

Response to Reviewer 1

We greatly appreciate the time and effort the reviewer spent reviewing our manuscript. The comments are thoughtful and helpful in improving the quality of our paper. Below, we make a point-by-point response to these comments. The response to the reviewer is structured in the following sequence: (1) Comments from the reviewer in black color; (2) Our response in blue color; (3) Our changes in the revised manuscript in red color.

The authors present a study of styrene ozonolysis in the presence of ammonia, and report the suppression of SOA formation in the presence of ammonia and observations of species that indicate reactions of stabilised Criegee intermediates with ammonia.

The authors present some interesting results, but the manuscript is generally lacking in detail. At present the manuscript does little more than present observations. Real-time measurements are referred to, which indicate the potential to determine reaction kinetics, but none are reported. It would be beneficial to at least report timescales/kinetics for production of the species observed and, ideally, estimated yields that could be used in atmospheric models. The manuscript should be significantly improved prior to publication to include further details of the experiments and more comprehensive description of the analysis and modelling of results.

We thank the reviewer for providing valuable suggestions to enhance the quality of our paper. Based on the reviewer's valuable suggestions, we have provided more experimental details, conditions, and kinetic results in our revised manuscript. Specifically, we have moved the experimental details from the *supplementary material* to the *Materials and methods* section of the manuscript. In addition, we have provided point-to-point responses to the corresponding questions in the *Other Comments*. Furthermore, we provided a more detailed description of the analysis and modeling of the results, particularly in the determination of the reaction kinetics. The specific modifications are as follows.

Pages 9, Lines 177-196: Accurate quantification of C₇H₉O₂N and its degradation

products typically requires the use of standard gases to establish a calibration coefficient between mass spectrometry signal abundance and actual concentration. However, due to the current unavailability of standard materials for C₇H₉O₂N and its products, direct quantification is challenging. Nevertheless, a previous study (Ma et al., 2018) estimated the rate constant for the reaction of C₇-SCI with NH₃ forming C₇H₉O₂N ($1.65 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) via quantum chemical calculations. Based on this rate constant, we added the corresponding reaction into the MCM mechanism. Under Exp.10 experimental conditions, the simulated maximum concentration of C₇H₉O₂N after 50 minutes of reaction was 28 ppb. Since the decomposition of C₇H₉O₂N was not considered in the simulation, this concentration actually represents the total concentration of C₇H₉O₂N and its two decomposition products. To further distinguish the specific concentrations of C₇H₉O₂N and its two decomposition products, it needs to determine their decomposition rate constants. Fortunately, using online GAIS-Orbitrap MS monitoring data on abundance-time evolution, we can obtain the relative proportions among the three species: C₇H₉O₂N (m/z 140): C₇H₇N (m/z 106): C₇H₇ON (m/z 122). Based on this ratio, we introduced two decomposition reactions into the MCM mechanism and adjusted their rate constants so that the simulated concentration ratios matched the experimentally observed values. The corresponding concentrations of C₇H₉O₂N (m/z 140), C₇H₇N (m/z 106) and C₇H₇ON (m/z 122) at the 50th minute were determined to be 23.8 ppb, 1.6 ppb and 2.7 ppb in Exp. 10, with a deviation of $\pm 17\%$. This allowed us to derive the two decomposition rate constants as $(3.0 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$ and $(5.1 \pm 0.6) \times 10^{-5} \text{ s}^{-1}$. To date, only Banu et al. (2018) have reported theoretical values for the two decomposition rate constants of C₇H₉O₂N, which are $7.02 \times 10^{-16} \text{ s}^{-1}$ and $1.22 \times 10^{-13} \text{ s}^{-1}$, respectively. It shows that the experimentally derived decomposition rate constants are approximately eight orders of magnitude higher than the theoretical values, indicating that C₇H₉O₂N is a highly unstable compound. Then, the maximum yields of C₇H₉O₂N, C₇H₇N and C₇H₇ON can be determined to be 8.1%, 3.0%, and 5.1% in styrene-O₃ system under conditions of Exp.10, respectively.

Other comments are listed below:

Line 14: Criegee intermediates should be more correctly referred to as zwitterions than radicals.

According to the reviewer's advice, we have revised "radicals" to "zwitterions" on Page 1, Line 14:

NH₃ efficiently scavenges stable Criegee intermediates (SCI) - critical zwitterions in organic aerosol formation.

