



Assessing the NO and SO₂ pollution impacts on the Δ^3 -carene photooxidation mechanisms

Ya Zhao^{a,b,c}, Chong Wang^{d,e}, Yufeng Shao^{a,b}, Yingqi Zhao^{a,b}, Yifei She^{a,b},
Hua Xie^{a,b}, Jiayue Yang^{a,b}, Weiqing Zhang^{a,b}, Gang Li^{a,b,*},
Ling Jiang^{a,b,f,**}, Xueming Yang^{a,b,c,d,f,g}

^a State Key Laboratory of Chemical Reaction Dynamics and Dalian Coherent Light Source, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

^b University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing, 100049, China

^c School of Chemistry, Dalian University of Technology, Dalian, 116024, China

^d Institute of Advanced Light Source Facilities, Shenzhen, 518107, China

^e Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China

^f Hefei National Laboratory, Hefei, 230088, China

^g Department of Chemistry and Guangdong Provincial Key Laboratory of Catalytic Chemistry, Southern University of Science and Technology, Shenzhen, 518055, China

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ABSTRACT

Investigating the influences of gaseous pollutants on volatile organic compound photooxidation mechanisms is essential for establishing robust air quality management strategies. Here, a set of well-defined experiments were conducted to elucidate the roles of NO and SO₂ in Δ^3 -carene-derived secondary organic aerosol (SOA) formation. Employing electron ionization time-of-flight aerosol mass spectrometer, we found that high NO concentration significantly inhibited new particle formation (NPF) by reducing the O:C rate of products. With the presence of SO₂ pollution, the trend of SOA yield exhibited two distinct regimes governed by SO₂ concentration. At low SO₂ concentrations ([SO₂]₀ ≤ 119 ppb), H₂SO₄ nucleation promoted the NPF and elevated the SOA yields; with the increase of SO₂ pollution level (119–178 ppb), the consumption of stabilized Criegee intermediates increased, which reduced particle number concentrations and SOA yields. Significantly, two distinct NPF events were observed in the Δ^3 -carene photooxidation. Leveraging the unique capabilities of vacuum ultraviolet free electron laser photoionization online aerosol mass spectrometer, we detected the dynamic chemical evolution of SOA across reaction stages and elucidated the differences between such two NPF mechanisms. The results show that the introduction of SO₂ progressively accelerated the onset of NPF, with a maximum shift of approximately 1 h. H₂SO₄ formed from SO₂ oxidation promoted earlier nucleation, while the generation of particulate formation was dominated by Δ^3 -carene oxidation. By integrating experimental observations with theoretical calculations, we identified a series of key organosulfates and elucidated their formation mechanisms. These results highlight the NO and SO₂ pollution impacts on Δ^3 -carene photooxidation and advance our understanding of NPF in polluted environments.

1. Introduction

High concentrations of particulate matter (PM) not only pose significant risks to human health and ecosystems (Maji, 2020; Qiang et al., 2025; Zhang et al., 2022), but also disrupt Earth's climate systems (Wu

et al., 2020; Wu et al., 2019). Secondary organic aerosols (SOA) are produced by the atmospheric oxidation of various biogenic and anthropogenic volatile organic compounds (VOCs) (Atkinson and Arey, 2003; Seinfeld and Pankow, 2003) and constitute a major fraction of PM (Alramzi et al., 2025; Zhou et al., 2020). Due to the complexity of SOA

* Corresponding author. State Key Laboratory of Chemical Reaction Dynamics and Dalian Coherent Light Source, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

** Corresponding author. State Key Laboratory of Chemical Reaction Dynamics and Dalian Coherent Light Source, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

E-mail addresses: gli@dicp.ac.cn (G. Li), ljiang@dicp.ac.cn (L. Jiang).

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sources (i.e., different oxidants, multiple environmental parameters, and diverse VOC precursors), well-defined experiments are essential to advance our understanding of their physicochemical properties.

In China, air pollution is predominantly photochemical haze and smog, with the reactive nitrogen oxide (NO_x) cycle as the primary driver and important precursors of air pollution (Fan et al., 2024; Wang et al., 2025; Yan et al., 2025). In pure NO_x cycle, light irradiation initiates the photolysis of NO_2 to form NO , which is subsequently oxidized back to NO_2 by generated ozone (O_3). VOCs can be readily oxidized by the oxidants produced during the NO_x cycle, generating various peroxy radicals (RO_2 and HO_2) (Perring et al., 2013). In turn, these radicals accelerate the oxidation of NO to NO_2 , consequently leading to a rapid accumulation of O_3 (Wang et al., 2025; Zhang et al., 2024). Previous studies on the VOC photooxidation have shown that in the low NO_x regime, the bimolecular reaction between RO_2 and HO_2 is prevailing; in the high NO_x regime, the reactions of RO_2/HO_2 with NO become more dominant (Sarrafzadeh et al., 2016; Yang et al., 2020; Zhao et al., 2018; Zhao et al., 2025). NO_x governs the dominant pathways of radical chemistry, thereby regulating the formation and growth mechanisms of SOA. Numerous studies have demonstrated that the formation of SOA is also closely linked to the components of NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) (Deng et al., 2017; Nihill et al., 2021; Zhao et al., 2026a; Zhao et al., 2024a). Recent research on Δ^3 -carene photooxidation have elucidated the key roles of NO_2 and SO_2 , detailing how the contributions of dominant oxidants shift with varying NO_2 concentrations (Zhao et al., 2025). Meanwhile, NO not only regulates oxidants formation but also engages in critical reactions with RO_2 , which are central to the underlying mechanism. Thus, a deeper understanding of the specific role of NO in photooxidation is essential for refining atmospheric chemical mechanisms.

As another key gaseous pollutant in China, sulfur dioxide (SO_2) is released mainly from coal and biomass combustion, with concentration exceeding $300 \mu\text{g m}^{-3}$ in high-pollution areas (Li et al., 2017; Zhang et al., 2015a). In the atmosphere, the oxidation of SO_2 is a major cause of acid rain, as evidenced by the Great Smog in London and Haze in Asia (Zhang et al., 2015b). The $\text{SO}_2 + \text{OH}/\text{stabilized Criegee intermediates (sCIs)}$ reactions can yield gaseous sulfuric acid (H_2SO_4), which serves as a critical precursor that drives new particle formation (NPF) (Berndt et al., 2008; Mauldin et al., 2012; Shang et al., 2022). Currently, extensive laboratory and theoretical efforts have been made in nucleation processes and models, including binary, ternary, and ion-induced nucleation theories (Almeida et al., 2013; Kürten et al., 2015; Sipilä et al., 2010). It has been found that during the growth process of particles, H_2SO_4 continues to condense onto the surfaces of nanoparticles, which simultaneously adsorb organic aerosol precursors (Lehtipalo et al., 2018; Tröstl et al., 2016). A large number of smog chamber studies have demonstrated that organosulfates (OSs) can be formed via acid-catalyzed reactions with H_2SO_4 as the sulfate group donor, consequently influencing the chemical compositions and yields of SOA (Xu et al., 2021b; Yang et al., 2023; Yang et al., 2020; Yang et al., 2021; Zhao et al., 2025). OSs are important components of aerosols, accounting for up to approximately 30% of organic matter in atmospheric particles (Brüggemann et al., 2017; Glasius et al., 2018; Shakya and Peltier, 2015). Due to the diverse impacts of SO_2 on NPF, the characterization of OSs is key for assessing the detailed effects of SO_2 on SOA formation.

