

Contents lists available at ScienceDirect

Atmospheric Environment



journal homepage: www.elsevier.com/locate/atmosenv

Anthropogenic effects on Δ^3 -carene photooxidation: Different oxidants induce significant changes of secondary organic aerosol formation mechanisms

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HIGHLIGHTS

- The key oxidant of Δ^3 -carene photooxidation is found to be OH under low-NO₂ conditions and O₃ under high-NO₂ conditions.
- SO₂ significantly promotes the formation of highly oxidized molecules via the acid-catalyzed pathway.
- Newly-developed threshold photoionization technique enables the observation of a series of new compounds.

G R A P H I C A L A B S T R A C T



https://doi.org/10.1016/j.atmosenv.2025.121313

Received 9 April 2025; Received in revised form 19 May 2025; Accepted 23 May 2025 Available online 23 May 2025

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ARTICLE INFO

Keywords:

 $\begin{array}{l} \mbox{Anthropogenic-biogenic interactions}\\ \mbox{Secondary organic aerosol}\\ \mbox{Photooxidation mechanism}\\ \Delta^3\mbox{-}\mbox{arene} \end{array}$

ABSTRACT

Elucidating the effects of anthropogenic pollutants on the formation mechanism of secondary organic aerosol (SOA) is crucial for the improvement of atmospheric models toward the development of effective control strategies. It is extremely challenging to precisely clarify the impacts of concentrations of anthropogenic pollutants on the molecular compositions and particle number/mass concentrations of SOA under complicated conditions. Here, we report a series of the studies on the effects of anthropogenic pollutants (NO₂ and SO₂) on the photo-oxidation of a representative monoterpene, Δ^3 -carene, by using the scanning mobility particle sizer spectrometer, recently-developed vacuum ultraviolet free electron laser (VUV-FEL) photoionization aerosol mass spectrometry, and quantum chemical calculations. The results indicated that with the increase of NO₂ concentration, the SOA yields increased under low-NO₂ conditions, whereas O₃ became the dominant oxidant under high-NO₂ conditions. SO₂ substantially enhanced the formation of highly oxidized molecules via the acid-catalyzed pathway. A series of new compounds (i.e., organic peroxides, organic nitrates, and organosulfates) were observed and their formation mechanisms were proposed. The present findings highlight the critical role of anthropogenic pollutants in the photooxidation of monoterpene under low and high pollution environments and also open new avenues toward systematic studies of a broader class of volatile organic compounds.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are globally the main precursors for the formation of secondary organic aerosol (SOA), which make great impacts on air quality, human health, climate, and ecosystem (Mellouki et al., 2015; Shiraiwa et al., 2017). Monoterpenes (C10H16), a class of BVOCs with high emission rates and reactivity, have a relatively short atmospheric lifetime of several hours or less and are susceptible to atmospheric oxidation. Once emitted into the atmosphere, BVOCs can undergo reactions with atmospheric oxidants such as hydroxyl radical (OH), ozone (O₃), and nitrate radicals (NO₃) (Mellouki et al., 2015). OH and O3 are two main oxidants during the daytime photooxidation with the relative dominance influenced by NO_x levels (Atkinson, 2000; Sarrafzadeh et al., 2016). In recent years, most studies have elucidated the mechanisms of BVOCs oxidation with single oxidant and identified a series of characteristic products (D'Ambro et al., 2022; DeVault and Ziemann, 2021; Fang et al., 2016). However, the formation of SOA from BVOCs in real environment exhibits intricate characteristics influenced by the types of atmospheric oxidants and multiple atmospheric environmental parameters. Hence, precise elucidation of chemical compositions and oxidation pathways of BVOCs-derived SOAs under complex conditions is a very important but challenging task.

The anthropogenic pollutants, such as nitrogen oxides ($NO_x = NO +$ NO₂) and sulfur dioxide (SO₂), are involved in the formation of biogenic SOA formation by affecting the gas-phase oxidation and gas-particle partitioning processes (Fan et al., 2022; Ma et al., 2023). NO_x enters the atmosphere primarily as nitric oxide (NO), which is subsequently oxidized to NO₂ and then to organic nitrates. The effects of NO_x on the reaction pathways of organic peroxy radicals (RO₂) formed during the VOCs oxidation are generally known to be pronounced (Zhao et al., 2018). The fate of RO_2 is highly sensitive to the NO_x levels, for which RO_2 mainly reacts with HO_2 at low NO_x concentration or with NO at high NO_x concentration (Fan et al., 2022; Sarrafzadeh et al., 2016). Previous experiments have generally evidenced that the correlation between the SOA yield and the NOx concentration is nonlinear (Aruffo et al., 2022; Liu et al., 2022; Qi et al., 2020). The likely reason is that NO_x can regulate the balance of oxidants (i.e., OH, O₃, and NO₃) to influence the proportion between organic peroxides (POs) and organic nitrates (ONs) (Draper et al., 2015; Sarrafzadeh et al., 2016).

Besides the heavy NO_x emissions, SO_2 is another significant gas pollutant, which is generally released into the troposphere via the combustion of fossil fuels and volcanic emissions (Smith et al., 2001). Generally, the oxidation of SO_2 in the atmosphere involves the reactions with OH and stabilized Criegee intermediates (sCIs), resulting in the formation of sulfuric acid (H₂SO₄) or organosulfates (OSs) (Mauldin Iii et al., 2012; Sipilä et al., 2010; Ye et al., 2018). Modeled or field-observed H₂SO₄ serves as the primary precursor for nucleation particle formation (NPF) in the atmospheric environments, acting as seeds to facilitate the condensation of product vapors by increasing the available surface area and volume (Sipilä et al., 2010; Zhou et al., 2023). Recent chamber studies have demonstrated that the effects of SO_2 on biogenic SOA formation involve not only the NPF processes but also the enhancement of acid-catalyzed heterogeneous reactions (Xu et al., 2021; Yang et al., 2021, 2023).