Line 17: What is the expected atmospheric lifetime of the species C₇H₉O₂N?

The C₇H₉O₂N molecule contains an unstable peroxide bond (-O-O-), which makes it highly reactive. Our experimental observations have confirmed its rapid decomposition into C₇H₇N and C₇H₇ON. In the actual atmosphere, in addition to self-decomposition, C₇H₉O₂N may also react with OH radicals and undergo photolysis. After considering these 3 pathways, the atmospheric lifetime of C₇H₉O₂N was estimated to be 2.1 hours. According to the reviewer's comments, we have provided a detailed analysis and explanation on Lines 197-205 of Pages 9-10.

To quantify the expected atmospheric lifetime of C₇H₉O₂N, we have considered 3 primary removal pathways: (1) Reaction with OH radicals, the reaction rate constant between C₇H₉O₂N and OH was estimated to be $4.77 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using a tool of AOPWIN (Atmospheric Oxidation Program for Microsoft Windows) in EPI (Estimation Program Interface). Using an average OH radical concentration of $1.0 \times 10^6 \text{ molecules cm}^{-3}$, the atmospheric lifetime of $\tau_{\text{OH}} = 5.8 \text{ hours}$; (2) Photolysis: Based on the general photolysis rates of peroxides $1.3 \times 10^{-6} \text{ s}^{-1}$ (Roehl et al., 2007), the photolytic lifetime $\tau_{\text{hv}} = 214 \text{ hours}$; (3) Thermal decomposition: Based on our results, the decomposition rate of C₇H₉O₂N is $8.1 \times 10^{-5} \text{ s}^{-1}$, and its self-decomposition lifetime $\tau_{\text{decomp}} = 3.4 \text{ hours}$. The total atmospheric lifetime was calculated to be 2.1 hours based on $1/\tau = 1/\tau_{\text{OH}} + 1/\tau_{\text{hv}} + 1/\tau_{\text{decomp}}$. This suggests that C₇H₉O₂N predominantly exists in the atmosphere as its more stable transformation products, namely the imine C₇H₇N and the amide C₇H₇ON.

Line 35: What are typical emission rates or atmospheric concentrations of styrene in urban/industrial regions? How significant is the atmospheric loss of styrene to reaction with ozone compared to the reaction with OH?

The typical atmospheric concentration of styrene varies between urban and industrial areas from 0.06 to 45 ppb (Okada et al., 2012; Cho et al., 2014; Sun et al., 2016; Sheng et al., 2018). Ozone oxidation is an important atmospheric sink for styrene. Based on MCM mechanism, the rate constant (k_{OH}) for the reaction of styrene with OH is $5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, and the rate constant (k_{O_3}) for the reaction with O_3 is $1.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Under typical atmospheric conditions ($[\text{OH}] \sim 1.0 \times 10^6 \text{ molecule cm}^{-3}$, $[\text{O}_3] \sim 50 \text{ ppb} = 1.3 \times 10^{12} \text{ molecule cm}^{-3}$), the estimated loss ratio for the reaction of styrene with OH and O_3 is about 2.6:1. This indicates that about 30% of styrene will be consumed by O_3 in atmospheric conditions. According to the reviewer's comments, we have added the following content to the *Introduction* section.

Page 2, Lines 41-44: The typical atmospheric concentration of styrene varies between urban and industrial areas from 0.06 to 45 ppb (Okada et al., 2012; Cho et al., 2014; Sun et al., 2016; Sheng et al., 2018). Under typical atmospheric conditions, about 30% of styrene may be consumed by O_3 , thus ozone oxidation is an important sink for styrene, especially in areas with high O_3 pollution.

Line 37: It would help to give the structures of the Criegee intermediates (and for other species discussed in the manuscript).

Based on the reviewer's suggestion. We have added the structures of Criegee intermediates and several other key species discussed in the manuscript on Page 1, Line 15 in the *supplementary material*:

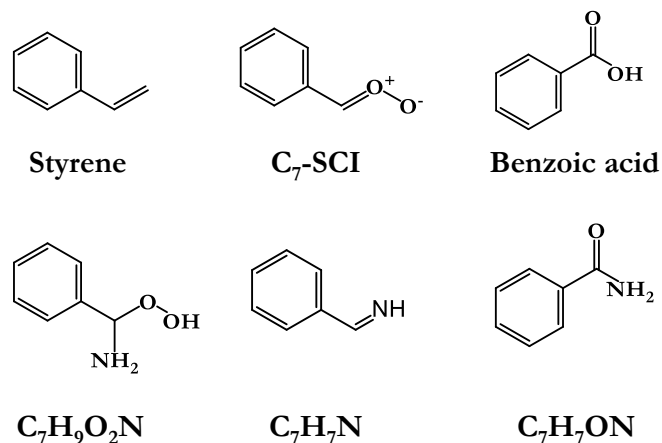


Figure S1. The structures of the key species

Line 52: Define FEP.