Global emissions of biogenic VOCs are estimated at approximately 760 Tg year^{-1} , which is about ten times the amount emitted from anthropogenic sources (Sindelarova et al., 2014). Investigating the chemical compositions and formation mechanisms of biogenic VOCs-derived SOA is crucial to understand atmospheric processes and to improve air quality. Δ^3 -Carene is a highly reactive bicyclic monoterpene and readily reacts with oxidants such as O_3 ($k_{\text{O}_3,298\text{K}} = 3.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), OH ($k_{\text{OH},298\text{K}} = 8.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and NO_3 radical ($k_{\text{NO}_3,298\text{K}} = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson and Arey, 2003). The oxidation processes of Δ^3 -carene by single oxidants (e. g., OH , NO_3 radical and O_3) have been reported, and a series of key

species have been identified (D'Ambro et al., 2022; Day et al., 2022; DeVault and Ziemann, 2021; Song et al., 2025). Recently, a growing body of studies have confirmed that gaseous pollutants significantly influence the oxidation processes of monoterpenes (Xu et al., 2021b; Zhao et al., 2025; Zhao et al., 2024a, b), but the precise identification of chemical speciation and evolution mechanisms of Δ^3 -carene-derived SOA remain elusive. Therefore, this work aims to elucidate the roles of gaseous pollutants (NO and SO_2) in Δ^3 -carene photooxidation and to characterize the generation of OSs. We utilized the newly-built vacuum ultraviolet free electron laser (VUV-FEL) photoionization online aerosol mass spectrometer to investigate the chemical compositions of SOA. This work is expected to provide valuable insights into SOA formation mechanisms under the influence of typical gaseous pollutants.

2. Experiment methods

2.1. Experimental procedure

The experiments were designed to simulate the formation of SOA under highly polluted conditions in the presence of both NO and SO_2 . Considering that the typical background levels in densely populated megacities such as Beijing, Wuhan, and Xi'an, where concentrations often exceed 100 ppb (Hui et al., 2019; Liu et al., 2022; Zheng et al., 2021), the NO and SO_2 concentrations in this work were set between 50 and 200 ppb. Such concentration range has also been used in previous studies of isoprene, β -pinene, and cyclooctene (Masoud et al., 2022; Xu et al., 2021b; Yang et al., 2023).

The designed experiments (Table 1) were performed in a 2 m^3 Teflon smog chamber (Conway Nite Environmental Tech, Beijing, China), which equipped with 40 black light lamps (F40BLB). An overview of the experimental procedure is provided in this section, while comprehensive details are available in the Supplementary Material (SM). First, an aliquot of Δ^3 -carene (>90.0%, Aladdin, Shanghai, China) was introduced into the reactor using dry and purified zero air. Next, NO (497 ppm in N_2 , Kylingas, Dalian, China) and SO_2 (495 ppm in N_2 , Kylingas, Dalian, China) were added to the reactor via the corresponding gas pipelines. Following the introduction of all components, the smog chamber was kept in the dark for 0.5 h to ensure the complete mixing. Upon recording the initial concentrations of all reactants, the black light lamps were turned on to initiate photooxidation and this moment was marked as time zero for the reaction. Throughout all the experiments, the temperature was maintained at $296.0 \pm 0.5 \text{ K}$, while the relative humidity remained below 5%. While the humidity conditions in this study deviate from typical atmospheric environments, the results provide insights into the atmospheric chemical mechanisms underpinning drought scenarios.

2.2. Gas-phase measurements

The smog chamber was equipped with a series of online instruments that enabled the quantification of gas-phase species. The concentration of Δ^3 -carene was determined by using a proton-transfer reaction mass spectrometer (PTR-QMS 3500, East & West Analytical Instruments, Beijing, China). Specially, the initial concentration of Δ^3 -carene ($[\Delta^3\text{-carene}]_0$) in Table 1 was defined as the actual concentration of Δ^3 -carene introduced into the chamber and was quantified directly via PTR-QMS. The concentrations of reaction gases (NO and SO_2) were continuously monitored throughout the experiments by gas analyzers (Model 42i and 43i, Thermo Fisher Scientific, USA). The concentration of O_3 were characterized by using another instrument (Model 49i, Thermo Fisher Scientific, USA).

2.3. Particle-phase measurements

For all experiments, the particle size distribution, volume, and number concentrations were monitored by using a commercialized

Table 1Summary of conditions and results for Δ^3 -carene smog chamber experiments.

Experiment ID	$[\Delta^3\text{-carene}]_0$ (ppb)	$[\text{NO}]_0$ (ppb)	$[\text{SO}_2]_0$ (ppb)	$[\Delta^3\text{-carene}]_0/[\text{NO}]_0$	$[\text{O}_3]_{\text{max}}$ (ppb)	ΔROG (ppb)	ΔM ($\mu\text{g m}^{-3}$)	SOA Yield (%)
CN1	407	51	-	8.0	89	292	236.5	14.5
CN2	409	70	-	6.1	100	307	257.6	15.1
CN3	396	92	-	4.3	115	309	186.1	10.8
CN4	387	149	-	2.6	107	314	131.2	7.5
CN5	400	199	-	2.0	69	312	66.9	3.9
CNS1	392	65	56	6.0	102	291	90.7	5.6
CNS2	390	64	80	6.1	105	292	85.5	5.3
CNS3	398	64	119	6.2	111	302	128.5	7.6
CNS4	395	61	138	6.5	104	300	99.1	5.9
CNS5	387	65	178	6.0	90	294	46.7	2.9

Abbreviations in experimental IDs represent the reactants introduced into the chamber, i.e., “C” stands for Δ^3 -carene, “N” for NO, and “S” for SO_2 . $[\text{X}]_0$ denotes the initial concentration of X; $[\text{O}_3]_{\text{max}}$ represents the maximum accumulation of O_3 ; ΔROG stands for the amount of reacted Δ^3 -carene; ΔM for particle mass concentrations.

