138

Edited by Barbara Ervens, Institut de Chimie de Clermont-Ferrand, Clermont-Ferrand, France; received July 19, 2021; accepted December 11, 2021 by Editorial Board Member Akkihebbal R. Ravishankara

Formaldehyde (HCHO), the simplest and most abundant carbonyl in the atmosphere, contributes to particulate matter (PM) formation via two in-cloud processing pathways. First, in a catalytic pathway, HCHO reacts with hydrogen peroxide (H2O2) to form hydroxymethyl hydroperoxide (HMHP), which rapidly oxidizes dissolved sulfur dioxide (SO2,aq) to sulfate, regenerating HCHO. Second, HCHO reacts with dissolved SO2,aq to form hydroxymethanesulfonate (HMS), which upon oxidation with the hydroxyl radical (OH) forms sulfate and also reforms HCHO. Chemical transport model simulations using rate coefficients from laboratory studies of the reaction rate of HMHP with SO2,aq show that the HMHP pathways reduce the SO2 lifetime by up to a factor of 2 and contribute up to ~18% of global sulfate. This contribution rises to >50% in isoprene-dominated regions such as the Amazon. Combined with recent results on HMS, this work demonstrates that the one-carbon molecules HMHP and HCHO contribute significantly to global PM, with HCHO playing a crucial catalytic role.

Particulate matter (PM) formation has a significant impact on cloud properties, climate, and human health (1). Higher toxicity has been attributed to small-size particles (particles with aerodynamic diameter smaller than 2.5 μm) due to their ability to enter the respiratory and cardiovascular system, causing adverse health effects in highly polluted environments (2–7). A substantial fraction of PM corresponds to sulfate, which is primarily formed from atmospheric oxidation of SO2 emitted anthropogenically by coal combustion and smelters (8). Important SO2 oxidation pathways include reaction with the hydroxyl radical (OH) in the gas phase and reaction with hydrogen peroxide (H2O2), ozone, multifunctional organic hydroperoxides (RXOOH), and NO2 in cloud droplets (9–13). Simple organic hydroperoxides, such as methyhydroperoxide and peroxyacetic acid, are unlikely to contribute due to their low Henry’s law constants, on the order of 102 to 103 M−1 atm−1 of9. Formaldehyde, revealing the catalytic role of formaldehyde, and demonstrating the importance of hydroxymethyl hydroperoxide, which can be formed by gas-phase reactions and in-cloud reaction of hydrogen peroxide with the simplest aldehyde, formaldehyde, strongly influences the Earth’s climate and air quality. Particle composition depends on anthropogenic and biogenic emissions. Thus, in order to understand climate change, knowledge of the difference between preindustrial and current conditions is critical. Under preindustrial conditions, multifunctional organic hydroperoxides, which are strong oxidants and have the ability to contribute to particulate matter formation, are in higher concentrations in the atmosphere. In this work, we focus on the previously unknown importance of hydroxymethyl hydroperoxide, which can be formed by gas-phase reactions and in-cloud reaction of hydrogen peroxide with the simplest aldehyde, formaldehyde, revealing the catalytic role of formaldehyde, and demonstrate that this chemistry is of great importance for particle formation.

Significance

Particulate matter, often formed via cloud processing, strongly influences the Earth’s climate and air quality. Particle composition depends on anthropogenic and biogenic emissions. Thus, in order to understand climate change, knowledge of the difference between preindustrial and current conditions is critical. Under preindustrial conditions, multifunctional organic hydroperoxides, which are strong oxidants and have the ability to contribute to particulate matter formation, are in higher concentrations in the atmosphere. In this work, we focus on the previously unknown importance of hydroxymethyl hydroperoxide, which can be formed by gas-phase reactions and in-cloud reaction of hydrogen peroxide with the simplest aldehyde, formaldehyde, revealing the catalytic role of formaldehyde, and demonstrate that this chemistry is of great importance for particle formation.

Author contributions: E.D. and F.N.K. designed research; E.D., J.M.M., L.J.M., D.J.J., and F.N.K. contributed new reagents/analytic tools; E.D. and K.H.B. analyzed data; and E.D., K.H.B., and F.N.K. wrote the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission. B.E. is a guest editor invited by the Editorial Board.

This open access article is distributed under Creative Commons Attribution License 4.0 (CC BY).

1To whom correspondence may be addressed. Email: dovrouel@gmail.com or keutsch@eas.harvard.edu.

2Present address: Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz 55128, Germany.

This article contains supporting information online at http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2113265119/-/DCSupplemental.

Published January 31, 2022.

PNAS 2022 Vol. 119 No. 6 e2113265119

https://doi.org/10.1073/pnas.2113265119
Another important compound that could contribute to PM formation is formaldehyde. Formaldehyde (HCHO) is the most abundant and simplest carbonyl in the atmosphere, formed primarily via photochemical oxidation of volatile organic compounds, such as isoprene, its main biogenic precursor (25). Having a high Henry’s law constant (~5.5 \times 10^4 M \cdot atm^{-1}) (26), HCHO can partition into cloud and fog water. The term HCHO, as used in this work, refers to both free HCHO and its hydrated form, which is the dominant form in clouds and fog droplets. In cloud droplets, HCHO reacts with SO_2 to form hydroxymethanesulfonate (HMS; HOCH_2SO_3^-) (27–30). HMS is stable at pH <6 and resistant to oxidation by hydrogen peroxide (H_2O_2) and ozone (O_3) but can be oxidized by OH to form sulfate and oxo sulfonate (HMSO; HOCH_2SO_2O). The literature values for this reaction are not well established (27–30).

In this work, NMR spectroscopy (1H-NMR) was used to determine the equilibrium constant and kinetics of HMHP for- mation from formaldehyde.

The rate of change in [HMHP] is

\[ \frac{d[H M H P]}{d t} = k_1 \cdot [H C H O]^2 - k_2 \cdot [H M H P] \]

for our experimental conditions and at equilibrium.