We have defined FEP in the experiments section on Page 3, Line 60:

The chamber experiments were conducted in Fluorinated Ethylene Propylene (FEP, 200A, DuPont) reactors under dark conditions, with background air supplied by purified zero air.

Line 54: What were the typical concentrations/concentration ranges used in the experiments?

The reactants and their concentration ranges used in the exp.1-5 are: styrene (0.34~0.36 ppm), O₃ (1 ppm), and NH₃ (0~0.8 ppm), respectively. The concentration ranges used in the exp.6-10 are: styrene (0.4~0.7 ppm), O₃ (2 ppm), and NH₃ (0~10 ppm), respectively. The concentration used in the exp.11 is styrene (3 ppm), O₃ (10 ppm), and NH₃ (0.8 ppm), respectively. We have listed the initial concentrations used in each experiment in Table S1, and added the concentration ranges in the *Materials and methods* section.

Page 3, Lines 63-64: The reactants and their concentration ranges used in the experiment are styrene (0.3~3 ppm), O₃ (1~10 ppm), and NH₃ (0~10 ppm), respectively.

Line 75: It would help to provide more details of the experimental procedures and conditions in the main text. Which species were measured? What was the timescale for the measurements?

According to the reviewer's advice, we have moved some of the experimental details from the *supplementary material* to the *Materials and methods* of the main text in manuscript, and provided a detailed introduction to the species measured during the experiment and their corresponding timescales on Pages 3, Lines 60-80:

Experiments and Measurements: The chamber experiments were conducted in Fluorinated Ethylene Propylene (FEP, 200A, DuPont) reactors under dark conditions, with background air supplied by purified zero air. Styrene was injected into the reactor with zero air using a glass microsyringe, O₃ was produced by an ozone generator with pure O₂, and NH₃ was directly injected into the reactor. The reactants and their concentration ranges used in the experiment are styrene (0.3~3 ppm), O₃ (1~10 ppm), and NH₃ (0~10 ppm), respectively. Because ozonolysis of styrene can form OH radicals, n-Hexane was used as an OH radical scavenger (>100ppm with a removal efficiency >90%). Detailed experimental conditions are provided in Table S1.

To collect particles and determine the SOA yields, experiments 1-5 were conducted in a 1.2 m³ chamber. During these experiments, styrene was measured online using a proton transfer reaction-mass spectrometer (PTR-MS P1000-L-AI, Anhui Province Key Laboratory of Medical Physics and Technology) with a time resolution of 20 s in the gas phase. O₃ was measured every 0.5 hours lasting for 5 minutes with an O₃ analyzer (Model 49C, Thermo Scientific) with a time resolution of 10 s in the gas phase. The particle concentrations and size distributions were determined by a scanning mobility particle sizer (SMPS, Model 3936, DMA-3080, CPC-3776, TSI) with a time resolution of 5 minutes. The online measurements covered the entire experimental process (4~5h). Particles were collected on a 25 mm polytetrafluoroethylene (PTFE) membrane with a pore size of 0.45 μm at the 4th hour, and the sample flow rate was 6 L/min and lasted for 40 min. The collected particles were extracted with methanol for composition analysis in the particle phase, which were injected by a high-performance

liquid chromatography (HPLC, Thermo Scientific), ionized by a heated electrospray ionization source (ESI), and then the molecular composition was measured by a high-resolution Orbitrap mass spectrometer (Orbitrap MS, Q-Exactive, Thermo Scientific) with a resolution $R = 70,000$ at m/z 200. To determine the kinetics and mechanism of the reaction between C_7 -SCI and NH_3 , experiments 6-10 were performed with higher concentrations in a 150 L chamber. During these experiments, the products were online ionized by a gas aerosol in-situ ionization source (GAIS), and then measured by Orbitrap MS in the gas phase. The time resolution of GAIS-Orbitrap MS measurement is about 0.5 s, and all the experiments lasted about 1 h.