Based on modelling estimates, Δ^3 -carene contributes 6 % to global annual monoterpene emissions, ranking as the sixth most abundant monoterpene species (Sindelarova et al., 2014). Recent studies have demonstrated that the oxidation of Δ^3 -carene is significantly influenced by multigenerational reactions and cross-reaction pathways, which play a critical role in the formation of Δ^3 -carene-derived SOA (DeVault and Ziemann, 2021; Thomsen et al., 2022; Zhang et al., 2025). These processes result in a substantial reduction of molecular volatility, leading to a higher SOA yield and a more diverse distribution of SOA products as compared to other monoterpenes (Liu et al., 2022; Thomsen et al., 2021; Zhang et al., 2024a). Strikingly, several oxidized Δ^3 -carene dimers were proposed to significantly contribute to NPF and aerosol growth, as evidenced by laboratory-generated SOA studies (Thomsen et al., 2021). While the oxidation mechanisms of Δ^3 -carene by specific oxidants has been proposed and some oxidation products has been identified, understanding of chemical compositions and reaction pathways of photooxidation products in complex environments is very limited. In this study, we investigated the effects of NO2 and SO2 on aerosol formation during Δ^3 -carene photooxidation and discussed the formation mechanisms of SOA. The chemical properties and molecular compositions of SOA were studied systematically with the laboratory-developed online instruments. A series of new products (including organic peroxides, organic nitrates, and organosulfates) were observed and their formation pathways were proposed. The present results provide new insights into the complex interactions between Δ^3 -carene, NO₂, and SO₂ during the daytime, which advance our understanding of the underlying mechanisms of anthropogenic-biogenic interactions and have important implications for the improvement of atmospheric models.

2. Materials and methods

2.1. Smog chamber experiments

To investigate the effects of NO₂ and SO₂ on the photooxidation of Δ^3 -carene, three groups of experiments (Table 1) were conducted by using the DICP-CAS chamber (Dalian Institute of Chemical Physics, Chinese Academy Sciences). The DICP-CAS smog chamber consists of a 2 m³ cylindrical fluorinated ethylene propylene film reactor (Zang et al., 2022). Before the start of experiment, the chamber was purged with purified and dried zero air for 12 h to ensure a clean background. The

experimental procedure involved the following steps: (1) injection of a precisely measured volume of Δ^3 -carene (>90.0 %, Aladdin) into the smog chamber using zero air; (2) introduction of NO₂ (497 ppm in N₂, Kylingas) and SO₂ (495 ppm in N₂, Kylingas) into the chamber via the calibrated gas cylinders; (3) allowing the chamber to equilibrate for 30 min to ensure thorough mixing of all components; (4) turning on the blacklights to initiate the reaction, in which the reaction's time zero was the moment of light turning on. The cyclohexane (>99.9 %, Innochem) was used as OH scavenger. With the concentration ratio of Δ^3 -carene to cyclohexane as 1:100, the initial concentration of cyclohexane was about 40 ppm.

The concentrations of Δ^3 -carene were measured by using a protontransfer reaction mass spectrometer (PTR-QMS 3500, East & West Analytical Instruments, China). The concentrations of NO, NO₂ and NO_x were monitored with a gas analyzer (Model 42i, Thermo Fisher Scientific, USA), and those of SO₂ were measured using a separate gas analyzer (Model 43i, Thermo Fisher Scientific, USA). The O₃ concentrations were determined with another gas analyzer (Model 49i, Thermo Fisher Scientific, USA). The number concentrations, volume and size distributions of particles were analyzed by using a scanning mobility

Table 1 Initial experimental conditions and results for all Δ^3 -carene photooxidation experiments.

particle sizer spectrometer (SMPS 3938L76, TSI Incorporated, USA). Particle mass concentrations were determined based on an assumed density of 1.0 g/cm^3 and the SMPS-determined volume concentration. All the mass concentrations have been wall-loss corrected.

2.2. Product analysis

The chemical compositions of the particles were detected by a homebuilt time-of-flight aerosol mass spectrometer (TOF-AMS) based on vacuum ultraviolet free-electron laser (VUV-FEL) photoionization (abbreviated as VUV-FEL-TOF-AMS), as described in our previous study (Zang et al., 2022). The VUV-FEL-TOF-AMS enables online detection of particle phase products, with a mass-to-charge ratio (m/z) detection range of 0–500. The full particles were transported from the reaction chamber to the TOF-MS chamber via a silicone tubing and aerodynamic lens assembly without pre-separation. The deposited particles were vaporized by using a cartridge heater, ionized by VUV-FEL, and detected by TOF-MS in positive ion mode. In our work, the detected mass spectral peaks correspond to the molecular weight (MW) values. A key advantage of this approach is able to measure neutral compounds via

