Author Comment on egusphere-2025-6276

Title: Revisiting the critical role of stabilized Criegee intermediates (sCIs) in sulfuric acid formation: coupling mechanistic updates with interpretable machine learning
Authors: Yuhuan Zhu et al.
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Correspondence to: Qiang Chen (chenqqh@lzu.edu.cn)

Dear Editor and Referees,

We sincerely thank the Editor and the Referees for their careful evaluation of our manuscript and for their constructive comments and suggestions. We especially appreciate the comments concerning the updates to the MCM v3.3.1 mechanism, particularly the selection and justification of reaction rate coefficients and kinetic parameters related to stabilized Criegee intermediates (sCIs), as well as the suggestions for improving the interpretation and presentation of the machine learning results. These comments have been very helpful in guiding us to further refine the mechanism updates, improve the clarity and interpretability of the machine learning results, and strengthen the overall scientific rigor of the manuscript. Specifically, we further revised the sCI-related gas-phase mechanism, expanded the AtChem-MCM simulations, reconstructed the XGBoost-based diagnostic framework, and reinterpreted the relative roles of sCI+SO_2 pathways in H_2SO_4 formation. These revisions have changed several quantitative results compared with the discussion manuscript, but the main qualitative conclusion remains unchanged: the revised mechanism still supports an important, regime-dependent role of sCI chemistry in atmospheric H_2SO_4 formation.

We have carefully considered all comments and revised the manuscript accordingly. Below, we provide a point-by-point response to each comment. For clarity, the Referees' comments are shown in black, our responses are shown in blue, and the corresponding revisions to the manuscript are summarized in red. Because these revisions required substantial new simulations and a near-complete rewriting of several sections, we are finalizing the revised manuscript and will submit it together with a complete "final author reply to the editor" as soon as permitted by the editor. In this public author comment, we provide detailed responses to the reviewers' major concerns and summarize the main changes and new results that will be incorporated into the revised manuscript.

Note: As the revised manuscript is still being finalized, the section, figure, table, and line numbers referred to in this public author comment should be regarded as provisional.

Reviewer #1
General Comment:

The authors present the results of a study to investigate the significance of stabilized Criegee intermediate (sCI) chemistry for the production of sulfuric acid in the atmosphere using model calculations. While investigation of the role of such chemistry does warrant attention, there are a number of significant flaws in the study that should be addressed before publication can be considered.

In general, the paper is poorly written and details of the aims, methods, and results are unclear. The authors acknowledge the use of ChatGPT “to proofread and refine the English expression of the manuscript”, but the result is a manuscript that lacks specific detail relating to the study undertaken. The aims and use of the machine learning method and the analysis of the data needs to be explained much more clearly, with the descriptions specifically linked to the study in question. The descriptions given are too generic to be useful. It is not clear what analysis has been performed and what is being assessed.

The manuscript refers to uncertainties in the mechanisms used in models, Examples or details of the uncertainties should be given. Do the main uncertainties relate to rate coefficients, product yields, or missing reactions in the mechanisms? Do the results of the study help to clarify what we need to know better in order to better understand the production of sulfuric acid in the atmosphere?

Importantly, the study described in the manuscript is an incomplete assessment of sCI chemistry. The authors compare the results from model calculations using the MCM v3.3.1 with those from model calculations using an updated mechanism with rate coefficient recommendations taken from Cox et al. which was published in 2020. However, there have been a number of studies since the Cox et al. recommendation that should be considered. The authors note the potential impact of temperature, but all calculations have been performed using rate coefficients obtained at ~298 K. Measurements of the temperature and pressure dependence of sCI reactions with SO2 and water have been reported in the literature since 2020 and these should be considered in the study to enable a more complete assessment. The study also neglects Z-isomers for sCIs where E/Z isomers are possible, and studies have shown that sCI reactivity is very different for E and Z isomers.

In addition, the study assumes that all sCI reactions with SO2 produce SO3 and thus lead to production of sulfuric acid. The reaction of the sCI CH2OO with SO2 has been shown to produce SO3, but this is not the case for other sCIs at atmospheric pressure and there is evidence that larger sCIs may produce secondary ozonides at atmospheric pressure rather than SO3. The impact of the assumption that all sCI reactions with SO2 produce SO3 and lead to sulfuric acid production should be investigated.

Author Response:

We sincerely thank the reviewer for the thorough and highly constructive evaluation of our manuscript. The comments have substantially helped us improve the clarity, rigor, and completeness of our work. Below we provide a detailed, point-by-point response organized into two parts: (1) Reply to Comments on Manuscript Writing, and (2) Reply to Comments on Mechanism Revision.