scanning mobility particle sizer spectrometer (SMPS 3938L76, TSI Incorporated, USA), comprising a differential mobility analyzer (Model 3082, TSI Incorporated, USA) and a condensation particle counter (Model 3776, TSI Incorporated, USA). Assuming that particles were spherical, particle mass concentrations were derived by applying a commonly-used density of 1.0 g cm^{-3} to the SMPS-measured volume concentrations. The aerosol density of a number of VOCs was measured to be about 1.0 g cm^{-3} (Kim et al., 2024), which value was thus used in this work. The wall loss rate of small smog chamber is approximately 10^{-6} s^{-1} (see details in the SM), which is comparable to that of large smog chambers ($2.2\text{--}2.4 \times 10^{-6} \text{ s}^{-1}$) (Zang et al., 2022). Wall-loss corrections were applied to all particle mass concentrations. Given that no seed aerosols were introduced in any of the experiments, particle wall loss was corrected by assuming a first-order kinetic process with an independent of particle size (Pathak et al., 2007). Accordingly, the corrected mass concentration ($[\text{M}(t)]_{\text{corr}}$) was calculated: $[\text{M}(t)]_{\text{corr}} = [\text{M}(t)]_{\text{meas}} + k \sum ([\text{M}(t)]_{\text{meas}} \Delta t)$, where $[\text{M}(t)]_{\text{meas}}$ was the measured particle mass concentration at time t and k was the fitted wall-loss rate constants (see SM for the details). The uncertainty of wall-loss correction mainly arises from particle mass concentrations, which is about 10% (Zhao et al., 2026a).

The chemical compositions of Δ^3 -carene-derived SOA were characterized by using VUV-FEL photoionization time-of-flight aerosol mass spectrometer (abbreviated as VUV-FEL-TOF-AMS) (Zang et al., 2022). The tunability of the VUV-FEL (50–150 nm/8.3–24.8 eV) enables selective measurement of SOA via threshold photoionization, allowing for the detection of SOA components that are typically undetectable with conventional ionization sources (Normile, 2017; Zhao et al., 2025). In this study, the VUV-FEL-TOF-AMS mass spectral peaks denoted the molecular weights (MWs) of the molecular ions.

The oxidation states of SOA were detected by another online electron ionization TOF-AMS (abbreviated as EI-TOF-AMS) (DeCarlo et al., 2006; Zang et al., 2024). The detection of the characteristic ion fragmentation of $m/z = 44$ (mainly CO_2^+) and $m/z = 43$ (predominantly $\text{C}_2\text{H}_3\text{O}^+$) via EI-TOF-AMS enables the extraction of the elemental ratios H:C and O:C (Aiken et al., 2008; Canagaratna et al., 2015; Ng et al., 2011; Ng et al., 2010), which allows for the determination of the overall SOA oxidation states throughout the reaction processes.

Both home-built online aerosol mass spectrometers were calibrated every month by using a set of calibration organic compounds, including vanillin ($\text{C}_8\text{H}_8\text{O}_3$, 99%, Aladdin, Shanghai, China), 1-pentadecanol ($\text{C}_{15}\text{H}_{32}\text{O}$, 99%, Alfa Aesar, Shanghai, China), n-eicosane ($\text{C}_{20}\text{H}_{42}$, 99%, Alfa Aesar, Shanghai, China) and n-triacontane ($\text{C}_{30}\text{H}_{62}$, 99%, Alfa Aesar, Shanghai, China). More detailed descriptions of VUV-FEL-TOF-AMS and EI-TOF-AMS are provided in SM.

2.4. Theoretical methods

Quantum chemical calculations were performed by using Gaussian

16 software package at the $\omega\text{B97XD/def2-TZVP}$ level to evaluate the feasibility of the proposed oxidation pathways for Δ^3 -carene (Frisch et al., 2016). The computational methodology involved geometry optimization and vibrational frequency calculations for all intermediates, transition states (TSs), and products. The structures of TSs were optimized with the Berny algorithm and verified through intrinsic reaction coordinate (IRC) analysis. All relative energies incorporated zero-point vibrational energy (ZPVE) corrections. Quantum chemical calculations in this study were aimed to theoretically deduce the formation process of SOA and to evaluate its feasibility at the molecular level, thereby providing a theoretical basis for the structural assignment and rationalization of the experimentally observed products. The thermodynamic and kinetic feasibility of the proposed reaction pathways was systematically evaluated by comparing the relative energies between reactants and products ($\Delta E_r < 0.0 \text{ kcal/mol}$) and by analyzing the energy barriers of the key TSs ($\Delta E_b < 25.0 \text{ kcal/mol}$).

3. Results and discussion

3.1. The influences of $[\text{NO}]_0$ on Δ^3 -carene SOA formation

A series of photooxidation experiments were conducted at different $[\text{NO}]_0$ which were varied from 51 to 199 ppb (Table 1, CN1–5). As shown in Fig. 1a₁, there is no NPF at the beginning of photooxidation. After 1.2 h, particle number concentration undergoes a rapid increase. The particle number concentration increases as $[\text{NO}]_0$ rises from 51 to 70 ppb, then decreases as $[\text{NO}]_0$ rises from 70 to 199 ppb. Notably, the maximum particle number concentration decreases from $1.2 \times 10^5 \text{ particles cm}^{-3}$ to $5.6 \times 10^4 \text{ particles cm}^{-3}$ over the $[\text{NO}]_0$ range of 70 to 199 ppb (Fig. S1). These results reveal that NO plays a clear inhibitory role in the process of NPF. Indeed, previous studies have reported that the $\text{RO}_2 + \text{NO}$ reaction is a key oxidation pathway, and the resulting organic nitrate exhibits a volatile nature, which is resistant to entering the particle-phase and thus suppresses NPF (Capouet and Müller, 2006; Lim and Ziemann, 2005; Nie et al., 2023; Orlando and Tyndall, 2012; Perring et al., 2013). Additionally, across the investigated range of $[\text{NO}]_0$ (51–199 ppb), the generation time of PM gradually increases from 1.2 h to 2.4 h (Fig. 2a). In this study, the generation time of PM is defined as the period from the start of photooxidation reactions (marked as t_0 upon switching on the black light lamps) to the initial detection of stable particle formation by SMPS. This corresponds to the inflection point at which the particle number concentration begins to exhibit sustained exponential growth. The generation time of PM for all experiments is summarized in Table S1. Fig. S2 shows that high NO concentration prolongs its conversion to NO_2 , which in turn postpones the production of key oxidants (O_3). The formation kinetics of O_3 is closely linked to the dynamics of PM generation and is likely one of factors for the delayed appearance of PM. Considering that RO_2 and HO_2 are also involved in the conversion of NO to NO_2 , the oxidation process of Δ^3 -carene may be