Exp. ID ^a	$[\Delta^3$ -carene $]_0$	[NO ₂] ₀	[SO ₂] ₀	$[\Delta^3$ -carene] ₀ /	[O ₃] _{max}	ΔROG	ΔM (µg/	SOA Yield	RH	T (K)
	(ppb) ^b	(ppb) ^b	(ppb) ^b	$[NO_2]_0^{D}$	(ppb) ^b	(ppb) ^c	m ³) ^d	(%)	(%)	
CN-1	399	50	_	8.0	110	284	301.5	19.1	1.2	295.5
CN-2	411	117	-	3.5	148	309	405.5	23.6	0.8	294.8
CN-3	406	192	-	2.1	201	321	485.6	27.2	1.2	295.6
CN-4	408	328	-	1.2	215	316	591.8	33.6	1.9	295.5
CN-5	406	388	-	1.0	175	317	535.4	30.3	1.8	295.1
CN-6	417	479	-	0.9	157	331	528.5	28.7	1.8	295.5
CN-7	412	697	-	0.6	149	335	487.7	26.1	2.2	296.0
CNS-200-	403	203	22	2.0	145	327	647.1	35.5	1.8	295.3
1										
CNS-200-	418	198	42	2.1	137	328	657.7	36.0	1.2	295.5
2		100	0.6		107	01.6	505.0	41.0	1.0	005 5
CNS-200-	393	196	96	2.0	137	316	727.0	41.3	1.3	295.7
3 CNE 200	400	101	157	0.1	196	21.0	741 4	41.0	2.6	205.7
CNS-200-	402	191	157	2.1	130	518	/41.4	41.9	2.0	295.7
T CNS-200-	300	104	105	2.1	130	317	785.0	44 5	0.2	205.8
5	555	1)4	155	2.1	155	517	705.0	11.0	0.2	295.0
CNS-200-	415	182	270	2.3	116	317	849.0	48.1	2.3	296.0
6										
CNS-200-	410	197	466	2.1	112	311	924.8	53.4	1.8	296.3
7										
CNS-200-	429	204	665	2.1	115	336	1060.4	56.7	1.4	296.3
8										
CNS-400-	371	386	24	1.0	210	334	755.1	40.6	1.9	295.3
1										
CNS-400-	399	388	48	1.0	164	339	1044.6	55.0	1.9	295.3
2										
CNS-400-	398	388	77	1.0	155	338	902.8	47.3	1.8	295.7
3										
CNS-400-	397	388	92	1.0	161	336	866.0	46.3	2.3	295.4
4 CNE 400	205	205	170	1.0	146	222	056.6	F0 F	1.4	205.7
CINS-400-	395	395	1/8	1.0	140	332	950.0	50.5	1.4	295.7
5 CNS 400	307	306	297	1.0	140	303	021.2	51.2	15	205.3
6	397	390	207	1.0	140	323	921.2	51.2	1.5	293.3
CNS-400-	401	302	477	1.0	152	330	1059 5	57 7	12	205.4
7	101	072	.,,	1.0	102	550	1009.0	0/1/	1.2	2,0.4
, CNS-400-	395	398	670	1.0	149	326	1067.7	58.8	1.8	295.3
8										

^a Exp. ID is named by the initial letter of the reactants introduced into the smog chamber and experimental sequence number. Letter "C", "N" and "S" stands for Δ^3 -carene, NO₂ and SO₂, respectively. Here, the experiment with the $[\Delta^3$ -carene]_0/[NO₂]_0 ratio larger than 1.2 is referred as low-NO₂ conditions, whereas that smaller than 1.2 is referred as the high-NO₂ conditions. Numbers "200" and "400" represent the 200 ppb of [NO₂]_0 in the low-NO₂ conditions and the 400 ppb of [NO₂]_0 in the high-NO₂ conditions, respectively.

 \overline{D} [X]₀ stands for the initial concentration of the species X and $[O_3]_{max}$ for the maximum accumulation of O_3 in the experiments.

 $^{\rm c}~\Delta {\rm ROG}$ stands for the amount of reacted organic gas.

 $^{\rm d}$ ΔM is particle mass concentrations at steady state obtained by multiplying SMPS-determined volume concentrations by the assumed density of 1 g cm⁻³ and has been wall-loss corrected.

threshold photoionization using a tunable VUV-FEL. Since different aerosol components may exhibit varying ionization potentials, the use of different VUV-FEL wavelengths (photon energies) facilitates threshold ionization and minimizes the fragment formation. As demonstrated in our previous studies, new neutral compounds can be detected by optimizing the VUV-FEL wavelength and pulse energy (Zhang et al., 2024b; Zhao et al., 2024). During the experimental optimization, the dependence of the mass spectral signal on VUV-FEL pulse energy was evaluated to avoid photoionization saturation.

The chemical characteristics of particles was analyzed by using another TOF-MS based on thermal desorption and electron ionization (abbreviated as EI-TOF-AMS) (Zang et al., 2024). The sampling process involved the introduction of particles through an aerodynamic lens, followed by thermal desorption at approximately 873 K to volatilize the particulate compounds. The vaporized compounds were subsequently ionized via electron ionization (about 70 eV) and analyzed by using a W-mode TOF-MS instrument. While the detailed working principle of EI-TOF-AMS has been previously reported (DeCarlo et al., 2006), the EI-TOF-AMS was mainly employed to investigate the oxidation states of SOA particles in this work. This analysis was based on two characteristic ions in the mass spectra: m/z = 44 (indicative of di- and poly-carboxylic acid functional groups, CO_2^+) and m/z = 43 (representative of non-acidic oxygenates, $C_2H_3O^+$) (Ng et al., 2010).

The VUV-FEL-TOF-AMS and EI-TOF-AMS have been calibrated by a series of standard organic compounds (i.e., vanillin, 1-pentadecanol, n-Eicosane, etc.). These calibrations were performed every month to ensure the accuracy of measurement.