(1) Reply to Comments on Manuscript writing:

We sincerely apologize for the lack of clarity in the original manuscript. We have thoroughly revised the manuscript to address the issues of unclear research objectives, vague methodology, and insufficient logical coherence among the three components of the study.

Regarding research objectives and logical framework:

Since the laboratory discovery that sCIs can react with SO_2 in the gas phase, extensive experimental and theoretical studies have been conducted to elucidate the relevant reaction pathways, and field observations together with atmospheric modeling studies have confirmed and quantified the important contribution of sCIs to gas-phase SO_2 oxidation. From the perspective of atmospheric pollution science, "the oxidation of SO_2 by sCIs to produce H_2SO_4" can be framed as a problem of "secondary pollutant formation governed by atmospheric oxidative capacity". The current consensus for addressing such secondary pollution issues is to establish quantitative relationships between precursors and secondary pollutants, and to elucidate the roles of key intermediate products (e.g., free radicals) within these relationships, thereby enabling a comprehensive understanding of pollution formation from both mechanistic and control perspectives. Existing studies on the contribution of sCIs to atmospheric H_2SO_4 or SO_4^{2-} aerosol formation have primarily focused on quantifying their contributions in specific regions and identifying key precursor alkene species through their production pathways. While these studies are highly valuable for characterizing sCI contributions and identifying the dominant alkene species in specific locations and time periods, their conclusions are not necessarily transferable to other regions, due to the site-specific nature of environmental conditions and precursor compositions. Consequently, a systematic understanding of the key drivers governing sCI contributions remains lacking. Furthermore, the production and loss processes of OH and sCIs are deeply coupled. This coupling implies that when evaluating the drivers controlling the sCI+SO_2 pathway contribution, one cannot ignore the concomitant effects on the OH+SO_2 pathway and the overall SO_2 oxidation rate. In particular, how the dominant controlling factors and the direction of their influence change as the gas-phase SO_2 oxidation regime transitions from being strictly OH-dominated to being co-driven by OH and sCIs remains an unresolved question.

Building on these motivations, our study presents a systematic assessment of the role of sCIs in atmospheric SO_2 gas-phase oxidation, structured around three progressive components:

Section 3.1 – Diagnosing key drivers of sCI-mediated SO_2 oxidation: We developed an interpretable machine-learning framework (XGBoost-SHAP) to elucidate the dependence of the sCI+SO_2 reaction rate on key controlling variables, including O_3, specific alkene species, and major competing sinks (H_2O, $(H_2O)_2$, and NO_x). Particular attention was given to quantifying the distinct effects of different alkene precursors and to examining how updates to the CI mechanism modify their relative importance.

Section 3.2 – Surrogate modeling of sCI contributions and regime analysis: Building on the diagnostic results in Section 3.1, we designed simulation scenarios covering perturbations to all control factors. An atmospheric box model coupled with the updated mechanism (MCM v3.3.1g) was then used to generate a comprehensive dataset of sCI contributions under diverse environmental conditions, from which an XGBoost-based surrogate model was constructed. Sobol sensitivity analysis and Partial Dependence Plots (PDPs) were integrated to quantify the magnitude and direction of each factor's influence. By stratifying the dataset based on the median sCI contribution, we further examined how the sensitivity of the total SO_2 oxidation rate differs between high- and low-sCI regimes, and identified the key reaction pathways responsible for these contrasts through mechanistic budget analysis.

Section 3.3 – Validation against ambient observations: The predictive performance of the surrogate model was evaluated by comparing its predictions with box model simulations for an actual ambient case. Additionally, direct XGBoost modeling of hourly observational data was performed to evaluate the sensitivity of SO_4^{2-} to various factors under different sCI contribution levels, thereby assessing whether the regime-dependent sensitivity relationships predicted by our model framework are consistent with ambient observations.

Regarding the Methods section:

In the revised manuscript, we have substantially expanded and reorganized Section 2 so that each method is explicitly linked to the corresponding scientific question addressed in this study.

In Section 2.1, “Updating the sCI gas-phase chemical mechanism,” we have added a more detailed description of the mechanism revision. In particular, we now describe how the concentration of water dimers was calculated using a temperature-dependent equilibrium constant and the square of the water monomer concentration, rather than prescribing it as a fixed fraction of water vapor. We also provide more detailed information on the updated kinetic parameters and branching treatments used in the revised mechanism, including the implementation of temperature-dependent rate coefficients for relevant sCI+H_2O/$(H_2O)_2$ reactions.