By observing the increase in the HMHP signal intensity over time, the forward rate constant of HMHP, \( k_1 \), was experimentally determined with lower limit of \( k_{1,\text{meas}} \geq 1.3 \pm 0.8 \) M\(^{-1}\) s\(^{-1}\), the value in agreement with the average forward rate constant reported in the literature (38, 39). The reverse rate constant, \( k_2 \), calculated from \( K_{eq} = \frac{k_1}{k_2} \), is \( k_{2,\text{calc}} \geq 7.6 \pm 0.4 \times 10^{-3} \) s\(^{-1}\) (Materials and Methods). By observing the decrease of the HMHP signal intensity upon dilution, the reverse rate constant was measured to be \( k_{2,\text{meas}} = 6 \pm 2 \times 10^{-3} \) s\(^{-1}\), and the forward rate constant calculated from this is \( k_{1,\text{calc}} = 1.0 \pm 0.2 \) \times 10\(^{-4} \) M\(^{-1}\) s\(^{-1}\). The literature values for \( k_2 \) also vary by more than an order of magnitude between 9.4 \times 10^{-1} and 7.5 \times 10^{-2} M\(^{-1}\) s\(^{-1}\), with the higher value being in close agreement with the one determined here; for \( k_1 \), the literature values vary between 6.3 \times 10^{-3} and 5.9 \times 10^{-3} s\(^{-1}\) (SI Appendix, Table S1). The literature values were obtained by observing the decrease and increase of H_2O_2 using either equal concentrations of HCHO and H_2O_2 or excess of HCHO (SI Appendix, Supplementary Discussion 2), whereas, in our study, HCHO and HMHP were both directly measured (38, 39). We were not able to resolve the discrepancy between \( k_{1,\text{meas}} \) and \( k_{2,\text{meas}} \). For that reason, and as \( k_{1,\text{meas}} \) is only a lower limit, we used three scenarios that correspond to fast, medium, and slow equilibria, \( k_1 \), \( k_2 \), and \( k_r \), respectively: 1) \( k_1 \): an upper-bound formation rate constant is considered equal to \( k_{1,\text{max}} = 100 \pm 35 \) M\(^{-1}\) s\(^{-1}\), with the reverse rate constant equal to \( k_{r,\text{max}} = 0.6 \pm 0.2 \) s\(^{-1}\); 2) \( k_1 \): the lower limit measured \( k_{1,\text{meas}} = 1.3 \pm 0.8 \) M\(^{-1}\) s\(^{-1}\) and \( k_{2,\text{calc}} = 7.6 \pm 0.6 \) \times 10^{-3} s\(^{-1}\); and 3) \( k_2 \): the measured decomposition rate constant, \( k_{d,\text{calc}} = 1.0 \pm 0.2 \times 10^{-4} \) M\(^{-1}\) s\(^{-1}\) and \( k_{2,\text{meas}} = 6 \pm 2 \) \times 10^{-3} s\(^{-1}\). The impact of the different rate constants on our conclusions is discussed later.

Rate of Oxidation of SO_2 via HMHP. Experiments to determine the rate constant of oxidation of SO_2 via HMHP followed the protocol for recent work on the ISOPOOH and H_2O_2 + SO_2 reactions (SI Appendix, Table S2) (12). Sulfate formation was so rapid under experimental conditions (completion within 30 s; Fig. 1 and SI Appendix, Fig. S1) that only a lower limit for the rate constant was determined. Slower reaction rates could not be accessed due to the detection limit of the ion chromatography (IC). The lower limit of this rate
constant, \( k(\text{HMHP}) \geq 8.0(\pm 1.2) \cdot 10^3 \text{ M}^{-1} \text{s}^{-1} \) at \( \text{pH} = 5.5 \), shows that reaction of HMHP with \( \text{SO}_2^{aq} \) is significantly faster than reaction with \( \text{H}_2\text{O}_2 \) \( [k(\text{H}_2\text{O}_2) = 1.6 \cdot 10^3 \text{ M}^{-1} \text{s}^{-1}] \). or ISOPOOH \( [k(1,2\text{-ISOPOOH}) = 1.65 \cdot 10^2 \text{ M}^{-1} \text{s}^{-1}] \) \((\text{SI Appendix}, \text{Table S4}) (9, 10, 12, 40–42)\). From experiments at lower \( \text{pH} \) of 4.5 and 3, we estimate a further increase in rate constants to \( \geq 1.5(\pm 0.7) \cdot 10^4 \text{ M}^{-1} \text{s}^{-1} \) and \( \geq 1.4(\pm 0.8) \cdot 10^4 \text{ M}^{-1} \text{s}^{-1} \), respectively, similar to \( \text{H}_2\text{O}_2 \) and in contrast to ISOPOOH.

**GEOS-Chem Model Results.** To examine the effect of HMHP/HCHO reactions on sulfate and HMS formation, GEOS-Chem simulations under current, \( \text{C} \), and “preindustrial,” \( \text{PI} \), atmospheric conditions were performed \((\text{Materials and Methods})\). Two HMHP pathways of sulfate formation were considered for the GEOS-Chem simulations: 1) HMHP formed in the gas-phase ozonolysis of terminal alkenes with subsequent partitioning into cloud water (HMHP-direct), where it decomposes to HCHO and \( \text{H}_2\text{O}_2 \), dependent on the equilibration rate, and 2) HMHP formed in the aqueous phase from the reaction of \( \text{H}_2\text{O}_2 \) with HCHO (HCHO-catalysis), also dependent on the rate of equilibration. Three HMHP equilibrium cases were considered in the GEOS-Chem simulations, all with \( K_{eq} = 172 \text{ M}^{-1} \): 1) fast equilibrium, \( K_f \), 2) medium equilibrium, \( K_m \), and 3) slow equilibrium, \( K_s \). We present the model contribution of all RXOOH (i.e., ISOPOOH, HMHP-direct and HCHO-catalysis) to sulfate formation \((\text{Fig. 2 and SI Appendix, Fig. S2})\) as well as to changes in the sulfate burden, \( \tau\text{SO}_2 \) \((\text{Fig. 3 A and C})\) and the HMS/sulfate production ratio \((\text{Fig. 3 B and D})\) and \( \text{SI Appendix, Fig. S3 B and D}) \).