2.3. Theoretical methods

To understand the experimental results and the photooxidation mechanisms of Δ^3 -carene, quantum chemical calculations were conducted at the ω B97XD/def2-TZVP level of theory by using the Gaussian 16 computational chemistry software package (Frisch et al., 2016). Theoretical calculations include geometric optimization and frequency calculation of the intermediates, transition states (TSs), and products. TSs were optimized by using the Berny algorithm, and their validity was

verified through rigorous intrinsic reaction coordinate (IRC) analysis. The relative energies included the zero-point vibrational energy (ZPVE) corrections. The using of present theoretical methods was based on our recent studies on the effects of isoprene on the ozonolysis of Δ^3 -carene and β -caryophyllene (Zhang et al., 2025).

3. Results and discussion

3.1. Effects of [NO₂]₀ and [SO₂]₀ on SOA formation

Experiments CN-X (X = 1-7) were designed to study the effects of $[NO_2]_0$ on the Δ^3 -carene + NO₂ photooxidation reactions. As shown in Fig. 1a₁, the particle mass concentration increases with the increase of [NO2]0 from 50 ppb to 328 ppb and then decreases with further increasing $[NO_2]_0$ up to 697 ppb. Note that the variation in particle mass concentration arises from the combined effects of particle number concentration and size distribution. As demonstrated in Fig. S3a and b, we analyzed the particle number concentration and size distribution for the CN-X experiments. The particle number concentration sharply increases with the increase of [NO₂]₀ from 50 ppb to 192 ppb and then converges with further increasing $[NO_2]_0$ up to 697 ppb (Fig. S3a). In contrast, with the increase of $[NO_2]_0$ from 50 ppb to 697 ppb (Fig. S3b), the particle size of peak A remarkably decreases and that of peak B slightly decreases. In the low-NO2 conditions, the increase of [NO2]0 enhances the formation of oxidants in the photochemical cycle, which facilitates the VOC oxidation. This leads to an increase in the particle number concentrations and consequently mass concentrations. However, for high-NO2 conditions, the conversion of NO in the system increases significantly. NO can alter the reaction pathways of RO₂, resulting in an increase of highly volatile organic compounds. This higher volatility is detrimental to particle formation and condensation, resulting in a decreasing particle size and a reduced particle mass concentration. Particularly, as shown in Fig. 1b1, all CN-X experiments exhibit bimodal particle size distributions (peaks A and B), which suggests that at least two dominant reaction channels exist in the Δ^3 -carene + NO₂ experiments.

Furthermore, particle mass concentration (Fig. 2a), SOA yield



Fig. 1. Particle mass concentrations (a_1-a_3) and particle size distributions (b_1-b_3) for all Δ^3 -carene photooxidation experiments. D_p : particle diameter. dN/dlogD_p: normalized number size distribution.



Fig. 2. Particle mass concentrations (a and d), SOA yields (b and e) and $[O_3]_{max}$ (c and f) as a function of $[NO_2]_0$ and $[SO_2]_0$, respectively. The black square, red dot and blue triangle represent the series experiments of CN-X, CNS-200-X and CNS-400-X, respectively. Letter "X" represents experimental sequence number as listed in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(Fig. 2b), and maximum ozone concentration $([O_3]_{max})$ (Fig. 2c) show a similar trend as a function of [NO₂]₀. The relationship between the SOA yields and the initial NO₂ concentrations in this work is consistent with the trends observed in previous studies (Aruffo et al., 2022; Lane et al., 2008; Zhao et al., 2018). The primary reason for this may lie in the NO_x cycle, where the variations in NO_x concentration disrupt the balance of oxidants in the photochemical cycle. Our study indicates that under low-NO2 conditions, HO2 and RO2 generated from NO2/NO interconversion are rapidly converted to OH, a reactive species that is capable of triggering Δ^3 -carene oxidation. Under high-NO₂ conditions, while NO contributes to O₃ formation, it also terminates the RO₂ fate, thereby inhibiting the OH production and shifting the primary oxidant to O₃. Notably, the maximum accumulation of O₃ in this work shows a nonlinear response, which is similar to the previous results (Zang et al., 2024; Zhang et al., 2024b). This finding corroborates our earlier discussion, demonstrating that OH dominates the oxidation process under low-NO₂ conditions, whereas O₃ gradually becomes the predominant oxidant under high-NO2 conditions.

To further understand the combined effect of NO2 and SO2 on the photooxidation of Δ^3 -carene, two series of comparative experiments were performed under low-NO₂ (~400 ppb Δ^3 -carene + ~200 NO₂ ppb + X ppb SO₂ (CN-200-X)) and high-NO₂ (~400 ppb Δ^3 -carene + ~400 $NO_2 ppb + X ppb SO_2$ (CN-400-X)) conditions, respectively. Fig. 1a₂ and a3 shows the influence of SO2 on the particle mass concentrations at low-NO2 and high-NO2 conditions, respectively. Under low-NO2 conditions (Fig. $1a_2$), an increase of $[SO_2]_0$ leads to a gradual rise in the particle mass concentrations (Fig. 2d, red curve). In contrast, under high-NO2 conditions (Fig. 1a3), a different trend emerges: the particle mass concentration first increases with the increase of [SO₂]₀ from 24 ppb to 48 ppb, decreases with the increase of [SO₂]₀-92 ppb, and then increases again with the further increase of [SO₂]₀-670 ppb (Fig. 2d, blue curve). Such trend at high-NO₂ conditions is confirmed by several replicating experiments, with detailed conditions listed in Table S1 and the results shown in Fig. S4.