In Section 2.2, “Model setup and observation data,” we have expanded the description of the AtChem simulations and chemical diagnostics. The revised text now distinguishes the different types of box-model simulations used in the study, explains how the rates of SO_2 oxidation by sCIs and OH were calculated, and clarifies how the observational dataset was used in different parts of the analysis. For the observation data, we no longer simply list the measured variables; instead, we now explain their specific roles in constraining the box model, constructing observationally based machine-learning models, and evaluating whether the sensitivity relationships inferred from the box-model surrogate are reflected in the real atmosphere.

We have also added a new Section 2.3, “Machine learning surrogate and interpretation framework,” to clearly describe the machine-learning methods used in the study. This section explains the purpose of each model, the target variable, the input features, the training dataset, and the interpretation method. In this way, the machine-learning analysis is now directly connected to the scientific objectives of the study, rather than being presented as a generic data-driven method.

Compared with the original manuscript, we have also substantially increased the size and representativeness of the modeling datasets. For Section 3.1, the number of box-model simulations used to train the XGBoost-SHAP model was increased from 768 to 3898. For Section 3.2, the number of simulation cases was increased from 243 to 1352. In this section, we also added two additional explanatory variables: ARI, representing the alkene-specific sCI production potential, and RH, representing the influence of atmospheric water vapor and water dimers on sCI loss. These additions improve the connection between Sections 3.1 and 3.2 and allow the surrogate model to better capture both sCI production and competitive loss processes. In addition, we replaced the ANOVA-based interpretation with Sobol sensitivity analysis, which is more appropriate for quantifying the contribution of individual variables and their interactions to the variance of the model output. In addition, we added a new analysis in Section 3.2 to examine whether the sensitivity of the total gas-phase SO_2 oxidation rate differs between conditions with relatively high and low sCIs contributions. Specifically, the simulation dataset was divided into high- and low-μ_{sCIs} subsets according to the median value of μ_{sCIs}. We then evaluated and compared the sensitivity relationships between the explanatory variables and the total SO_2 oxidation rate in these two subsets. This analysis allows us to assess how the relative importance of the sCI pathway modifies the response of overall SO_2 oxidation to changes in O_3, alkenes, NO_x, RH, and other environmental variables. Therefore, the revised Section 3.2 now more directly addresses the question of how the transition from an OH-dominated regime to a regime co-influenced by OH and sCIs changes the controlling factors of sulfuric acid production. These additions improve the connection between Sections 3.2 and 3.3. For Section 3.3, we replaced the Random Forest model used in the original manuscript with XGBoost to maintain methodological consistency across the study. The observational period used to evaluate the sensitivity relationships was also extended from 18 days, 1-18 July 2021, to 45 days, 1 June-15 July 2021, thereby improving the robustness of the observational analysis.

Regarding the Results and Discussion:

we have substantially revised Section 3 because the revised treatment of key kinetic processes changed the box-model simulations. Specifically, the rate coefficients for relevant sCI reactions with SO_2 and $H_2O/(H_2O)_2$ were updated from fixed 298 K values to temperature-dependent expressions where recommended, and the water dimer concentration was recalculated using the temperature-dependent equilibrium constant and the square of the water monomer concentration. Together with the increased number of simulations, the expanded feature set, the longer observational period, and the replacement of the interpretation method in Section 3.2, these changes led to updated results throughout the manuscript.

In revising Section 3, we have also strengthened the interpretation of the results. Rather than only reporting numerical rankings from SHAP values, Sobol indices, or PDPs, the revised text now focuses on the physical and chemical meaning behind these diagnostics. In the original manuscript, we discussed the impact of the mechanism revision in both Sections 3.1 and 3.3 and emphasized these comparisons in the Abstract. Our original intention was to demonstrate the necessity and reasonableness of the mechanism revision by showing the magnitude of the resulting changes. However, this presentation blurred the focus of the study and may have given the impression that the manuscript was primarily an assessment of the completeness of sCI chemistry. In the revised manuscript, we have therefore refocused the discussion. The comparison between the original and updated mechanisms is now retained only in Section 3.1, where it serves a specific and focused purpose. This analysis is used to quantify how the relative importance of individual alkene precursors to $L_{SO2,sCIs}$ changes after updating the sCI mechanism, and to identify which revised kinetic processes are mainly responsible for these changes. The results indicate that one of the dominant sources of uncertainty in MCM v3.3.1 lies in the rate coefficients that govern the competition between the sCI + SO_2 pathway and the major water sinks (H_2O and $(H_2O)_2$). This revised treatment keeps the mechanism comparison directly connected to the main research question: which chemical processes control the ability of sCIs to oxidize SO_2 and contribute to sulfuric acid formation? It also provides practical guidance for future mechanism development, particularly for deciding which CI kinetic processes should be prioritized when incorporating CI chemistry into reduced chemical mechanisms used in three-dimensional atmospheric models. At the same time, we have removed unnecessary mechanism-comparison statements from Section 3.3 and the Abstract, so that the later sections focus more clearly on the environmental conditions under which sCIs can effectively compete with OH and on whether the inferred sensitivity relationships are supported by ambient observations.