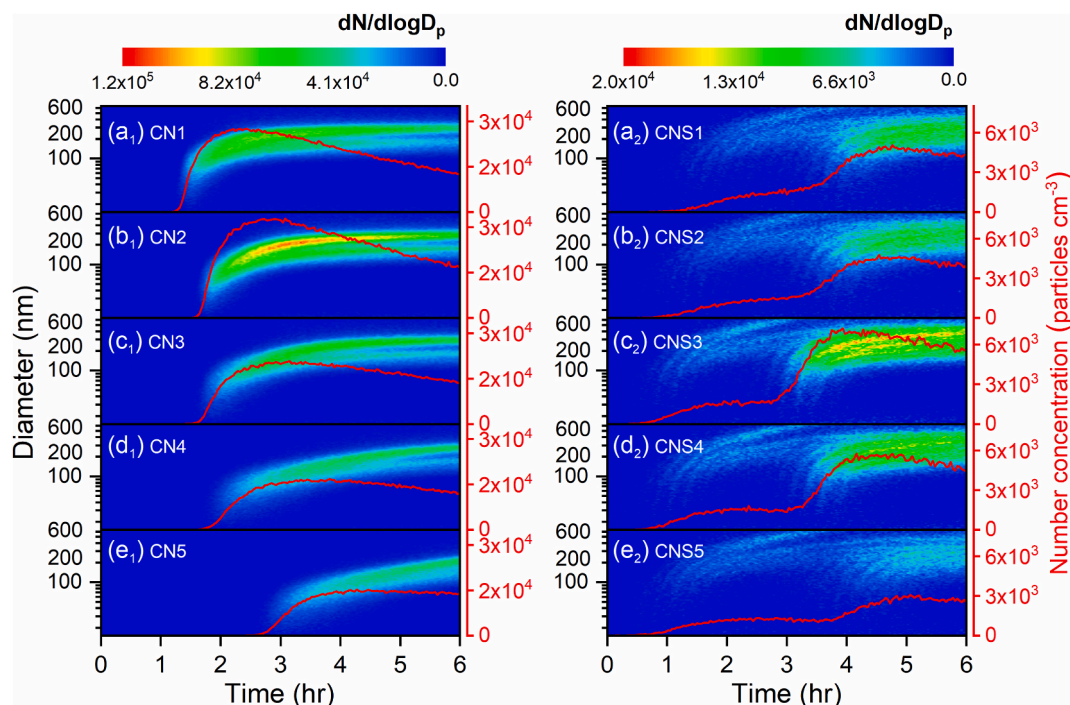


Fig. 1. Temporal evolution of the particle size distribution and number concentration in the Δ^3 -carene photooxidation experiment based on $[\text{NO}]_0$ (a₁-e₁) and $[\text{SO}_2]_0$ (a₂-e₂). Specifically, (a₁) 407 ppb Δ^3 -carene + 51 ppb NO; (b₁) 409 ppb Δ^3 -carene + 70 ppb NO; (c₁) 396 ppb Δ^3 -carene + 92 ppb NO; (d₁) 387 ppb Δ^3 -carene + 149 ppb NO; (e₁) 400 ppb Δ^3 -carene + 199 ppb NO; (a₂) 392 ppb Δ^3 -carene + 65 ppb NO + 56 ppb SO₂; (b₂) 390 ppb Δ^3 -carene + 64 ppb NO + 80 ppb SO₂; (c₂) 398 ppb Δ^3 -carene + 64 ppb NO + 119 ppb SO₂; (d₂) 395 ppb Δ^3 -carene + 61 ppb NO + 138 ppb SO₂; (e₂) 387 ppb Δ^3 -carene + 65 ppb NO + 178 ppb SO₂. D_p for particle diameter; $dN/d\log D_p$ denotes normalized number size distribution.

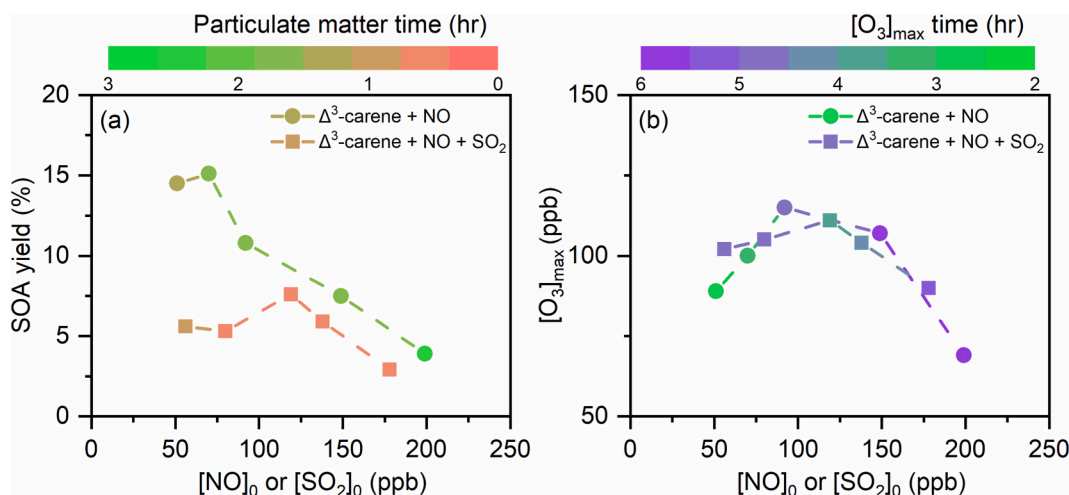


Fig. 2. SOA yield and the generation time of particulate matter as a function of the $[\text{NO}]_0$ and $[\text{SO}_2]_0$ (a). The maximum ozone concentration and the occurrence time of $[\text{O}_3]_{\text{max}}$ as a function of $[\text{NO}]_0$ and $[\text{SO}_2]_0$ (b). Specially, in the Δ^3 -carene + NO conditions, $[\text{NO}]_0$ was the principal variable; in the Δ^3 -carene + NO + SO₂ conditions, the main variable was $[\text{SO}_2]_0$, with a constant $[\text{NO}]_0$ at 70 ppb.

prematurely terminated. This leads to the formation of products with higher volatility, thereby limiting their partitions into the particle-phase.