The particle size distributions under low-NO₂ (CN-200-*X*) and high-NO₂ (CN-400-*X*) conditions are depicted in Fig. $1b_2$ and b_3 , respectively. Compared with the SO₂-free experiments, the results reveal notable differences: the particle size distribution exhibits a broader range and

enhanced intensities, indicating that the oxidation reaction in the system is enhanced. The corresponding temporal evolution of particle size distributions is shown in Fig. S2, indicating that the variations in the particle number concentrations align well with the trends observed for mass concentrations under different conditions. The trend of mass concentrations under the CN-200-X conditions (Fig. 2d) are similar to that of SOA yields (Fig. 2e). This also holds true for the CN-400-X conditions. For instance, the SOA yield in the CN-200-X conditions (Fig. 2e, red curve) shows a gradual increase with rising [SO₂]₀, suggesting that SO_2 facilitates the SOA formation in the Δ^3 -carene photooxidation under low-NO2 conditions. In contrast, the SOA yield in the CN-400-X conditions (Fig. 2e, blue curve) exhibits more variable behaviors, implying that SO₂ may play different roles in various [SO₂]₀ stages under high-NO₂ conditions. In addition, the maximum ozone concentration (Fig. 2f) decreases with the increase of [SO₂]₀ under both CN-200-X and CN-400-X conditions.

It can be inferred from the above discussion that the Δ^3 -carene oxidation via OH is favored in the low-NO2 conditions. When SO2 is introduced, it can be oxidized by OH to form sulfuric acid particles (Sipilä et al., 2010). The addition of SO₂ provides acid nuclei to promotes particle growth and gradually enhances acid catalysis. These factors contribute to the observed increase in the SOA formation. Simultaneously, SO₂ and Δ^3 -carene compete for OH, thereby leaving the chance for the O_3 oxidation reaction. This effect is corroborated by the trend chart of [O₃]_{max} as a function of [SO₂]₀ (Fig. 2f). Note that the O₃ oxidation reaction generates sCIs, which also could oxidize SO₂ to form H₂SO₄, thereby continuing to drive SOA growth (Du et al., 2023; Mauldin Iii et al., 2012; Ye et al., 2018). In the high-NO₂ conditions with SO2 addition, the decrease of [O3]max is relatively modest, suggesting that O3 is likely still the dominant oxidant. Regarding the variability of SOA yields at high-NO2 conditions with SO2 addition (Fig. 2e, blue curve), it is hypothesized that when $[SO_2]_0 < 48$ ppb, SO₂ primarily promotes nucleation, as evidenced by the increased particle number concentrations. In the range of $[SO_2]_0 = 48-92$ ppb, Fig. S2 shows a significant decline in the particle number concentrations, suggesting that a substantial portion of oxidation products is adsorbed onto the sulfuric acid particles. While the gas-particle partitioning and acid-catalysis processes are somewhat enhanced, they are insufficient to compensate for the loss of sCIs, consequently reducing the particle mass concentrations and SOA yields. As $[SO_2]_0$ increases further, the number concentrations rise significantly again. This indicates that the numbers and states of oxidation products may approach to the saturation levels, with sulfuric acid nucleation once again becoming the primary driver of SOA formation, leading to an increase of both particle mass concentrations and SOA yields.

3.2. General molecular characteristics

A series of photooxidation experiments under the ~400 ppb Δ^3 carene + X NO₂ ppb (CN-X), ~400 ppb Δ^3 -carene + ~200 NO₂ ppb + X ppb SO₂ (CN-200-*X*), and ~400 ppb Δ^3 -carene + ~400 NO₂ ppb + *X* ppb SO₂ (CN-400-X) conditions were also conducted using EI-TOF-AMS and the results are shown in Fig. 3. The observed differences in the mass spectra primarily stem from the m/z = 44 (predominantly CO₂⁺) and m/z= 43 (mainly $C_2H_3O^+$) peaks. Therefore, the ratio of m/z = 44 to total organic aerosol (f_{44}) is plotted as a function of f_{43} . Notably, m/z = 44 and O/C have significant correlation (Aiken et al., 2008), which justifies f_{44} values serve as a reliable indicator of atmospheric aging and are employed to assess the oxidation states of SOA. The triangular region in the f_{44} vs. f_{43} plot signifies the typical range of SOA oxidation states. For semi-volatile oxygenated organic aerosols (SV-OOA), the average f_{44} values range from 0.07 \pm 0.04, whereas low-volatile oxygenated organic aerosols (LV-OOA) exhibit higher average f_{44} values of 0.17 \pm 0.04 (Ng et al., 2010). Most of the SOA mass spectral tests derived from smog chamber experiments are located in the lower portion of the triangle in the f_{44} vs. f_{43} plot (Chen et al., 2017; Sato et al., 2012; Zang et al., 2024). This observation is likely attributed to the fact that the experimental conditions in the laboratory are significantly more intense than atmospheric loads, leading to the incorporation of less oxidized, more volatile products into the aerosol phase. Additionally, the size constraints and limited residence time of the laboratory chambers can hinder the SOA from achieving the oxidation levels observed in field measurements. The results obtained in this study also fall within the lower section of the triangular region, suggesting that the aerosol exhibits relatively low oxidation states and should be classified as SV-OOA.

Fig. 3a shows the triangle plot for all the SOA components formed from the Δ^3 -carene photooxidation in the presence of NO₂. The result indicates that as [NO₂]₀ increases, the f_{44} value decreases progressively, suggesting that higher NO₂ concentration leads to a lower oxidation state of the oxidation products. This trend is likely due to the fact that with increasing [NO₂]₀, the reaction pathways involving RO₂ and NO become increasingly significant, favoring the formation of ONs. Indeed, the introduction of nitrogen atom was found to be able to enhance the vapor pressures of oxidation products (Capouet and Müller, 2006). ONs is highly volatile, which hinders their transition from the gas phase to the particle phase and consequently reduces the SOA yields. Additionally, the increase of RO₂ and NO oxidation pathway not only enhances the production of ONs but also reduces the proportion of other RO_2 pathways (e.g., cross-reaction and autooxidation processes), thereby suppressing the formation of low-volatility organic compounds. This may also contribute to the observed decrease of the f_{44} values.