Line 92: How certain is the mechanism for benzoic acid formation? It would help to show a schematic of the mechanism. Is there any evidence for combined effects of ammonia and water? Studies of Criegee intermediate kinetics using photolytic precursors have demonstrated cooperative effects of water and ammonia on Criegee intermediate chemistry (e.g. Chao et al., J. Phys. Chem. A, 123, 1337-1342, 2019).

The formation mechanism of benzoic acid through reaction between C_7 -SCI and H_2O has been reported by previous studies (Na et al., 2006; Banu et al., 2018). In this study, the chemical mechanism of styrene was taken from the MCM mechanism v3.3.1 (<http://mcm.york.ac.uk/>), which is built using published experimental data, theoretical studies, and evaluated kinetic data (Jenkin et al., 2003). According to the reviewer's advice, we have added a schematic of the mechanism in Figure 1 d.

Thank you for recommending the important study by Chao et al. (2019), which revealed the strong synergistic effect of NH_3 and H_2O on the reaction of C_1 -SCI. We have cited this work in the *Introduction* section. In the present study, our primary focus is on the reaction between C_7 -SCI and NH_3 . It should be noted that the Q-Exactive mass spectrometer used here can only detect ions with an m/z greater than 50. Since the reaction products of C_1 -SCI with H_2O or NH_3 have molecular weights below 50 Da, we were unable to detect any of these products. Consequently, no synergic enhancement effect between water and NH_3 was observed under our experimental

conditions. According to the reviewer's suggestions, we have revised the following content.

Page 2, Lines 33-38: Quantum calculations suggest that NH_3 may influence the SOA formation from styrene through reactions with stable Criegee intermediates (SCIs) (Ma et al., 2018; Banu et al., 2018), and NH_3 and H_2O have a synergic effect on the reaction of C_1 -Criegee intermediate (Chao et al., 2019a,b). The reaction rate between NH_3 and C_1 -Criegee intermediate (CH_2OO) has been determined by theoretical calculations (Jørgensen and Gross, 2009; Misiewicz et al., 2018) and experiments (Liu et al., 2018; Chao et al., 2019; Chhantyal-Pun et al., 2019). Our recent study has shown new laboratory evidence that NH_3 can also react with isoprene-derived SCIs to form NOCs, thereby changing the chemical characteristics of SOA (Li et al., 2024).

Page 4, Lines 115-116: Since benzoic acid is mainly formed from the reaction of C_7 -SCI with H_2O (Na et al., 2006; Banu et al., 2018), the presence of NH_3 apparently competes with H_2O for SCIs and inhibits the formation of benzoic acid (Fig.1d).

Page 6, Line 131:

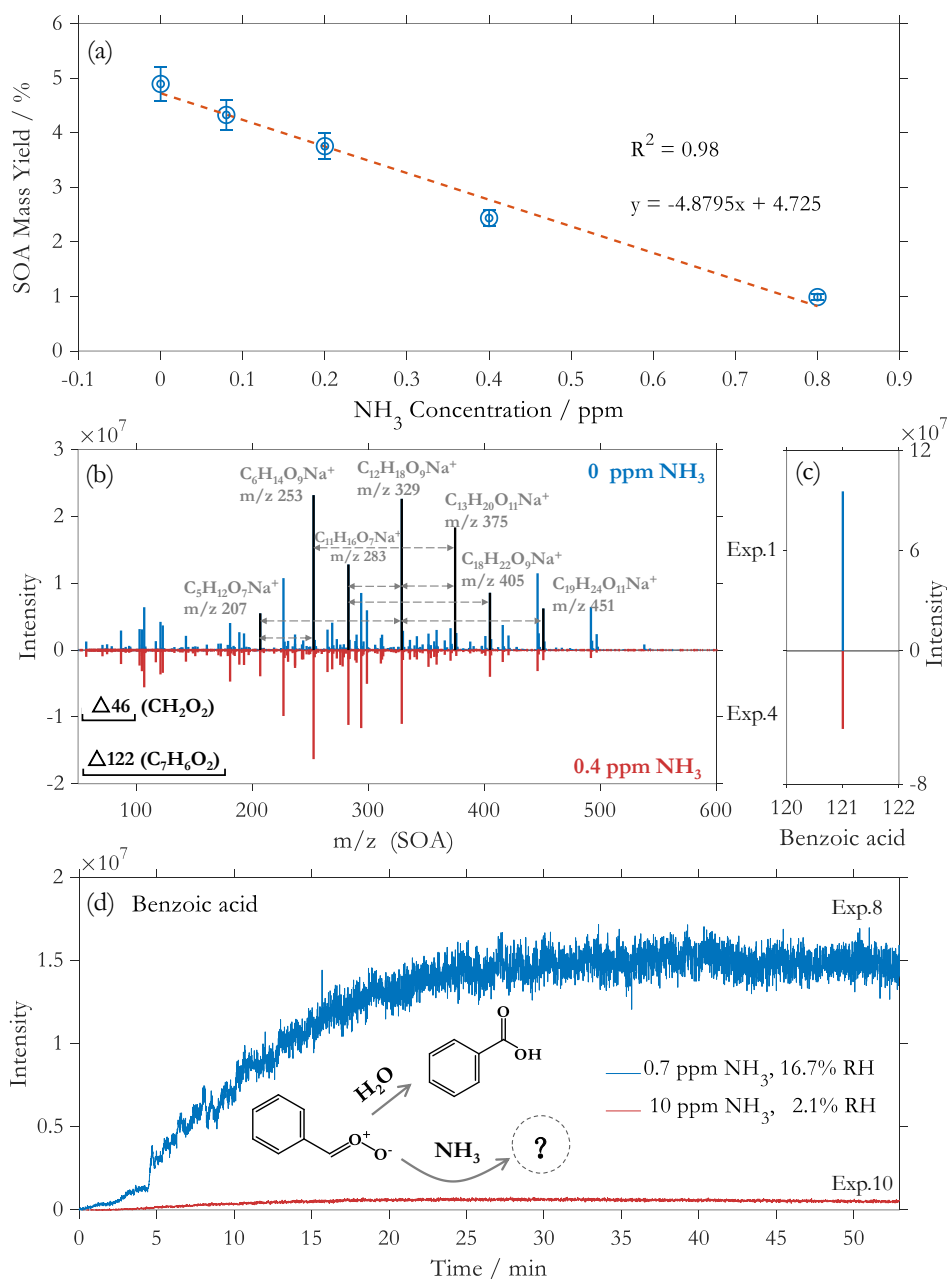


Figure 1: SOA mass yields from styrene ozonolysis under different NH_3 concentrations (a); Positive mode mass spectra of SOA from styrene ozonolysis systems with 0 ppm (blue) and 0.4 ppm NH_3 (red) (b), several top ion peaks assigned to SCI-derived oligomer are marked in black; The mass spectra of benzoic acid from styrene ozonolysis systems with 0 ppm (blue) and 0.4 ppm NH_3 (red) (c); Online observation of benzoic acid in the experiments with low concentration NH_3 with normal humidity (Ex.8, blue) and high concentration NH_3 with low humidity (Ex.10, red) (d).

Line 140: What is ‘the general decomposition principle of peroxides’? References and

details are needed here. What is known about the stability of the species being discussed?

Dehydration and dehydroperoxidation are common decomposition pathways for peroxides (Smith and March, 2020). Due to the high reactivity of peroxide bonds, the peroxide amine $C_7H_9O_2N$ is expected to be highly unstable and easily decomposed by removing one H_2O_2 or H_2O (Smith and March, 2020; Banu et al., 2018; Ma et al., 2018).

Regarding the stability of species $C_7H_9O_2N$, our online mass spectrometry experimental evidence shows that the appearance of the $C_7H_9O_2N$ signal is accompanied by an increase in the signals of its decomposition products (C_7H_7N and C_7H_7ON), demonstrating the instability of $C_7H_9O_2N$ on the experimental time scale. In addition, we also discussed the expected atmospheric lifetime of $C_7H_9O_2N$, and the result obtained was only 2.1 hours, further proving the instability of $C_7H_9O_2N$.

According to the reviewer's advice, we have added some sentences on Page 9, Lines 168-170:

Due to the high reactivity of peroxide bonds, the peroxide amine $C_7H_9O_2N$ is expected to be highly unstable and easily decomposed by removing one H_2O_2 or H_2O (Smith and March, 2020), and may further decompose into imines and amides based on theoretical calculation (Banu et al., 2018; Ma et al., 2018).

References:

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