In the Δ^3 -carene + NO experiments, the trends in mass concentrations (Fig. S3a) and SOA yields (Fig. 2a) are consistent with those of particle number concentrations. It is likely that the $[\text{NO}]_0$ increase elevates the proportion of the $\text{RO}_2 + \text{NO}$ reaction, thereby altering the chemical compositions of SOA, suppressing the mass concentration and SOA yield. As shown in Fig. 2b, the measured $[\text{O}_3]_{\text{max}}$ initially rises with increasing $[\text{NO}]_0$ from 51 ppb to 92 ppb (green-dotted curve), but begins to decline when $[\text{NO}]_0$ reaches 149 ppb. This nonlinear response is

consistent with previous studies (Zhang et al., 2024; Zhao et al., 2024a, b) and may be attributed to a modification in the NO reaction pathway, subsequently affecting accumulative $[\text{O}_3]_{\text{max}}$. Notably, as $[\text{NO}]_0$ increases, the occurrence time of $[\text{O}_3]_{\text{max}}$ gradually shifts from 2.6 h to 6.0 h. Furthermore, a significant decrease of $[\Delta^3\text{-carene}]_0$ occurs only after O_3 begins to accumulate. While OH and O_3 are the principal oxidants in photooxidation process, OH oxidation is generally the dominant sink of precursors (Atkinson, 2000; Chu et al., 2022). Nevertheless, Recent studies have shown that O_3 also plays an important role in the photo-oxidation of monoterpenes, especially in environments with high VOC concentrations (Zhang et al., 2024; Zhao et al., 2024a, b; Zhao et al.,

2026b). A comparison of SOA formation pathways has demonstrated that derived from monoterpene ozonolysis possesses lower volatility than that generated via OH-initiated oxidation (Watne et al., 2017). Smog chamber study has indicated that SOA yield from monoterpene ozonolysis exceeds that from OH oxidation (Zhao et al., 2015). The significant O₃ accumulation observed in our study implies that ozonolysis is likely a non-negligible process. The quantitative assessment of relative contribution of OH and O₃ oxidation processes is difficult due to the absence of OH measurement in this work, which will be taken into consideration in the future experiments.

3.2. The influences of [SO₂]₀ on Δ³-carene SOA formation

To understand the specific influences of SO₂ on Δ³-carene photooxidation, a series of experiments (Table 1, CNS1-5) were performed under different [SO₂]₀. As illustrated in Fig. 1a₂-e₂, particle size distribution of CNS1-5 increases significantly, whereas the maximum particle number concentrations are lower than those in the CN1-5 experiments. Furthermore, the generation time of PM is remarkably advanced with the presence of SO₂. Under dry conditions, SO₂ is primarily oxidized to SO₃ by sCIs and then SO₃ rapidly reacts with H₂O to produce H₂SO₄ (Heine et al., 2018; Ye et al., 2018). Due to the low saturated vapor pressure, H₂SO₄ readily condenses and nucleates, serving as a key precursor for NPF. Therefore, the formation of H₂SO₄ could be a key factor for the earlier generation time of PM. Moreover, the H₂SO₄ acidic nuclei not only adsorbs other organic compounds but also facilitates the generation of OSs via acid-catalyzed reactions, thereby significantly promoting the growth of particles. Besides, the growth of particles may reduce the particle number concentration. This is one reason for the experiment of CNS3 with SO₂ exhibits lower maximum particle number concentration (2.0×10^4 particles cm⁻³) than the experiment of CN2 without SO₂ (1.2×10^5 particles cm⁻³). In particular, the addition of SO₂ consumes a portion of sCIs, consequently suppressing the generation of oxidation products. This scavenging effect leads to a significant reduction in particle number concentration. In Fig. 1(a₂-e₂), the maximum particle number concentration first increases and then decreases as [SO₂]₀ rises. Mass concentrations (Fig. S2b) and SOA yields (Fig. 2a) are found to vary in parallel with particle number concentrations, indicating that particle number concentration serves as the governing factor in these series of experiments. In low [SO₂]₀ (CNS1-3), the formation of H₂SO₄ promotes acidic nuclei, thereby enhancing particle number concentration. At [SO₂]₀ = 138 ppb, the system reaches an SO₂ concentration of approximately 3.4×10^{12} molecule cm⁻³, where the rate of the bimolecular reaction between SO₂ and sCIs ($k_{bi,298K} = 10^{-11}$ - 10^{-13} cm³ molecule⁻¹ s⁻¹) becomes comparable to that the partial unimolecular reaction of sCIs ($k_{uni,298K} = 10^{-2}$ - 10^8 s⁻¹) (Berndt et al., 2012; Heine et al., 2018; Taatjes et al., 2013; Wang et al., 2019). Thus, excessive SO₂ enhances the consumption of sCIs, ultimately reducing the yield of oxidation products. Notably, the NPF event occurs twice in the series experiments of CNS1-5 (Fig. 1(a₂-e₂)). The NPF appears at the first hour, which process is likely driven by H₂SO₄ with the enhancement of nucleation and growth via the condensation of gaseous species. However, incomplete conversion of NO to NO₂ restricts the yield of O₃, thereby limiting the oxidation of Δ³-carene. NPF reappears at the third hour, coinciding with the occurrence of [NO₂]_{max} and a large accumulation of [O₃]. These findings demonstrate that intensive Δ³-carene oxidation produces a burst of oxidation products, which promotes the gas-phase to particle-phase partition. To further investigate the formation mechanisms of the two NPF events, additional experiment of 70 ppb NO + 117 ppb SO₂ (NS) without Δ³-carene has been performed and the results are shown in Fig. S4. A comparison of the NS (Fig. S4a) and CNS3 (Fig. 1c₂) experiments shows that the NPF event in the NS experiment also begins within 1 h, which is in accord with the first NPF event in CNS3. Thus, it is inferred that the first NPF in the Δ³-carene photooxidation with the presence of SO₂ is primarily driven by H₂SO₄ formation, whereas the second NPF event could be attributed

to the oxidation of Δ³-carene.

Fig. 2b shows that [O₃]_{max} initially increases with rising [SO₂]₀ (56-119 ppb) but declines at [SO₂]₀ = 138 ppb. This suggests that the bimolecular reaction between SO₂ and sCIs promotes the ozonolysis at high [SO₂]₀, thereby inhibiting the O₃ accumulation. In addition, the occurrence time of [O₃]_{max} in the experiments of CNS1-5 exhibits notable fluctuations, following a trend of initial advancement and subsequent delay. This temporal shift is closely linked to variations in the NO_x cycle. As shown in Fig. S3(a₂-e₂), at [SO₂]₀ = 56-119 ppb, the time of [NO₂]_{max} occurs progressively earlier, indicating that SO₂ promotes the conversion of NO to NO₂. At this stage, sCIs are mainly oxidized to RO₂, which stimulates the NO_x cycle and in turn leads to an earlier occurrence time of [O₃]_{max}. With increasing [SO₂]₀ (CNS3-5), the fraction of SO₂ oxidized by sCIs gradually approaches or may even exceed that of the unimolecular reaction of sCIs. This prolongs the conversion of NO to NO₂, thereby delaying the occurrence time of [O₃]_{max}.

The aforementioned results exhibit the multifaceted roles of SO₂, modulating the formation of PM through both direct and indirect pathways. On one hand, the oxidation of SO₂ by sCIs can provide the acidic nuclei (H₂SO₄), which promotes NPF and thereby initiating other reactions (such as condensation and acid-catalysis) to drive particle growth. On the other hand, the concentration of SO₂ is closely linked to the consumption of sCIs, which influences the formation of RO₂. This competition subsequently affects SOA formation and NO_x cycle. These findings are particularly relevant for regions such as the North China Plain, Northwest China and the Guanzhong Basin, where the SO₂-initiated organic aerosols are one of the major factors of haze (Li et al., 2017; Li et al., 2021; Liu et al., 2021; Zhou et al., 2022).