The GEOS-Chem contribution of all RXOOH pathways to sulfate in the global troposphere for the \( K_f \) case is 18%/24% for \( \text{C}/\text{PI} \). For the \( K_m \) case, the corresponding contributions are 7%/8%, and for \( K_s \) this is reduced to 4%/3%. For \( K_f \), \( \text{H}_2\text{O}_2 \) remains the most important oxidant globally but HCHO-catalysis is significant, contributing the majority of RXOOH pathways with 17%/23% of \( \text{C}/\text{PI} \) of sulfate \((\text{Fig. 2 and SI Appendix, Figs. S2 and S5})\). The contribution of HCHO-catalysis to global sulfate decreases as the equilibrium slows down to 5%/7% \( \text{C}/\text{PI} \) for the \( K_m \) case and 0.4%/0.6% for \( K_s \). The contribution of the HMHP-direct pathway increases but never exceeds 2.2% contribution to sulfate for the global troposphere, and \( \text{H}_2\text{O}_2 \) remains the dominant oxidant \((\text{SI Appendix, Tables S5–S7})\).

Regionally, RXOOH pathways contribute more to sulfate formation than other oxidation pathways (i.e., \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \)) in isoprene-rich regions \((\text{SI Appendix, Figs. S4 and S5})\), where they are dominant. Field measurements in the Amazon region have shown that local \( \text{SO}_2 \) conversion to sulfate is important for \( \text{PM} \) formation 70% of the time \((43)\). For \( K_f \), RXOOH pathways account for 79%/72% \( \text{C}/\text{PI} \) of sulfate formation in the lowest kilometer of the troposphere in the Amazon, 62%/52%.

![Fractional sulfate production under current atmospheric conditions](https://doi.org/10.1073/pnas.2113265119)

**Fig. 2.** Contribution of the two HMHP pathways to column sulfate production. (A–C) The contribution is estimated for fast \((A)\), medium \((B)\), and slow \((C)\) HMHP equilibrium under current atmospheric conditions from GEOS-Chem simulations at altitudes of \( 0 \) to \( 10 \text{ km} \). If the equilibrium is reached under the fast rate, the HCHO-catalysis pathways are dominant compared to the direct HMHP pathway for the oxidation of dissolved \( \text{SO}_2 \).
in the Congo Basin, and 20%/58% in the SE-US. For K_s, HCHO-catalysis contributes more than H_2O_2 itself in the Amazon and Congo Basin. The contribution of ISOPOOH is also significant in isoprene-rich regions (e.g., 24%/22% on average in the Amazon for K_f). These regional increases in sulfate burden are reflected in corresponding reductions of rSO_2 (Fig. 3A and C and SI Appendix, Fig. S3A and C and Tables S8–S10). For the global troposphere, rSO_2 is reduced only by 5%/7% C/PI, but in regions such as the Amazon and Congo Basin, rSO_2 is roughly halved, a large change that decreases the already low gas-phase SO_2 concentrations even further, especially under PI conditions. The increase in the regional sulfate burden is due to the increase in the local oxidation of SO_2, which reveals that the oxidation is outcompeting the sum of SO_2 transport and deposition.

The RXOOH pathways also have significant impacts on the contribution of HMS to PM. The global HMS/sulfate production ratio is reduced by 19%/44% C/PI for the K_f case, and 15%/44% for the K_m case, and 13%/58% for the K_s case (Fig. 3B and D and SI Appendix, Fig. S3B and D and Tables S5–S7). The reductions on regional scales can be much larger; for example, in the Amazon, the HMS/sulfate production ratio is reduced by 75 to 81% over all equilibrium cases. The same trend in impact on HMS/sulfate production ratio is observed in the Congo Basin and SE-US (Fig. 3B and D and SI Appendix, Fig. S3B and D and Tables S5–S7).

**Fig. 3.** Percent change in column sulfate and HMS production and ratio of SO_2 lifetime and HMS to sulfate production. (A and B) Percent change in column sulfate (A) and HMS (B) production considering fast, medium, and slow HMHP equilibrium under current atmospheric conditions at altitudes of 0 to 10 km. The GEOS-Chem model described in this work was used to perform the simulations. (C) The percentages presented in the table represent the ratio of SO_2 lifetime, τ_SO_2, of the value obtained from the equilibrium cases to that from the base simulation for the Amazon, SE-US, Congo Basin, and Indonesia. The percentages are all lower than 100%; thus, the equilibrium cases reduce the SO_2 lifetime. (D) The percentages presented in the table represent the ratio of the parameter p = production_HMS / production_SO_2, of the value obtained from the equilibrium cases to that from the base simulation for the Amazon, SE-US, Congo Basin, and Indonesia. The percentages are all lower than 100%; thus, the equilibrium cases reduce the production of HMS compared to sulfate (SI Appendix, Tables S5–S7).
Discussion

Within cloud droplets and fog water, there exist competing pathways for HMHP (reaction with SO$_2$aq versus dissociation to H$_2$O and HCHO), H$_2$O (reaction with SO$_2$aq versus HCHO), HCHO (reaction with SO$_2$aq versus H$_2$O$_2$), and SO$_2$aq (reaction with H$_2$O$_2$ versus HMHP versus HCHO). The latter, SO$_2$aq (reaction with H$_2$O$_2$ versus HMHP versus HCHO), is the most important to explain model results (Fig. 4A and SI Appendix, Fig. S6). Although the equilibrium constant for HMHP is large, the majority of HCHO and H$_2$O remain in the free, or, for HCHO, hydrated, form under cloud droplet conditions. The fact that inclusion of the HMHP-direct and HCHO-catalysis pathways in the model greatly reduces the HMS/sulfate production ratio reflects not a direct competition between H$_2$O$_2$ and SO$_2$aq for HCHO but, rather, that the oxidation via HCHO-catalysis or HMHP-direct is so rapid that less HMS is formed.