(2) Reply to Comments on Mechanism Revision:

Selection of Basis for Mechanism Revision:

We appreciate the reviewer's concern and would like to clarify our rationale for selecting (Cox et al., 2020) as the primary basis for mechanism revision. Our study is not intended as a comprehensive re-evaluation of sCI chemistry per se, but rather investigates the importance of sCIs in gas-phase SO_2 oxidation and identifies the key controlling factors. For this purpose, the mechanism update serves as a prerequisite to minimize the propagation of kinetic uncertainties into our conclusions. Our selection of the IUPAC Task Group evaluation(Cox et al., 2020) as the revision basis was guided by the following considerations:

- Scientific consensus and reliability: The IUPAC evaluation critically assesses and synthesizes multiple experimental and theoretical studies to provide recommended kinetic parameters that have undergone extensive peer scrutiny. The description in the original manuscript was imprecise: we stated that the mechanism was updated using “the latest research findings”. This has now been accurately rephrased as “the most recent systematically evaluated kinetic data by IUPAC”.
- Benchmarking against MCM v3.3.1: The MCM v3.3.1 is one of the mainstream mechanisms widely coupled in atmospheric models. Rate coefficients for reactions of O_3 with alkenes within MCM v3.3.1 were previously reviewed by (Saunders et al., 2003), (Jenkin et al., 1997) and (Jenkin et al., 2015) with recommendations. Adopting the 2020 IUPAC evaluation — which represents the same category of authoritative, community-vetted assessment — provides robust basis for updating this mechanism while maintaining the credibility that the international modeling community widely accepts.
- Practical requirements for mechanism implementation: Mechanisms intended for integration into computational models require precise functional expressions. For example, if temperature dependence is to be considered, Arrhenius expressions with well-defined parameters are needed. The IUPAC evaluation provides such expressions where available. In contrast, some frontier studies, while scientifically valuable, do not report explicit kinetic parameters and therefore cannot be directly

integrated into the MCM v3.3.1 mechanism.

Compared with the original MCM v3.3.1 parameters, the IUPAC-evaluated values reveal order-of-magnitude differences in sCI bimolecular reaction rate coefficients, and the original mechanism entirely omits the unimolecular decomposition of sCIs, reactions with $(H_2O)_2$, and the distinct reactivities of different sCI stereoisomers. These fundamental deficiencies fully justify the mechanism revision. Because the IUPAC-evaluated data sufficiently addresses these critical gaps, we opted for a more conservative approach: rather than incorporating newer studies published post-2020, we strictly adopted these comprehensively evaluated recommendations.

Temperature and Pressure Dependence:

We acknowledge that the original manuscript insufficiently addressed the temperature dependence of sCI reactions. In the revised manuscript, we have made the following changes:

- Temperature dependence of $k_{(sCIs+H2O)}$ and $k_{(sCIs+(H2O)2)}$: The IUPAC evaluation provides both 298 K preferred values and temperature-dependent expressions for the reactions of C_1-C_4 sCIs with H_2O and $(H_2O)_2$. In the original manuscript, we adopted the 298 K values for consistency with the sCI yields and other bimolecular rate coefficients, which are predominantly derived from direct kinetic studies at 298 K. However, we recognize that the reactions of sCIs with $H_2O/(H_2O)_2$ exhibit significant negative temperature dependence (e.g., the $CH_2OO + (H_2O)_2$ reaction), whereas the sCIs+SO_2 reactions show weaker temperature sensitivity. This differential temperature dependence means that using only 298 K values does not adequately capture the competitive balance between these pathways. In the revised mechanism (MCM v3.3.1g), we have updated all $k_{(sCIs+H2O)}$ and $k_{(sCIs+(H2O)2)}$ for C_1-C_4 sCIs to their recommended temperature-dependent expressions $k(T)$.
- Pressure dependence of $k_{(sCIs+SO2)}$: The IUPAC evaluation indicates that for C_1-C_4 sCIs, there is no significant pressure dependence for reactions with SO_2 within the range relevant to atmospheric applications.