3.3. Oxidation state and chemical evolution of Δ³-carene photooxidation

All the experiments of Δ³-carene (Table 1) were analyzed via an EI-TOF-AMS, for which the results of Van Krevelen (V-K) diagrams are shown in Fig. 3. Aging time is one of the important factors influencing the chemical composition of aerosols in photooxidation processes. Aerosol aging is a highly complex process that leads to the continuous enrichment of oxygen-containing functional groups and an increase in the O:C ratio of the resulting photooxidation products (Hall et al., 2013; Hodshire et al., 2019; Ng et al., 2010). In this study, all experiments in Fig. 3 employed a continuous sampling mode with a uniform sampling interval of 10 min. Under consistent time-series observation, variations in oxidation levels under different conditions provide insights into the changes of the oxidation pathways. The elemental ratios of O:C and H:C can reflect the changes of the functional groups and the oxidation states of the products (Heald et al., 2010; Li et al., 2023). In Fig. 3a, the O:C ratio significantly decreases with increasing [NO]₀, suggesting that NO lowers the overall oxidation states of the products. The addition of nitrogen-containing groups enhances the saturation vapor pressure of products (Capouet and Müller, 2006). Even for some RONO₂ molecules with carbon numbers up to C12, the vapor pressure remains sufficiently high to inhibit their partitioning into the particulate phase (Lim and Ziemann, 2005). Moreover, the reaction of RO₂ + NO → RONO₂ can divert RO₂ from autooxidation pathways, suppressing the formation of highly oxygenated products and thereby lowering the O:C ratio. Zhao et al. (2025) reported that the H:C ratio was lower under low NO₂ conditions (O₃-dominant) as compared to high NO₂ conditions (OH-dominant). Similarly, α-pinene ozonolysis yielded products with a notably lower H:C ratio as compared to those formed via OH oxidation (Chhabra et al., 2010; Chhabra et al., 2011; Shilling et al., 2009). In contrast with our experimental results of CN1-5, the observed H:C ratios show the similarity to those obtained from ozonolysis, indicating that ozonolysis is a viable pathway in Δ³-carene photooxidation, without precluding contributions from other pathways in the photooxidation system. It should be noted that experimental results may exhibit some variability due to differences in smog chamber size, residence time, and other factors. Nonetheless, the overall trend remains generally

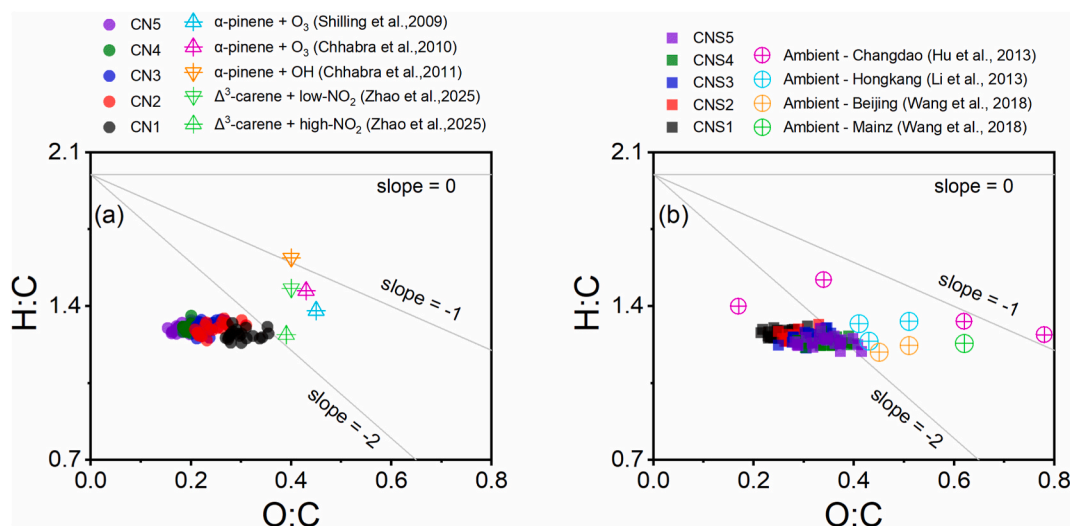


Fig. 3. Van Krevelen diagram for Δ^3 -carene photooxidation experiments. In (a), the principal variable was $[NO]_0$, whereas in (b), the main variable was $[SO_2]_0$. CN1: 407 ppb Δ^3 -carene + 51 ppb NO; CN2: 409 ppb Δ^3 -carene + 70 ppb NO; CN3: 396 ppb Δ^3 -carene + 92 ppb NO; CN4: 387 ppb Δ^3 -carene + 149 ppb NO; CN5: 400 ppb Δ^3 -carene + 199 ppb NO; CNS1: 392 ppb Δ^3 -carene + 65 ppb NO + 56 ppb SO_2 ; CNS2: 390 ppb Δ^3 -carene + 64 ppb NO + 80 ppb SO_2 ; CNS3: 398 ppb Δ^3 -carene + 64 ppb NO + 119 ppb SO_2 ; CNS4: 395 ppb Δ^3 -carene + 61 ppb NO + 138 ppb SO_2 ; CNS5: 387 ppb Δ^3 -carene + 65 ppb NO + 178 ppb SO_2 . Specifically, slope = 0 means the replacement of a hydrogen atom (-H) on an aliphatic carbon ($-CH_2-$) by an alcohol group (-OH) or a peroxide group (-OOH); the slope of -1 corresponds to the formation of a carboxylic acid group ($-C(=O)OH$); and the slope of -2 represents a ketone or aldehyde group ($-C(=O)-$) replaces an $-CH_2-$.

consistent in these studies.