The lifetime of HMHP with respect to dissociation to HCHO and H$_2$O increases from 1.7 s for K$_f$ to 5 min for K$_m$ and, finally, to 19 d for K$_z$. For K$_z$, the HMHP that partitions from the gas phase to the aqueous phase can be assumed to be instantaneously in equilibrium with HCHO and H$_2$O. In contrast, for K$_f$, the dissociation of HMHP in the aqueous phase from the gas phase is so slow that it is irrelevant, whereas oxidation of SO$_2$aq forming HCHO is an important pathway. This explains the shift of the contribution from HCHO-catalysis to HMHP-direct with slower equilibration observed for the Amazon. For K$_f$, H$_2$O$_2$ and HMHP are effectively not chemically coupled, and both can oxidize SO$_2$aq. In locations with high-HMHP mixing ratios (SI Appendix, Fig. S7), HMHP thus becomes an important oxidant due to the much higher rate constant (SI Appendix, Table S4) for K$_f$ than for K$_m$. For K$_f$, H$_2$O$_2$ and HMHP are coupled due to the fast equilibrium. In this case, the HCHO-catalysis pathway is very efficient as, despite low concentrations of HMHP, the rate constant is very high and HMHP is “instantaneously” regenerated from reformed HCHO and H$_2$O, which can be replenished from the gas phase. Although HMHP concentrations cannot be higher than those of H$_2$O$_2$, the HMHP turnover rate can be very high. This pathway is particularly effective, as HCHO is not consumed but regenerated. For medium equilibrium for k$_z$ = 1.3 M$^{-1}$ s$^{-1}$ and the literature lower limit k$_z$literature = 7.5×10$^{-2}$ M$^{-1}$ s$^{-1}$, the estimated kinetic chain length is between 24 and 1.5 (Materials and Methods). This unexpected finding reveals the truly catalytic nature of this pathway, in which the oxidant can be viewed as H$_2$O$_2$, but with addition of HCHO as the catalyst.

The largest uncertainty in this work is the HMHP equilibration rate. Zhou and Lee showed that the equilibration rate is inversely dependent on [H$^+$], increasing with higher pH (base catalysis) (36, 39). However, a critical finding is that regardless of this equilibration rate, HCHO-catalysis and/or HMHP-direct pathways are significant contributors to sulfate formation. This results in increased sulfate burdens in regions such as the Amazon and Congo Basin, accompanied by a reduction of SO$_2$O$_2^-$ and HMHP (Fig. 5 and SI Appendix, Fig. S8 and Tables S8–S10). The effect is largest for the K$_f$ case, but it is only slightly reduced for the K$_z$ case, as the decrease in the contribution of HCHO-catalysis is largely balanced by increasing contribution of HMHP-direct. The reduction in SO$_2^-$ results in reductions in gas-phase SO$_2$, in particular in regions that are already low in SO$_2$, which acts as a limiting reagent in sulfate production so that H$_2$O$_2$ or HCHO concentrations are not affected. The reduced gas-phase SO$_2$ in turn reduces production and concentration of gas-phase sulfuric acid. Analysis of the impact on new particle formation (NPF) is beyond the scope of this work, but, as formation of gas-phase sulfuric acid is critical for NPF, we expect this to have a significant impact on regional NPF.

The effects of PI versus C are more pronounced in regions that currently have high anthropogenic emissions, showing that the role of RXOOH could increase substantially as NO$_x$ emissions decrease in such regions. In the SE-US, the contribution of HCHO-catalysis/HMHP-direct for the PI scenario is about three times that of C for the lowest km (SI Appendix, Tables S5–S7). Similar increments are revealed via the model simulations for the ISOPOOH contribution. For the C and PI scenario, inclusion of the RXOOH pathways reduces the HMS particulate sulfur production fraction by 20 to 26% and 85 to 88% compared to the base C/PI case, depending on the HMHP equilibration rate assumed. For India and East China, the contribution of RXOOH increases by factors of 5 and 25, respectively, due to the large changes in the NO$_x$ regime for these regions. The Amazon and Congo Basin are low-NO$_x$ environments regardless of C and PI scenarios, and there is little change in the contribution of HMHP/HCHO. The global contribution of the one-carbon pathways increases slightly in the PI compared to the C scenario, (Fig. 4B and SI Appendix, Fig. S8). In summary, the changes between C and PI are driven by changes in both the yields of RXOOH, as in East China, also but by changes in model OH production at the surface.

It is likely that other α-hydroxyhydroperoxides, formed from highly water soluble, electron-poor aldehydes, such as hydroxyacetone, glyoxal, or butenedial, react similarly to HMHP. It also has been shown that aldehyde-S(IV) species, such as glyoxal-S(IV), hydroxyacetdehyde-S(IV), and the methyglyoxal adduct, are formed in cloud water and have faster formation rates than HMS at pH ≥4.5 (31). Although the solubility of these aldehydes is comparable to that of HCHO, their concentrations in the atmosphere are much lower (SI Appendix, Supplementary Discussion 1) (30, 34, 44–49). Nonetheless, studies are clearly needed to quantify their contribution and that of other multifunctional hydroperoxides, as only HMHP; an α-hydroxyhydroperoxide, and ISOPOOH, a β-hydroxyhydroperoxide, have been investigated, to our knowledge. Although these two likely are the most abundant multifunctional hydroperoxides, the sum of all multifunctional hydroperoxides could increase the importance of RXOOH pathways for the PM sulfur burden.