E/Z Isomer Consideration:

We sincerely apologize that our treatment of E/Z isomers was not clearly communicated in the original manuscript. In fact, our mechanism update accounts for the distinct reactivities of E- and Z-isomers, but this was not adequately described. We have added explicit descriptions in Section 2.1 and the Supplementary Material (Table S1) of the revised manuscript. The key points are as follows:

Among the sCIs covered in our revision, CH_3CHOO (from propene, cis/trans-but-2-ene ozonolysis), C_2H_5CHOO(from but-1-ene ozonolysis) and the C_4 intermediates from isoprene ozonolysis exist as E- and Z-conformers. E- and Z-conformers exhibit markedly different reactivities, particularly in their propensity for unimolecular decomposition versus bimolecular reactions:

- For CH_3CHOO: Z-$[CH_3CHOO]^*$ and Z-CH_3CHOO undergo extremely rapid unimolecular decomposition via the well-established 1,4 H-shift isomerization mechanism, producing vinyl hydroperoxide intermediates that decompose to OH. This rapid decomposition means that bimolecular reactions of Z-CH_3CHOO with SO_2, H_2O, and other species are kinetically uncompetitive under atmospheric conditions. In our revised mechanism, the unimolecular decomposition of Z-CH_3CHOO is combined with the prompt decomposition of excited CIs(Z-[CH_3CHOO]*), with the branching ratio determined by the recommended OH yield. The sCI yield and bimolecular reaction rate coefficients listed for CH_3CHOO in Tables 1 and 2 specifically refer to E-CH_3CHOO, which is the conformer that participates in bimolecular chemistry with SO_2 and H_2O/$(H_2O)_2$. A small contribution from E-[CH_3CHOO]* unimolecular decomposition is also accounted for and deducted from the total sCI yield.

- For C_2H_5CHOO (from but-1-ene): Similarly, Z-C_2H_5CHOO is assumed to undergo primarily unimolecular decomposition, with its contribution reflected in the OH yield, and the reported sCI yield represents predominantly the E-conformer.
- For C_4 sCIs from isoprene: Z-$(CH=CH_2)(CH_3)COO$ and Z-$(C(CH_3)=CH_2)CHOO$ undergo rapid 1,5 ring-closure reactions with rate coefficients of ~2,800 s^{-1} and ~14,000 s^{-1}, respectively. Their unimolecular decomposition processes are similarly accounted for in the OH yield, and their branching ratios are deducted from the total sCI yields. Only the E-conformers are treated as participating in bimolecular chemistry.

In summary: The sCI yields(CH_3CHOO, C_2H_5CHOO,and C_4 sCIs) reported in Table 2 of our revised manuscript have been adjusted to account for the rapid decomposition of Z-isomers, and thus represent only the E-isomers that are available for bimolecular reactions. This is now stated explicitly in the table caption and in Section 2.1: “In MCM v3.3.1g, the species CH_3CHOO and C_2H_5CHOO specifically denote the E-isomers. The unimolecular decomposition of Z-isomer sCIs is integrated with the prompt decomposition of excited CIs; consequently, their branching ratios are deducted from the total sCI yields.”

SO_3 Yield from sCI + SO_2 Reactions:

We thank the reviewer for raising this important point. In the revised manuscript, we have added an explicit discussion of this assumption and its implications.

Following the IUPAC evaluation, the reaction of small sCIs (C_1-C_4) with SO_2 proceeds via the barrierless formation of a chemically activated secondary ozonide (SOZ) intermediate. For CH_2OO+SO_2, the dominant product is SO_3 (+ HCHO), which is well-established by experimental evidence. There is evidence that larger sCIs may favor secondary ozonide formation at atmospheric pressure. However, the product branching ratios for sCIs + SO_2 reactions remain poorly constrained experimentally. In our mechanism, we follow the IUPAC recommendation that, in the absence of quantitative experimental branching ratio data for the primary (SO_3-forming) and secondary (SOZ-forming) channels, the sCI + SO_2 reaction is treated as predominantly producing SO_3 (and the corresponding carbonyl compound).

We now explicitly acknowledge this as an assumption in Section 2.1 of the revised manuscript and discuss its implications: By assuming 100% SO_3 yield, our calculated sCI contributions to H_2SO_4 production represent an upper bound. If a fraction of sCI + SO_2 reactions produces SOZs instead of SO_3, the actual contribution to H2SO4 would be proportionally reduced. It should be noted, however, that the SO_3 yield essentially acts as a linear scaling factor on our results: while it may overestimate the absolute

H_2SO_4 production rate via the sCI pathway as well as the sCI fractional contribution, this assumption does not alter the functional relationships between the controlling factors and the sCI contribution, nor does it affect our identification of the conditions under which their contribution becomes significant. Consequently, these core insights remain qualitatively robust despite uncertainties in the exact SO_3 branching ratio.

Specific Comments

Comment 1:

line 15: sCIs are not free radicals and ‘oxidated’ should be changed to ‘capable of oxidising’.