In V-K diagram (Fig. 3b), as $[SO_2]_0$ increases, the H:C ratio exhibits a slight decline, whereas the O:C ratio shows an increase. This trend is a typical characteristic of atmospheric oxidative aging of organic aerosols. During the oxidation process of VOCs, oxygenated functional groups (such as hydroxyl (-OH) and carboxyl (-COOH)) are introduced, leading to an increase in the O:C ratio; besides, hydrogen atoms in the carbon skeleton are often abstracted or replaced, accompanied by the reduction of H:C ratio. The observations in Changdao island showed that higher sulfate concentrations promoted a rise in the O:C ratio of SOA (Hu et al., 2013). Recently, some studies reported that the $ROH + H_2SO_4 \rightarrow ROSO_3H + H_2O$ reaction may occur in the oxidation process of monoterpene (Du et al., 2023; Xu et al., 2021b), which lead to an increase in the O:C ratio. Therefore, the products generated by Δ^3 -carene photooxidation (CNS1-5) may contain the functional group of $-OSO_3H$. In the experiments of CNS1-5, the H:C ratio falls within the range of approximately 1.19–1.32, which are closely aligned with the H:C ratios reported in studies from locations such as Changdao island (1.27–1.52), Hong Kong (1.10–1.60), Beijing (1.19 and 1.22), and Mainz (1.23) (Hu et al., 2013; Li et al., 2013; Wang et al., 2018). The H:C ratio reflects the structural characteristics of the carbon-hydrogen framework within aerosols and serves as a useful indicator for discerning their sources (Ng et al., 2011). Due to differences in the saturation and aromaticity of their precursor compounds, SOA derived from biogenic VOCs (e.g., α -pinene, isoprene) typically exhibits a higher H:C ratio than SOA formed from anthropogenic VOC (e.g., phenol, naphthalene) (Chhabra et al., 2010; Chhabra et al., 2011; Sato et al., 2012; Zhang et al., 2021; Zhao et al., 2015). In field observations, the H:C ratio can be employed to estimate the sources of aerosol precursors, thereby offering experimental evidence for quantifying the contribution of biogenic components to regional SOA. Moreover, the combination of O:C and H:C ratios serves as key parameters for characterizing the oxidation state of organic aerosols. Numerous studies indicate that low-volatility oxygenated organic aerosol (LV-OOA) typically displays higher O:C and lower H:C ratios, whereas semi-volatile OOA (SV-OOA) shows lower O:C and higher H:C ratios (Li et al., 2013; Ng et al., 2010). Furthermore, the overall results observed in Δ^3 -carene + NO + SO_2 experiments closely resemble to those of Hong Kong and Beijing. For instance, atmospheric organic aerosols in Beijing are predominantly attributable to anthropogenic

primary combustion sources, and their secondary aging and transformation are significantly enhanced during haze events; atmospheric organic aerosols in Hong Kong are primarily formed through secondary photooxidation processes that involve synergistic interactions between gas-phase and aqueous-phase reactions. This indicates that to some extent, our experimental results could reflect the characteristics of atmospheric organic aerosols, thereby providing a scientific support for advancing the control of complex air pollution.

3.4. Molecular composition and evolution of Δ^3 -carene photooxidation

To investigate the effect of SO_2 on the chemical compositions of SOA derived from Δ^3 -carene photooxidation, mass spectra were carried out by using the VUV-FEL-TOF-AMS. Previous works showed that optimization of VUV-FEL parameters (e.g. wavelength and pulse energy) could achieve high sensitivity and selectivity in threshold photoionization for monoterpene oxidation experiments (Zhang et al., 2025; Zhao et al., 2024a, b; Zhao et al., 2026b). The VUV-FEL-TOF-AMS experiments on the Δ^3 -carene + NO_2 + SO_2 system at different wavelengths (125 nm, 115 nm, and 105 nm) indicated that 115.0 nm was the optimal wavelength for threshold photoionization of most OSs (Zhao et al., 2025). The CN2 (409 ppb Δ^3 -carene + 70 ppb NO) experiment in the Δ^3 -carene + NO system and the CNS3 (398 ppb Δ^3 -carene + 64 ppb NO + 119 ppb SO_2) experiment in the Δ^3 -carene + NO + SO_2 system correspond to the maximum of SOA yields. Then, the conditions of CN2 and CNS3 were representatively selected to measure the mass spectra at $\lambda_{VUV-FEL} = 115$ nm (Fig. 4 and S5). In Fig. S5a and b, the known complexes with MW = 140 ($C_8H_{12}O_2$, 2,2-dimethylcyclopropyl-1,3-dicarboxaldehyde), 156 ($C_8H_{12}O_3$, 3-norcarallic acid), 168 ($C_{10}H_{16}O_2$, 3-caronaldehyde) and 184 ($C_{10}H_{16}O_3$, 3-caronic acid) are observed, which are consistent with in the literatures (Fang et al., 2016; Song et al., 2025), indicative of the reliability of our VUV-FEL-TOF-AMS. In contrast with the mass spectrum of Δ^3 -carene + NO (Fig. S5a), new peaks of MW = 182 ($C_4H_6O_6S$, 2, 3-dioxobutyl hydrogen sulfate), 198 ($C_4H_6O_6S$, 2,3-dihydroxy-3-methylbuty hydrogen sulfate), and 200 ($C_5H_{12}O_6S$, 3-hydroxy-3-methyl-2-oxobutyl hydrogen sulfate) can be seen in the Δ^3 -carene + NO + SO_2 experiment (Fig. S5b), indicative of important contribution from SO_2 . These peaks are new products and thus selected for discussions. To further assess the generation pathway of these oxidation products (MW

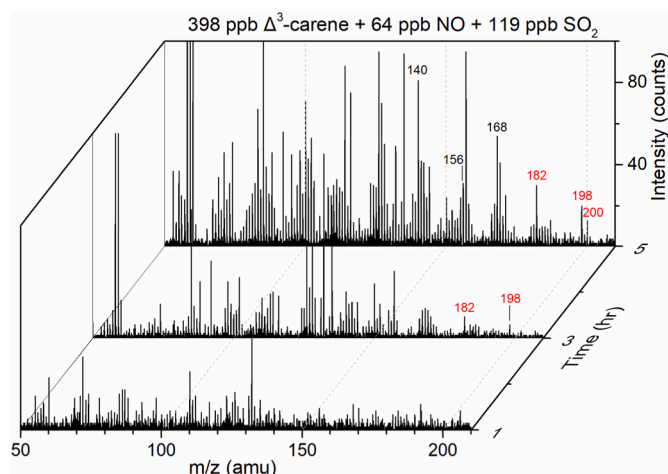


Fig. 4. Temporal evolution of VUV-FEL photoionization mass spectra. Newly-observed compounds are marked with red. All mass spectra were background-subtracted. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

= 182, 198, and 200), Δ^3 -carene ozonolysis experiments were designed (Table S2). A detailed description of the ozonolysis experiments and results could be found in SM (Fig. S6, S7 and S8). The peaks of MW = 182, 198, and 200 are both observed in the ozonolysis experiments with or without OH scavenger (Fig. S8), indicating that these complexes could be formed via the ozonolysis pathway.