The HCHO-catalysis pathway reveals the importance of HCHO in cloud chemistry and sulfate PM formation. The additional HCHO pathway in cloud water, which results in HMS formation, contributes to organic PM formation, as HMS is an S(IV) compound. HMS decomposition is favored at pH values of approximately ≥5, which are observed in regions with dust and agricultural activities (50), resulting in the regeneration of HCHO upon reaction with OH (30, 34), which suggests a possible additional catalytic pathway of HCHO at pH ≥5. Therefore, this pathway could provide a perspective on HMS, in which HCHO, in this case, as well, acts as a catalyst for PM production.

This analysis clearly demonstrates that regardless of the rate of HMHP equilibration, one-carbon molecules HCHO and HMHP can have a significant impact on PM formation in the condensed phase via formation of sulfate and HMS. The discrepancy between the experimentally determined forward and reverse rates could possibly be addressed by online analysis tracking the peroxide concentration directly over a wider pH range. We show that HCHO plays an important role in formation of PM, acting as a catalyst. The oxidative environment can greatly influence the contribution of HMS versus sulfate, as HMHP formation is favored in the presence of H$_2$O$_2$ and HCHO and can rapidly result in sulfate formation. Lastly, as shown in previous studies, HMS can contribute significantly to the sulfur and organic PM budget, especially under haze conditions (e.g., in the northern Chinese winter haze conditions, HMS can reach up to 20 μg · m$^{-3}$) (51). In such cases, the organic carbon PM contribution from the one-carbon molecule HCHO, via HMS, is estimated to be 2.2 μg · m$^{-3}$, in
accordance with the analysis in this work. In these conditions, a single chemical pathway of HCHO results in likely the most abundant single molecule, HMS, contributing to the PM carbon budget.

Comparing the GEOS-Chem simulations of this work with atmospheric models, it is observed that the implemented HMHP and ISOPOOH chemistry eliminates the underprediction of sulfate in some cases. Specifically, atmospheric models
underpredict sulfate concentrations by ~20% globally and >20% regionally (i.e., in the SE-USA by ~34%) (16–23). In the case of fast equilibrium, the pathways account for 18% of sulfate globally and 58% in the SE-USA, contributions that can explain the global underpredicted sulfate and reveal a change in the contribution of the oxidative pathways to sulfate formation. For the cases of medium and slow HMHP equilibrium, the pathways account for 7% globally and 44% in the SE-USA and 3% globally and 24% in the SE-USA, respectively. In both cases, the pathways’ contribution to sulfate formation in the SE-USA can explain the underpredicted values from previous model simulations. However, on a global scale, they contribute ~1/6 to 1/3 of the underpredicted sulfate values.

The contribution of HCHO to PM production via HMS and HMHP, regardless of the rate of equilibration, impacts air quality and the Earth’s radiative balance as well as the acidity of clouds (Fig. 4D and SI Appendix, Fig. S9). The simplest aldehyde present in the atmosphere, HCHO, via its contribution to PM sulfur and carbon, affects, in an unexpected way, both climate and human health.

Materials and Methods

Chemicals, Sample Preparation, and Sample Analysis for the Oxidation Reaction of Sulfur Dioxide with the Examined Peroxides in the Aqueous Phase. Sodium metabisulfite was purchased from Sigma-Aldrich (purity ≥99%) and used as the source of bisulfite (HSO3−) in the solutions. Sodium metabisulfite was synthesized in the laboratory following the method of Zhao et al. (35). H2O2 was purchased from Sigma-Aldrich (30 wt. % in H2O), and filtered Milli-Q water was used as a solvent. Each sample was prepared by using bisulfite and the examined peroxide. Separate experiments were conducted with H2O2 and HMHP as the dominant oxidant. For each examined reaction time, a new sample containing HSO3− and peroxide and a control sample containing only HSO3− was prepared and left to react. The reaction of sulfate (SO42−) due to oxidation by dissolved oxygen (O2) was monitored via the control sample and was subtracted from the results. Specifically, for each examined time, a control sample was prepared and analyzed prior to the analysis of the sample containing HSO3− and a peroxide. The amount of SO2 formed in the control sample was calculated and subtracted from the amount of SO2 formed in the sample of HSO3− and peroxide. The samples were analyzed at 25 °C over a pH range of 3 to 6. Reactant concentrations were in the micromolar range with reaction times of 0.5 to 3 min. The reactions were rapid relative to the sample analysis time; therefore, catalase (purchased from Sigma-Aldrich, catalase from bovine liver 2,000 to 50,000 units/mg protein) was used to quench the reaction after a given reaction time before the chromatographic analysis (12, 52).

Hydrochloric acid (purchased from Sigma-Aldrich) was used to control sample pH.

A Dionex ICS-5000+ IC system was used to analyze the samples. The AG12A guard column and the AS12A analytical column (Dionex Ionpac) were selected in order to separate sulfur-containing species (34) and quantify sulfate production. The mobile phase during the experiments was 4.5 mM:1.4 mM sodium carbonate/bicarbonate with flow rate 1.5 mL·min−1. The IC analysis was 10 min, as sulfate had a retention time of 7.5 min under the experimental parameters presented by Dovrou et al. (12). This modified chemical mechanism was used to include new isoprene chemistry (53) and the HMS chemistry described in the work of Meach and Kok (35). Reactions involving HMHP were taken from Allen et al. (58), with oxygenation rates and products from that study and formation yields from Nguyen et al. (59). Henry’s law constants for 1,4-ISOPOOH and 4,1-ISOPOOH, taken from Rivera-Rios (60), were computed as K∞ = exp(7761 · (1/T) – 14.415) M·atm−1 and K∞ = exp(7843.4 · (1/T) – 16.953) M·atm−1, respectively. Henry’s law constant for 1,4-ISOPOOH and 4,1-ISOPOOH was approximated at the average of the 1,2-ISOPOOH and 4,3-ISOPOOH values, although the small yields of the delta-ISOPOOH isomers make this value relatively unimportant. Henry’s law constant for HMHP was approximated as 3.0 · 106 M·atm−1, an average of the experimental values from Staffelbach and Kok (61).