Response 1:

We thank the reviewer for this clarification and for correcting our terminology. sCIs are reactive zwitterionic intermediates ($R_1R_2C{=}O^+\text{-}O^-$), rather than traditional free radicals. We have replaced the term ‘oxidated’ with ‘capable of oxidising’ to ensure accurate expression, and similar inaccuracies have been carefully reviewed and corrected throughout the manuscript.

Changes in Manuscript:

Modified version: “...stabilized Criegee intermediates (sCIs) are recognized as important atmospheric intermediates capable of oxidising sulfur dioxide (SO_2)…”

Comment 2

Line 17: No apostrophe in sCIs.

Response 2

We thank the reviewer for catching this error. The apostrophe has been removed from all instances of "sCIs" throughout the manuscript.

Changes in Manuscript:

The apostrophe has been removed from all occurrences of “sCIs” throughout the revised manuscript.

Comment 3

Line 18: Clarify the meaning of the factor reported.

Response 3

We thank the reviewer for this helpful comment. In the original manuscript, the reported factor referred to the ratio of the mean absolute SHAP values, mean(|SHAP|), obtained from the XGBoost models trained with MCM v3.3.1g and MCM v3.3.1, respectively. Thus, this 1.97- to 10.75-fold increase demonstrates that the updated mechanism significantly amplifies the importance of these precursors in predicting $L_{SO2,sCIs}$. Because the Abstract has been substantially rewritten, this potentially confusing statement has been removed from the Abstract.

Changes in Manuscript:

This sentence has been removed from the Abstract.

Comment 4

Line 32: ‘Fine particles … are …’ rather than ‘fine particles … is’, and ‘its’ to ‘their’.

Response 4

We thank the reviewer for pointing out these grammatical errors. We have thoroughly checked the manuscript for similar expression inaccuracies.

Changes in Manuscript:

Corrected to "Fine particles ... are ..." and "their".

Comment 5

Line 37: Which of the formation routes described is the primary route?

Response 5

We thank the reviewer for raising this important question. The primary formation route of sulfate depends on atmospheric conditions. During severe haze events, high humidity and aerosol loadings strongly promote aqueous-phase and heterogeneous SO_2 oxidation, making these multiphase processes the dominant pathways for secondary sulfate formation. As the atmosphere becomes progressively cleaner, conditions favorable for aqueous-phase and heterogeneous sulfate formation weaken, and the relative importance of the gas-phase pathway (i.e., oxidation of SO_2 by OH and sCIs) is expected to increase significantly. Furthermore, the gas-phase pathway remains fundamentally important regardless of the dominant sulfate formation pathway because its end product, sulfuric acid (H_2SO_4), is a key precursor for new particle formation (NPF). NPF governs aerosol number concentrations and is frequently observed even in highly polluted urban environments with strong condensation sinks. We have clarified this dependence on atmospheric conditions and the growing importance of the gas-phase route in the revised manuscript.

Changes in Manuscript:

The relevant paragraph in the Introduction has been revised

Comment 6

Line 45: The reference to ‘anon’ should be changed to reference the WHO

Response 6

We thank the reviewer for pointing out these citation errors. We have corrected. We thank the reviewer for pointing out this citation issue. The reference to “anon” has been corrected to the appropriate (WHO, 2021) citation in the revised manuscript and similar citation issues have been carefully checked and corrected throughout the manuscript.

Changes in Manuscript:

The citation has been corrected to (WHO, 2021), and the reference list has been updated accordingly.

Comment 7

Line 50: The reference to ‘anon’ should be changed to Mauldin et al. 2012

Response 7

We thank the reviewer for pointing out these citation errors. We have corrected. We thank the reviewer for pointing out this citation issue. The reference to “anon” has been corrected to Mauldin et al. and similar citation issues have been carefully checked and corrected throughout the manuscript.

Changes in Manuscript:

The citation has been corrected to (Mauldin et al., 2012), and the reference list has been updated accordingly.

Comment 8

Line 62: There are earlier references to the production of Criegee intermediates.

Response 8

We sincerely thank the reviewer for pointing out this historical detail. We have updated the citation to include the pioneering work by Criegee (1949), which first proposed the zwitterionic mechanism and the production of Criegee intermediates. The reference list has also been updated accordingly.

Changes in Manuscript:

The Introduction has been revised to include the suggested references.

Comment 9

Line 69: Clarify the description of gas phase sulfate ions.

Response 9

We thank the reviewer for catching this imprecise expression. We intended to describe the gas-phase formation pathway of sulfate (i.e., the gas-phase oxidation of SO_2 to H_2SO_4, which subsequently contributes to particulate sulfate), rather than implying the existence of SO_4^{2-} ions in the gas phase.

Changes in Manuscript:

The Introduction has been substantially revised, and the original sentence containing this expression has been removed.