As shown in Fig. 3b and c, the f_{44} vs. f_{43} values for the Δ^3 -carene photooxidation at different NO2 concentrations revealed how [SO2]0 affects the SOA characteristics. The results demonstrated that as $[SO_2]_0$ increases, the f_{44} value all gradually approaches the upper region of the triangle plot, indicative of the enhanced SOA oxidation states and altered oxidation product characteristics. However, when [SO₂]₀ exceeds 200 ppb, the change of f_{44} becomes negligible, suggesting that the capacity of SO2 is limited. The addition of SO2 to the experiments introduces sulfuric acid particles, which may facilitate the capture of low oxidation products from gas phase into the particle phase, thereby reducing the overall oxidation states of SOA. Conversely, the presence of acid nuclei provided sites for acid-catalyzed multiphase reactions, promoting the formation of OSs and further increasing the oxidation states of products. In this work, a significant increase of the f_{44} values with rising [SO₂]₀ is observed, indicating the production of particulate organics with high oxidation state (i.e., OSs), which have a very obvious promoting effect. OSs has also been observed in previous laboratory studies (Du et al., 2023; Surratt et al., 2007; Yang et al., 2021), which supports the present findings. Additionally, it is observed that both the mean and range of f_{43} in the SOA component decrease as f_{44} increases. This suggests that regardless of the oxidation pathways, SOA components become more chemically similar as oxygen content and photochemical aging increase.

3.3. Composition analysis

The chemical compounds generated from the Δ^3 -carene photooxidation were characterized by using the VUV-FEL-TOF-AMS. Recent studies have demonstrated that the optimization of VUV-FEL wavelengths and pulse energies enables threshold photoionization with high sensitivity, high selectivity, and minimal fragmentation (Zhang et al., 2024b; Zhao et al., 2024). The VUV-FEL photoionization mass spectra of the compounds generated under different experimental conditions are representatively shown in Figs. 4 and 5, respectively. Further details are provided in Figs. S5 and S6, respectively. The background of all mass spectra has been subtracted.

The above analyses suggest that the OH oxidation reactions are dominated under low-NO₂ conditions, whereas the O₃ oxidation becomes more significant under high-NO₂ conditions. This divergence leads to the different effects of SO₂ under [NO₂]-varying conditions. To further verify this finding, a series of experiments were carried out to differentiate the OH oxidation and O₃ oxidation pathways. Detailed experimental conditions are listed in Table S2 and the results are shown in Figs. S7 and S8, respectively.

Several important products of Δ^3 -carene photooxidation have been



Fig. 3. Triangle plot for Δ^3 -carene photooxidation of different experimental series.



Fig. 4. VUV-FEL photoionization mass spectra of the compounds generated under different experimental conditions. The compounds were ionized by the VUV-FEL at 125.0 nm. The background has been subtracted. New compounds are marked with red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. VUV-FEL photoionization mass spectra of the compounds generated under different experimental conditions. The compounds were ionized by the VUV-FEL at 115.0 nm. The background has been subtracted. New compounds are marked with red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

identified in previous studies, which have provided detail structural information and formation mechanism (Colville and Griffin, 2004; Fang et al., 2016; Hantschke et al., 2021; Ma et al., 2009; Thomsen et al., 2021). Table S3 lists the structural information of the MW = 168, 170, 198, 200 and 400 compounds. Notably, the MW = 198 compound is identified as an OH oxidation product, while the MW = 200 compound corresponds to an O_3 oxidation product (Fang et al., 2016). These products are also observed in the present mass spectra (Fig. 4). Considering that the ionization efficiency of the homologues could be similar, we mainly compared the mass spectral intensities of the known

products, such as MW = 198 and 200 (Table S3). Meanwhile, the mass spectral intensities of the same product under different experimental conditions could be compared to evaluate the influence of experimental conditions on the formation mechanism of the product. The MW = 198peak sharply appears in the mass spectra of the Δ^3 -carene ozonolysis (Fig. 4a). After adding the OH scavenger (Fig. 4b), the MW = 198 peak disappears, whereas the MW = 200 peak becomes apparent, indicating that the MW = 198 compound might be mainly generated from the OH oxidation pathway and the MW = 200 compound might be mainly generated from the O3 oxidation pathway. This result aligns with previous studies, indicating that the source of oxidation products could be identified through comparative analysis in mass spectrometry. New peaks at MW = 260, 304, and 306 are observed in the 394 ppb Δ^3 -carene +226 O₃ experiment (Fig. 4a) but not in the 402 ppb Δ^3 -carene +225 O₃ experiment with OH scavenger (Fig. 4b), suggesting that these new compounds may be formed from the OH oxidation pathway.

In Fig. 4c, the MW = 198 and 200 compounds are simultaneously observed, indicating the coexistence of the OH and O₃ oxidation pathways. Notably, the intensity of the MW = 198 peak is remarkably larger than that of the MW = 200 peak, suggesting that the OH oxidation pathway is more dominant under low-NO2 condition. The effect of OH scavenger on the newly-observed MW = 260, 304, and 306 peaks is similar to that of the MW = 198 peak, implying that OH is the primary oxidant for the formation of these new compounds. A new peak is observed at MW = 223 in the 406 ppb Δ^3 -carene +192 ppb NO₂ experiment (Fig. 4c), which is tentatively identified as an ON. As shown in Fig. 4d, the intensity of the MW = 200 peak is notably higher than that of the MW = 198 peak, indicating the dominance of the O_3 oxidation pathway under this condition. New product peaks at MW = 220, 232, 245, and 308 are observed in the 406 ppb Δ^3 -carene +388 ppb NO₂ experiment (Fig. 4d). The MW = 245 compound is hypothesized to originate from the RO_2 and NO reactions, while the MW = 220, 232, and 308 compounds are proposed to be formed via the O₃ oxidation (vide infra).