Simulations. Six simulations were performed to examine the effect of the oxidation reactions and the HCHO pathways described in this work. Simulation 1 incorporated the modifications described in “Model parameters” without making any additional changes to SO2 chemistry and including the HMS chemistry (35). Simulation 2 included the oxidation of HSO3− by HMHP and ISOPOOH (12) considering fast equilibration: kH = 100 M−1·s−1 and kH = 0.6 M−1·s−1. Simulations 2, 3, and 4 included the same chemistry but with medium (kH = 1.3 M−1·s−1 and kH = 7.6 · 10−5·s−1) and slow (kH = 1.0 · 10−4·s−1 and kH = 6 · 10−6·s−1) equilibria, respectively. Simulations 5 and 6 were sensitivity studies, where kH = 100 M−1·s−1, kH = 7.6 · 10−5·s−1, and kH = 6 · 10−7·s−1, respectively. The equations for the HMHP Synthesis and Measurement of HMHP Equilibrium Constant. The method described by Zhao et al. (36) was used to synthesize HMHP. Formaldehyde (37 wt. % in H2O, purchased from Sigma-Aldrich) was mixed with hydrogen peroxide and left to react for at least 2 h under dark conditions at 25 °C. The concentrations of formaldehyde and hydrogen peroxide were [HCHO]0 = 34% and [H2O2]0 = 1 M, and the mixture was analyzed using 1H-NMR to verify the formation of HMHP. Four sets of HCHO and H2O2 concentrations were examined to monitor HMHP formation in a wider concentration range. The concentrations were [HCHO] = [H2O2] = 1 mM, [HCHO] = 10 mM, [HCHO] = 30 mM, and [HCHO] = [H2O2] = 80 mM. Reactant concentrations were in the millimolar range due to the detection limit of the NMR system. Bis-HMHP, a byproduct of the reaction, was also formed at ~6% concentration compared to HMHP. Formaldehyde was predominantly present as hydrate.

The concentration of HMHP was determined using the equilibrium constant of HMHP, which was obtained experimentally and calculated to be Keq = 172 ± 2 M−1, comparable to the reported equilibrium constant by Zhao et al. (36) of Keq = 164 M−1. The equilibrium constant is defined as

Keq = [HMHP]iq /[HCHO]0 ([HSO3−]0)q

By solving Eq. 4, the HMHP concentration was calculated.

In order to verify the calculated concentration, the 1H-NMR analysis was repeated using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt ([CH3]3Si[CH2]3SO3Na) as a standard compound. The equation used to calculate the HMHP concentration according to the area provided by the NMR spectrum and the standard compound was used

Cstandard = Ccompound Nstandard Icompound Nstandard [C0, I0]eq

where I is the integral area, N is the number of protons, and C is the concentration of the compound of interest.

Experimental Parameters of HMHP Equilibrium Kinetic Studies. H2O2 and HCHO solutions of the same concentration were mixed and analyzed using 1H-NMR for 37 time points in the range of 2 to 65 min to determine the rate constant, kH of HMHP formation. The reactions were rapid relative to the sample analysis time; therefore, a lower limit of the formation rate constant was estimated: 1.3 (±0.8) M−1·s−1 (SI Appendix, Fig. S10). The upper bound of the formation rate constants, for our experimental conditions considering independent determination of the formation rate constant, was estimated equal to 100 (±35) M−1·s−1.

The decomposition of HMHP was examined in a time range of 2 min to 10 d to determine the corresponding rate constant, kH. A solution of HMHP was prepared and left for ~12 h under dark conditions. HMHP was diluted in a ratio of 1:100 in order to initiate the decomposition. In addition, kH was also calculated using the equilibrium constant (Eq. 4).

H2O2(aq) + HCHO(aq) = HMHP

Different sets of HCHO and H2O2 concentrations, as described in HMHP Synthesis and Measurement of HMHP Equilibrium Constant, were examined.

Model Parameters. Version 12.2.1 of GEOS-Chem, a global chemical transport model that incorporates NASA Goddard Earth Observing System Fast Processing (GEOS-FP)-assimilated meteorological observations, was used to conduct the simulations (53–56). The model parameters for the chemistry of the oxidation of HSO3− by ISOPOOH are described in detail in the work of Dovrou et al. (12). The original chemical mechanism was modified to include new isoprene chemistry (53) and the HMS chemistry described in the work of Meach and Kok (35). Reactions involving HMHP were taken from Allen et al. (58), with oxidation rates and products from that study and formation yields from Nguyen et al. (59). Henry’s law constants for 1,4-ISOPOOH and 4,3-ISOPOOH, taken from Rivera-Rios (60), were computed as K∞ = exp(7761 · (1/T) – 14.415) M·atm−1 and K∞ = exp(7843.4 · (1/T) – 16.953) M·atm−1, respectively. Henry’s law constant for 1,4-ISOPOOH and 4,1-ISOPOOH was approximated at the average of the 1,2-ISOPOOH and 4,3-ISOPOOH values, although the small yields of the delta-ISOPOOH isomers make this value relatively unimportant. Henry’s law constant for HMHP was approximated as 3.0 · 106 M·atm−1, an average of the experimental values from Staffelbach and Kok (61).
rate constants along with the mixing ratio of H$_2$O$_2$, ISOPOOH, and O$_3$ can be measured OH concentration in remote continental and remote marine regions equal to 8. 10$^{-15}$ M and 8. 10$^{-18}$ M (64).