As noted above, NPF event occurs twice in the E8 experiment. To explore the chemical compositions of SOA in these different NPF events, mass spectra at different time points are compared in Fig. 4. At the initial stage (the first hour), the mass spectrum shows sparse signal peaks with very low intensities, indicating that the concentration of SOA is low, consistent with minimal amounts of particles (Fig. 1c₂). At the third hour, the particle number concentration reaches its first peak, as indicated by a noticeable increase in the number of mass spectra peaks (Fig. 4). The peaks of MW = 140, 156, 168, 182 and 198 are observed. As discussed above, the formation of H_2SO_4 may be the key driver of the first NPF. With the emergence of H_2SO_4 , the new products of MW = 182 and 198 appeared in the presence of SO_2 are assigned to the OSs. Furthermore, the detection of oxidation products (MW = 140, 156, and 168) implies that the formation of H_2SO_4 contributes to adsorb the gas-phase products. At the fifth hour, both the number and intensity of mass spectra peaks significantly increase, which could be due to the substantial oxidation of Δ^3 -carene. Moreover, a new peak appears at MW = 200 and is identified as another OS. These findings indicate that the second NPF is primarily generated by Δ^3 -carene oxidation, and the product compositions comprehensively reflect the overall compositions of VOC oxidation. Notably, as photooxidation progresses, the number and intensity of lower MW peaks continuously increase, indicative of not only the continuous accumulation of small molecule oxidation products but also the gradual enrichment of oxidants in the system, promoting the overall oxidation process. Furthermore, lower MW peaks are formed preferentially in the early reaction stages, whereas high MW peaks mainly appear during the later phases of photooxidation. This differentiation underscores oxidation mechanisms: low MW products likely arise from initial rapid processes, including hydrogen abstraction, addition, and decomposition, which yield strong signals and are thus detected early by mass spectra. In contrast, high MW products depend on more complex reactions involving multiple oxidation processes and cross-reactions, leading to their gradual accumulation in the later stages.

3.5. Possible mechanisms of organosulfates

The VUV-FEL-TOF-AMS results indicate that SO_2 modifies the

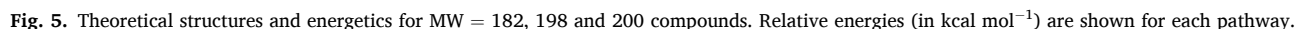
chemical composition of SOA significantly, with the observation of new OS compounds of MW = 182, 198 and 200. In this study, O_3 is generated by the NO_x photolysis cycle and is suggested to be the key oxidant from the above analyses. Recent studies of Δ^3 -carene ozonolysis provide important clues for this work (Fang et al., 2016; Song et al., 2025; Wang et al., 2019). Theoretical study at the $\omega\text{B97XD/def2-TZVP}$ level were conducted with the aim of elucidating the formation mechanisms of these newly-observed compounds. All the proposed mechanisms are thermodynamically favorable and kinetically feasible (Fig. 5). Nevertheless, we do not exclude alternative molecular structures or pathways. Specially, theoretical calculations were performed to determine the energy barriers for key processes including decomposition, H-shift, and isomerization. The corresponding results are illustrated in Fig. 5.

As shown in Fig. 5, Δ^3 -carene undergoes a [3 + 2] cycloaddition with O_3 to yield highly unstable POZ, which rapidly decomposes to produce a sCI (C-I1). This process is predicted to be facile with the exothermicity of $191.9 \text{ kcal mol}^{-1}$ and the barrier of $22.0 \text{ kcal mol}^{-1}$, respectively. C-I1 releases CO_2 and quickly reacts with an O_2 to form C-I2, which is thermodynamically exothermic with a calculated value of $45.8 \text{ kcal mol}^{-1}$. Considering that the $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ reaction is an important oxidation pathway in the presence of NO, C-I3 derives from the bimolecular reaction of C-I2 with NO. Since H-shift reaction and isomerization are generally the dominant fates of radicals, C-I3 may undergo 1,4-H-shift and isomerization to generate C-I4 with the predicted barrier of $9.6 \text{ kcal mol}^{-1}$ and $7.7 \text{ kcal mol}^{-1}$, respectively. Theoretical calculations confirm that the process C-I4 $\rightarrow$ C-I5 is exothermic ($43.3 \text{ kcal mol}^{-1}$). Obviously, the double bond in C-I5 makes it susceptible to oxidation by O_3 . Consequently, similar reaction pathways lead to the formation of multiple intermediates (C-Ix ($x = 6-12$)). The formation of a ketone group typically coincides with the loss of hydrogen atom from the carbon skeleton, whereas the formation of an aldehyde group is often associated with hydrogen addition. The formation of such multifunctional structures C-Py ($y = 1, 3$ and 5) are theoretically plausible, and the processes are exothermic. Finally, the OSs of MW = 182, 198 and 200 (C-Py ($y = 2, 4$ and 6)) compounds are formed from nucleophilic reactions, which are calculated to be exothermic by $4.9 \text{ kcal mol}^{-1}$, $3.1 \text{ kcal mol}^{-1}$, and $6.2 \text{ kcal mol}^{-1}$, respectively. Moreover, the proposed mechanisms of these structures match the trends of the V-K diagram (Fig. 3b), providing a molecular-level explanation for the observed impacts of SO_2 on the Δ^3 -carene photooxidation.

The smog chamber experiments in this study were conducted under very dry conditions ($\text{RH} < 5\%$), and the influence of H_2O on the reaction system was not considered. However, RH is a critical parameter in the actual atmosphere, influencing SOA formation mechanisms and physicochemical properties (Alramzi et al., 2025; Sun et al., 2013). Field observations have shown that variations in RH modify the growth factors of particles and influence the activity coefficients of organic compounds (Li et al., 2020; Nguyen et al., 2016). Additionally, laboratory studies have demonstrated that RH influences the ozonolysis of monoterpenes through multiple mechanisms, primarily driven by the reaction of H_2O with sCIs (Huang et al., 2023; Zhang et al., 2023). Moreover, reactions between H_2O and sCIs can perturb SO_2 oxidation, shifting the oxidation pathway of sCIs and SO_2 , which influences sulfate production and governs SOA formation (Xu et al., 2021a; Ye et al., 2018; Zhang et al., 2019). In the future, it will be interesting to systematically study the formation mechanisms of SOA under different RH conditions.

4. Conclusions

Due to the inherent chemical complexity of SOA and their high sensitivity to environmental factors, the clarification of the influence of gaseous pollution on SOA formation mechanisms has been proved to be a significant challenge in the precise measurements. In this study, a series of targeted photooxidation experiments were conducted in a small smog chamber. This experimental design enables effective control of



Both particle number concentration and SOA yield show an initial increase followed by a decrease with rising SO₂ concentrations. Based on the literatures, these results are likely due to the alteration in the reaction pathways of sCIs: at low SO₂ concentration, the dominant fate of sCIs points to the formation of RO₂; as the SO₂ concentration increases, the oxidation reaction with the involvement of SO₂ gradually becomes a significant sink for sCIs. Two distinct NPF events are observed with the presence of SO₂. The first NPF event is mainly caused by the nucleation of H₂SO₄, while the second one is attributed to the oxidation of Δ³-carene. Several previously-unreported OSs are tentatively identified by mass spectral analyses and their potential oxidation pathways are proposed. This study's findings on the impacts of SO₂ on SOA formation not only deepen our understanding of atmospheric chemical processes but also provide crucial scientific evidence for regional air quality

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2026.128185>.

Data availability

Data will be made available on request.

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