Since the oxidation state of the product reaches saturation when [SO₂]₀ is 200 ppb (Fig. 3b and c), this concentration is selected for the mass spectral measurement of the Δ^3 -carene + NO₂ + SO₂ experiments. As shown in Fig. 5, new compounds are observed at MW = 212, 240,256, 284, 400, and 414. As exemplified in the 395 ppb Δ^3 -carene +395 ppb $NO_2 + 178$ ppb SO_2 experiment (Fig. S6), the mass spectral intensities of the MW = 212, 256, and 414 peaks measured at the VUV-FEL wavelength of 115 nm are larger than those at the 105 nm and 125 nm. This could be rationalized that the photon energy at the VUV-FEL wavelength of 115 nm (10.78 eV) may be close to the ionization potentials of most OSs, whereas the photon energy at the VUV-FEL wavelength of 105 nm (11.81 eV) might be much higher than the ionization potentials of most OSs and the photon energy at the VUV-FEL wavelength of 125 nm (9.92 eV) might be lower than the ionization potentials of these OSs. These results support the conclusion that the addition of SO₂ promotes the formation of OSs.

In Fig. 5, the MW = 212 peak is consistently observed under different conditions, suggesting that this compound may have multiple isomers generated via different pathways (i.e., the OH and O3 oxidation). Upon comparing Fig. 5a and b, with the addition of the OH scavenger, the MW = 240 and 284 peaks disappear, whereas the intensities of the MW =256 and 400 peaks are obviously reduced but still observable, implying that the MW = 240 and 284 compounds could be derived from the OH oxidation pathway and the MW = 256 and 400 could be formed from both OH and O_3 oxidation pathways. A new peak appears at MW = 414, which is likely to originate from the O_3 oxidation pathway. The MW = 240 and 284 peaks are predominantly observed in the 399 ppb Δ^3 carene +194 ppb NO₂ + 195 ppb SO₂ experiment (Fig. 5c), whereas the MW = 256 and 414 peaks are notably prominent in the 395 ppb Δ^3 carene +395 ppb NO₂ + 178 ppb SO₂ experiment (Fig. 5d). These findings support the conclusion that OH is the primary oxidant under low-NO2 conditions, whereas O3 dominates the oxidation pathway under high-NO₂ conditions. Additionally, the differences in the product distributions may lead to the diverse effects of SO_2 on SOA formation.

3.4. Possible formation mechanisms of new compounds

In section 3.3, the individual and combined effects of NO₂ and SO₂ on the formation of SOA were investigated by using VUV-FEL-TOF-AMS. Several new compounds were observed through mass spectrometry, and their primary oxidation pathways were characterized. Based on these findings, we have carried out quantum chemical calculations to elucidate the specific molecular mechanisms of these new compounds and to propose their formation mechanisms. Nevertheless, the possibility of other structures/formation pathways is not excluded. The structural assignments of new compounds are summarized in Tables S4 and S5. The potential formation mechanisms of some key products are illustrated in Figs. 6-9 and those of other products are presented in Figs. S9-S13, respectively. The product is labeled as $C_{OHx/O3x}$ -P_y or $C_{OHx/}$ $_{O3x}$ -OS-P_v (x = 1–2; y = 1–3) sorted by the molecular weight, and the intermediate is successively labeled as $C_{OHx/O3x}$ - I_y (x = 1–2; y = 1–10). Two isomers were proposed for the MW = 212 compound as inferred from the aforementioned analyses of mass spectra (Fig. S12).

First, we analyze the new compounds of MW = 223 and 304 observed under low-NO₂ conditions. As shown in Fig. 6, OH adds to the double bond, forming a carbon-centered radical on the tertiary carbon (C_{0H1}-I1), which process is exothermic with a predicted value of 29.1 kcal/mol at the ω B97XD/def2-TZVP level of theory. Given that alkyl radicals on tertiary carbons are the primary addition pathways (Baptista et al., 2014), we focus on the most likely reactions at each stage. C_{OH1}-I1 undergoes a rearrangement over a small reaction energy barrier of 7.6 kcal/mol to form C_{OH1}-I2, which combines with O₂ to form C_{OH1}-I3.

Generally, the first-generation RO₂ radicals do not condense into the aerosol phase due to their relatively high saturated vapor pressures, but may undergo bimolecular reactions (with HO2, NO, or RO2) to form alkoxy radicals (D'Ambro et al., 2022; Hantschke et al., 2021). Considering the presence of NO_x in the present experimental conditions, COH1-I4 could be generated via the reaction of COH1-I3 with NO. The alkoxy group dissociates the three-carbon chain (CH₃COCH₃) and then combines with O_2 to form C_{OH1} -I5. This process is thermodynamically exothermic (30.4 kcal/mol) and kinetically favorable with a very small energy barrier of 4.9 kcal/mol. Previous studies indicated that RO2 can react with HO₂ to form ROOH products, with yields potentially reaching 80 % under suitable conditions (Orlando and Tyndall, 2012). Indeed, the C_{OH1} -I5 + HO₂ \rightarrow C_{OH1} -P1 + O₂ process is predicted to be facile with an exothermic value of 33.1 kcal/mol. CoH1-P1 contains unsaturated double bonds, which are further oxidized by OH and are incorporated with O_2 to form C_{OH1} -I6. This process is extremely exothermic by 60.8 kcal/mol. Since the reaction of RO_2 with NO_x can terminate the reaction chain, C_{OH1} -I6 could react with NO to form C_{OH1} -P2 (MW = 223), which is an ON. The process is exothermic by 39.9 kcal/mol. Recent laboratory studies have demonstrated that the larger structure of RO₂ produced by monoterpenes can undergo cross-reactions and self-reactions to form the accretion product ROOR' (Zhang et al., 2025; Zhao et al., 2024). Accordingly, it is speculated that COH1-I6 and COH1-I5 undergo a bimolecular reaction to form C_{OH1}-P3 (MW = 304), which is exothermic with a predicted value of 35.3 kcal/mol.