For the medium equilibration case rate constant of this work $k_2$ = 1.3 M$^{-1}$s$^{-1}$ and for the lower limit of the literature $k_2$ = 7.5 - 10$^{-2}$ M$^{-1}$s$^{-1}$ and Henry's law constant for H$_2$O$_2$ = 10$^4$ M atm$^{-1}$, the kinetic chain length for remote continental regions was equal to maximum value 24 and minimum value 1.5, respectively. The results show the catalytic nature of H$_2$O$_2$ for the examined reactions. Considering fast equilibrium, the kinetic chain length is in the order of 10$^4$, whereas for the slow equilibrium, the kinetic chain length is significantly low. Considering remote marine regions, the kinetic chain length increases by an order of magnitude.

When considering a closed system with liquid water content of 0.3 g m$^{-3}$ (cumulus cloud containing 800 droplets), the kinetic chain length values decrease by 40%. However, the decrease is not high, as the gas-phase mixing ratios are drawn down by the H$_2$O$_2$ partitioning to the condensed phase.

Data Availability. The GEOS-Chem modifications have been implemented and are available at https://geochem.seas.harvard.edu/. All other study data are included in the article and/or SI Appendix.

ACKNOWLEDGMENTS. We thank Jean C. Rivera-Rios and John D. Crouse for the helpful HHMP-related discussions, Scott T. Martin for useful discussions regarding sulfate in isoprene-rich regions, and Adam W. Birdall for the helpful discussions. This work was supported by the Harvard Global Institute and NSF Grant CHE-1808084. E.D. is grateful for the Onassis Foundation scholarship for Hellenes. K.H.B. and D.J.J. acknowledge support from the US Environmental Protection Agency (EPA) Science to Achieve Results Program. J.M.M. and J.L.M. acknowledge support from Assistance Agreement 83587201 awarded by the US EPA. This work has not been formally reviewed by the EPA.

Kinetic Chain Length. The kinetic chain length of the catalytic role of HCHO was calculated as

\[
\frac{\text{Kinetic chain length}}{k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})} = \frac{k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})}{k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})} \times \frac{k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})}{k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})}
\]

From GEOS-Chem, the annual average values obtained after our simulations are $[\text{HCHO}] = 3.99 \text{ ppb}, [\text{HCHO}] = 1.45 \text{ ppb},$ and $[\text{HCHO}] = 0.045 \text{ ppb}$. The $[\text{HCHO}]$ is two orders of magnitude lower compared to HCHO and H$_2$O$_2$. The kinetic rate of $\text{HCHO} \rightarrow \text{HCHO}$ is not considered.

For each equilibrium case, we calculated the kinetic chain length considering $k_2 = k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO})$ and $k_{\text{fi}}(\text{HCHO} \rightarrow \text{HCHO}) = 10^3 \text{ M}^{-1} \text{s}^{-1}$ (63). Arakaki et al. measured OH concentration in remote continental and remote marine regions equal to 8. 10$^{-15}$ M and 8. 10$^{-18}$ M (64).

1. S. Fuzzi et al., Particulate matter, air quality and climate: Lessons learned and future needs. Atmos. Chem. Phys. 15, 8217–8299 (2015).
2. H. J. Forman, C. E. Finch, A critical review of assays for hazardous components of air pollution. Free Radic. Biol. Med. 117, 202–217 (2018).
3. J. Xu et al., Macropores treated with particulate matter PM$_2.5$ induce selective neutrocytosis through glutaminase-mediated glutamate generation. J. Neurochem. 134, 315–326 (2015).
4. F. J. Kelly, J. C. Fussell, Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. 60, 504–526 (2012).
5. E. J. Bernstein, Environmental and occupational respiratory disorders Rostrum Health effects of air pollution. Environ. Occup. Resp. Dis. 117, 1116–1123 (2004).
6. T. M. Chen, J. Kokkale, S. Shofer, W. G. Kuschnr, Outdoor air pollution: Nitrogen dioxide, sulfur dioxide, and carbon monoxide health effects. Am. J. Med. Sci. 333, 249–256 (2007).
7. M. R. Miller et al., Inhaled nanoparticles accumulate at sites of vascular disease. ACS Nano 11, 4542–4552 (2017).
8. Q. Zhang et al., Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. Geophys. Res. Lett. 43, 1696–1705 (2016).
9. J. A. Lind, A. L. Lázrus, G. L. Kok, Aqueous phase oxidation of sulphur(IV) by hydrogen-peroxide, methylhydroperoxide, and peroxyacetic acid. J. Geophys. Res. 92, 4171–4177 (1987).
10. D. A. Hegg, P. V. Hobbs, Measurements of sulphate production in natural clouds. Atmos. Environ. 16, 2663–2668 (1982).
11. X. Shen et al., Aqueous phase sulphate production in clouds in eastern China. Atmos. Environ. 62, 502–511 (2012).
12. E. Dovrou, J. C. Rivera-Rios, K. H. Bates, F. N. Keutsch, Sulfate formation via cloud processing from isoprene hydroxydi-peroxides (ISOPOOH). Environ. Sci. Technol. 53, 249–259 (2019).
13. H. He et al., Mineral dust and NO$_x$ promote the conversion of SO$_2$ to sulfate in heavy pollution days. Sci. Rep. 4, 4172 (2014).
14. E. Harris et al., In-cloud sulfate addition to single particles resolved with sulfur iso- tope analysis during HCTT-2010. Atmos. Chem. Phys. 14, 4219–4235 (2014).
15. M. Chin, D. J. Jacob, G. M. Gardner, M. S. Forman-Fowler, R. A. Spivo, A global three-dimensional model of tropospheric sulfate. J. Geophys. Res. 101, 18667–18690 (1996).
16. L. A. Barrie et al., A comparison of large-scale atmospheric sulfate aerosol models (COSAM): Overview and highlights. Tellus 53B, 615–645 (2001).
17. T. F. Berglen, T. K. Berntsen, I. S. A. Isaksen, J. K. Sundet, A global model of the coupled sulfur/oxidant chemistry in the troposphere: The sulfur cycle. J. Geophys. Res. 109, 1–27 (2004).
18. D. A. Hegg, D. S. Covert, H. Jonsson, D. Khelif, C. A. Friehe, Observations of the impact of cloud processing on aerosol light-scattering efficiency. Tellus B Chem. Phys. Meteorol. 58B, 285–293 (2004).
19. A. L. Redington, C. S. Witham, M. C. Horta, Source apportionment of speciated PM$_{2.5}$ in the United Kingdom in 2008: Episodes and annual averages. Atmos. Environ. 145, 251–263 (2016).
38. S. Marklund, The simultaneous determination of bis(hydroxymethyl)-peroxide (BHMP), hydroxymethylhydroperoxide (HMP), and H$_2$O$_2$ with titanium(IV). Equilibria between the peroxides and the stabilities of HMP and BHMP at physiological conditions. Acta Chem. Scand. 25, 3517–3531 (1971).