Comment 10

Line 70: Ozone is not formed through direct reactions between VOCs and NOx. The statement should be clarified.

Response 10

We thank the reviewer for catching this imprecise expression. O_3 is formed through the combination of O_2 and O generated from NO_2 photolysis. This sequence is continuously driven by the complex photochemical cycles of its precursors, VOCs and NO_x.

Changes in Manuscript:

The Introduction has been substantially revised, and the original sentence containing this expression has been removed.

Comment 11

Line 101: Subscript in O3.

Response 11

We thank the reviewer for pointing out this formatting issue. We have corrected the O_3 notation and have carefully checked and revised the chemical notation throughout the manuscript.

Changes in Manuscript:

All instances have been checked and corrected.

Comment 12

Line 106: Clarify the meaning of 'bimolecular water'. Should this refer to water dimers, (H2O)2? If the statement is intended to refer to water dimers the following statement regarding the relative concentration to H2O (monomers) is incorrect. How were water dimer concentrations calculated?

Response 12

We thank the reviewer for pointing out these inaccuracies. First, we clarify that the term "bimolecular water" was indeed intended to refer to the water dimer, $(H_2O)_2$. We have corrected this non-standard terminology throughout the manuscript. Second, we acknowledge the writing error regarding the concentration ratio in the original manuscript. The intended value was 10^{-4} (not 10^4), which reflects the typical atmospheric relative abundance of water dimers to monomers(10^3~10^4) (Tretyakov et al., 2014).

However, addressing the valid question regarding the actual calculation of water dimer concentrations, treating this ratio as a constant introduces significant uncertainty. The actual dimer concentration scales quadratically with water monomer abundance and is highly temperature-dependent. To accurately represent the kinetics of the sCIs + $(H_2O)_2$ reaction in the box model, we employed a pre-equilibrium approximation. The dimer is assumed to be in steady-state equilibrium with the monomer. We rigorously parameterized the temperature-dependent equilibrium constant (K_{eq}^{D}) using high-accuracy thermochemical data from the Active Thermochemical Tables (ATcT) (Ruscic, 2013), allowing us to calculate an apparent third-order rate constant (k_{eff} = $k_{sCIs+(H2O)2} \cdot K_{eq}^{D}$). The complete mathematical derivation and parameter details have now been explicitly added to Section 2.1.

Changes in Manuscript:

The term "bimolecular water" has been replaced by "water dimer, $(H_2O)_2$".

Modified version:

To accurately represent sCIs+$(H_2O)_2$ in MCM v3.3.1 within the box model, a pre-equilibrium approximation was employed. Given the rapid exchange between water monomers and dimers, the concentration of $(H_2O)_2$ is assumed to be in steady-state equilibrium with the water monomer:

$$K_{eq}^{D} = \frac{[(H_2O)_2]}{[H_2O]^2}$$

where K_{eq}^{D} is the temperature-dependent equilibrium constant(Scribano et al., 2006). The reaction of sCIs with water dimers was parameterised using an apparent third-order rate constant(Lade et al., 2024b), k_{eff}, such that the total reaction rate (r) is expressed as:

$$r = k_b[sCI][(H_2O)_2] = k_b \times K_{eq}^{D}[sCI][H_2O]^2 = k_{eff}[sCI][H_2O]^2$$

The apparent rate constant is defined as the product of the bimolecular rate constant for the sCIs+$(H_2O)_2$ reaction (k_b) and the equilibrium constant (K_{eq}^{D}). To ensure the highest thermodynamic accuracy in calculating K_{eq}^{D}, thermochemical data were retrieved from the Active Thermochemical Tables (ATcT). Standard Gibbs free energies of formation

($\Delta_r G_T^\circ$) for both the water monomer and the water dimer were extracted from Table 1 and Table 3 of (Ruscic, 2013). These discrete data points were then used to calculate the reaction Gibbs free energy ($\Delta_r G_T^\circ$) over the temperature range of 200-360 K, which covers the typical conditions of the troposphere. The temperature dependence of K_{eq}^D was then obtained via a linear regression of K_{eq}^D against $\frac{1}{T}$, resulting in the following Arrhenius-type parameterisation used in the model:

$$K_{eq}^D(T) = Aexp\left(\frac{B}{T}\right)$$

where the coefficients A and B represent the intercept and slope derived from the fitting procedure respectively, with A = 1.15×10^{-23} $cm^3 \cdot molecule^{-1}$ and B = 1549.32 K.

Comment 13

Line 110: Some of the rate coefficients given are for unimolecular processes.

Response 13

We thank the reviewer for pointing out this inaccuracy. To accurately reflect that the table includes both unimolecular and bimolecular reactions, the title has been revised to refer generally to the loss processes of sCIs.

Changes in Manuscript:

The title of Table 1 has been revised to:

"Table 1. Comparison of rate coefficients for sCIs loss processes before and after the update."

Comment 14

Line 112: No rate coefficients are given in the table.

Response 14

We thank the reviewer for catching this omission and inaccuracy. We have added the missing rate coefficients for the alkene ozonolysis reactions (O_3 + alkenes) to Table 2. Accordingly, the table title has been revised to accurately reflect that it now presents both the kinetic rate coefficients and the corresponding OH/sCIs yields ($Y_{i,OH}$ and $Y_{i,sCIs}$).

Changes in Manuscript:

Tables 1 and 2 have been revised.

Comment 15

Line 130: 'Elements … were determined …' should be changed to 'elemental analysis … was performed …', but it's not clear that the elemental analysis is relevant.

Response 15

We thank the reviewer for pointing out the phrasing issue and for prompting us to clarify the relevance of these measurements. We have revised the text to "Elemental analysis was performed," as suggested. To avoid confusion, we have removed references to elements that were not used in the model, except for iron (Fe). Fe was retained because it is an important variable in this study and was included as a key input feature in the XGBoost model. As discussed in Section 3.3, the SHAP values of Fe were used as an indicator to assess the role of transition-metal-catalyzed aqueous-phase reactions in sulfate formation. This has now been clarified in the revised methodology section.

Changes in Manuscript:

Modified version: "Hourly observations from the Wuhai City Atmospheric Environment Super Monitoring Station were used for the observation-constrained simulations and observation-based machine learning analysis. The variables used in this study include trace gases ($PM_{2.5}$, CO, SO_2, NO_2, O_3, VOCs), meteorological parameters (WS, T, P, RH), photolysis frequencies, inorganic ions including SO_4^{2-} and NO_3^-, and Fe as an indicator of transition-metal-related aqueous-phase processes.". Variables measured at the station but not used in the present analysis have been removed from the revised description to avoid ambiguity.

Comment 16

Line 186 (and elsewhere): Check the units given for rates, is 'mole' rather than 'molecule' correct?

Response 16

We thank the reviewer for catching this unit error. In the manuscript, the intended unit was molecule (e.g., $\text{molecule}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$), but we incorrectly used "mole" as a shorthand for "molecule". We have now systematically checked and corrected all corresponding units throughout the manuscript and figures.

Changes in Manuscript:

All units corrected throughout.

Comment 17

Line 200: Subscripts in CH3CHOO and CH2OO.

Response 17

We thank the reviewer for pointing out this formatting issue. We have corrected the CH_3CHOO/CH_2OO notation and have carefully checked and revised the chemical notation throughout the manuscript.

Changes in Manuscript:

All chemical formulae have been checked and corrected for proper subscripts.

Comment 18

Line 206 (and elsewhere): The text in the figures is too small to read.

Response 18

We thank the reviewer for pointing out this issue. We have increased the font size and improved the resolution of all figures in the manuscript to enhance readability.

Changes in Manuscript:

All figures revised with improved readability.

Comment 19

Line 237: Why were these values chosen?

Response 19

We thank the reviewer for this helpful comment. In the revised manuscript, the factor levels are no longer defined as fixed percentages (e.g., 10%, 100%, and 190% of the baseline) for all variables. Instead, the range of each variable was determined separately based on its three-year hourly observational distribution in the Wuhai region. Specifically, the lower and upper bounds were selected with reference to the 5th and 95th percentiles, so that the design could cover a wide range of pollution conditions while avoiding unrealistic extreme scenarios. We have clarified this rationale in the revised manuscript and added the corresponding variable ranges in the figure showing the values at the normalized levels of 0, 0.5, and 1.

Changes in Manuscript:

Justification for the scenario design added in Section 2 or 3.2.

Comment 20

Line 321: Subscript in O3.

Response 20

We thank the reviewer for pointing out this formatting issue. We have corrected the O_3 notation and have carefully checked and revised the chemical notation throughout the manuscript.

Changes in Manuscript:

The O_3 notation has been corrected throughout the revised manuscript.

Comment 21

Line 328: It would be helpful to provide a summary of the input data. As a minimum, the mean, standard deviation, and median values should be reported for each input parameter.

Response 21

We thank the reviewer for this helpful suggestion. We have added a summary table reporting the mean, median, and standard deviation of the major constrained variables during the simulation period (2021.06.01-2021.07.15). We also added a time-series figure to show the temporal evolution of the major constrained species and meteorological parameters.

Changes in Manuscript:

A summary table and a time-series figure have been added to the Supplement.

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