39. X. Zhou, Y. N. Lee, Aqueous solubility and reaction kinetics of hydroxymethyl hydroperoxide. J. Phys. Chem. 96, 265–272 (1992).

40. M. R. Hoffmann, J. O. Edwards, Kinetics of the oxidation of sulfate by hydrogen peroxide in acidic solution. J. Geophys. Res. 79, 2096–2098 (1975).

41. S. M. Kunen, A. L. Lazrus, G. L. Kok, B. G. Heikes, Aqueous oxidation of SO$_2$ by hydrogen peroxide. J. Geophys. Res. 88, 3671–3674 (1983).

42. H. Hoß, H. Elias, K. J. Warnowius, Sulfur(IV) oxidation by hydrogen peroxide in aqueous suspensions of SO$_2$, Al$_2$O$_3$, TiO$_2$, and zeolite. Atmos. Environ. 25A, 1715–1717 (1991).

43. Q. Chen et al., Mass spectral characterization of submicron biogenic organic particles in the Amazon Basin. Geophys. Res. Lett. 36, 1–5 (2009).

44. T. M. Olson, L. A. Torry, M. R. Hoffmann, Kinetics of the formation of hydroxyacetaldehyde-sulfur(IV) adducts at low pH. Environ. Sci. Technol. 22, 1284–1289 (1988).

45. T. M. Olson, M. R. Hoffmann, Kinetics, mechanism, and thermodynamics of glyoxal-sulfur(IV) adduct formation. J. Phys. Chem. 92, 533–540 (1988).

46. T. M. Olson, M. R. Hoffmann, Hydroxalkylsulfonate formation: its role as a S(IV) reservoir in atmospheric water droplets. Atmos. Environ. 23, 985–997 (1989).

47. T. Salthammer, Formaldehyde in the ambient atmosphere: From an indoor pollutant to an outdoor pollutant? Angew. Chem. Int. Ed. Engl. 52, 3320–3327 (2013).

48. C. Stönnert, B. Derstroff, T. Klüpfel, J. N. Cronin, J. Williams, Glyoxal measurement with a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS): Characterization and calibration. J. Mass Spectrom. 52, 30–35 (2017).

49. M. Li, Q. Li, M. H. Nantz, X. A. Fu, Analysis of carbonyl compounds in ambient air by a microreactor approach. ACS Omega 3, 6764–6769 (2018).

50. V. Shah, D. J. Jacob, J. M. Moch, X. Wang, S. Zhai, Global modeling of cloud water acidity, precipitation acidity, and acid inputs to ecosystems. Atmos. Chem. Phys. 20, 12223–12245 (2020).

51. S. Song et al., Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze. Atmos. Chem. Phys. 19, 1357–1371 (2019).

52. Y. Tan, M. J. Perri, S. P. Seitzinger, B. J. Turpin, Effects of precursor concentration and acidic sulfate in aqueous glyoxal-OH radical oxidation and implications for secondary organic aerosol. Environ. Sci. Technol. 43, 8105–8112 (2009).

53. I. Bey, J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, Y. Liu, L. J. Mickley, and M. G. Schultz, Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. J. Geophys. Res. 106, 23073–23095 (2001).

54. R. J. Park, D. J. Jacob, B. D. Field, R. M. Yantosca, Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy. J. Geophys. Res. 109, 1–17 (2004).

55. B. Alexander et al., Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean. J. Geophys. Res. 117, 1–17 (2012).

56. K. H. Bates, D. J. Jacob, A new model mechanism for atmospheric oxidation of isoprene: Global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol. Atmos. Chem. Phys. 19, 9613–9640 (2019).

57. J. Quesada et al., Ground based gas phase measurements in Surinam during the LBA-Claire 98 experiment. J. Atmos. Chem. 39, 15–36 (2001).

58. H. M. Allen et al., Kinetics and product yields of the OH initiated oxidation of hydroxymethyl hydroperoxide. J. Phys. Chem. A 122, 6292–6302 (2018).

59. T. B. Nguyen et al., Atmospheric fates of Criegee intermediates in the ozonolysis of isoprene. Phys. Chem. Chem. Phys. 18, 10241–10254 (2016).

60. J. C. Rivera-Rios, "Atmospheric chemistry of isoprene hydroxyhydroperoxides," PhD thesis, Harvard University, Cambridge, MA (2018).

61. T. A. Staffelbach, G. L. Kok, Henry’s law constant for aqueous solutions of hydrogen peroxide and hydroxymethyl hydroperoxide. J. Geophys. Res. 98, 12713–12717 (1993).

62. A. B. Guenther et al., The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions. Geosci. Model Dev. 5, 1471–1492 (2012).

63. H. Herrmann et al., CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry. J. Atmos. Chem. 36, 231–284 (2000).

64. T. Arakaki et al., A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters. Environ. Sci. Technol. 47, 8196–8203 (2013).