There are also new peaks at MW = 260 and 306 observed at low-NO₂ conditions, which are speculated to originate from the OH addition and the formation of alkyl radicals on secondary carbons. Although this pathway was considered as minor contribution (Baptista et al., 2014), the intensities of these two peaks in our mass spectra suggest that it is



Fig. 6. Possible formation mechanisms of new compounds MW = 223 and 304 calculated at the ω B97XD/def2-TZVP level of theory. Relative energies are given in kcal/mol.



Fig. 7. Possible formation mechanisms of new compounds MW = 232 and 245 calculated at the ω B97XD/def2-TZVP level of theory. Relative energies are given in kcal/mol.



Fig. 8. Possible formation mechanisms of new compounds MW = 240 and 284 calculated at the ω B97XD/def2-TZVP level of theory. Relative energies are given in kcal/mol.



Fig. 9. Possible formation mechanisms of new compounds MW = 256 and 414 calculated at the ω B97XD/def2-TZVP level of theory. Relative energies are given in kcal/mol.

another oxidation pathway with high yield. Accordingly, the formation mechanisms of the MW = 260 and 306 compounds are proposed in Fig. S9.

Fig. 7 illustrates the possible formation mechanisms of the MW =232 and MW = 245 compounds observed under high-NO₂ conditions. Ozonolysis is known to be the dominant oxidation pathway in such conditions. Initially, Δ^3 -carene reacts with O₃ via a [3 + 2] cycloaddition to form a primary ozonide (POZ) (Wang et al., 2019). POZ is highly unstable and rapidly decomposes to generate sCI (C031-I1). In previous studies, it was suggested that 1,5-H-shift and 1,4-H-shift were more favorable during intramolecular H-shifts (D'Ambro et al., 2022; Dibble, 2002). Therefore, C₀₃₁-I1 might undergo a 1,4-H-shift to form C₀₃₁-I2, which is predicted to be slightly endothermic (2.1 kcal/mol) with a reaction energy barrier of 15.5 kcal/mol. Co31-I2 then rapidly reacts with an O2 molecule to form the important RO2 (Co31-I3). On one hand, C_{031} -I3 could continue to form C_{03} -I6 by autooxidation, with a reaction energy barrier of 22.4 kcal/mol and an exothermicity of 10.4 kcal/mol (Fig. 7). C_{031} -I6 then forms a PO (C_{031} -P1, MW = 232) via a bimolecular reaction. On the other hand, C_{031} -I3 could react bimolecularly with NO to form C₀₃-I4, which undergoes a 1,4-H-shift and combines with O₂ to form C_{031} -I5, with a reaction energy barrier of 14.4 kcal/mol and predicted exothermicity of 27.5 kcal/mol. Finally, NO terminates the oxidation reaction of C₀₃₁-I5, resulting in the formation of C₀₃₁-P2 (MW = 245).

Comparing the structures of products formed at low-NO2 and high-NO₂ conditions, we are surprised to find that at low-NO₂ conditions, the formation mechanisms of the MW = 260, 304, and 306 compounds are ultimately terminated in two RO2 bimolecular reactions, while at high- NO_2 conditions, only the MW = 308 compounds is identified as a product of ROOR' formation. This suggests that the RO₂ cross-reactions are more favorable in low-NO2 conditions. Generally, dimer esters formed via the $RO_2 + RO_2$ bimolecular reactions have low volatility and play a significant role in the SOA oxidation mechanism. The presence of RO2 cross-reactions during VOC oxidation has been reported recently, with contributions to SOA formation as high as 39 % (Chen et al., 2022). In this work, the variation in NO_x concentrations is identified as the direct cause of the nonlinear variation in the SOA yields. Further molecular-level investigations reveal that NOx indirectly alters the proportion of RO2 reaction pathways. The increase in NOx concentration inhibits the bimolecular reactions of RO2 which may be one of the key reasons for the observed decrease in SOA yields under high-NO2 conditions.

New compounds MW = 240 and 284 are observed in the Δ^3 -carene $+ NO_2 + SO_2$ experiments under low-NO₂ conditions, which possible structures and formation processes are shown in Fig. 8. CoH1-I5 and COH1-I3 are the RO2 radicals as shown in Fig. 6. Firstly, COH1-I5 reacts bimolecularly with another RO2 to form the COH1-I5-P1 with the predicted exothermicity of 88.9 kcal/mol. A new RO2 (CoH1-I5-I1) is then formed by OH-induced oxidation reaction. CoH1-I5-I1 reacts with NO to form a RO, which subsequently reacts with HO₂ to lose one O₂, ultimately forming COH1-I5-P2. This process is extremely exothermic with a predicted value of 74.9 kcal/mol. The addition of SO2 introduces sulfuric acid into the experimental system, which condenses with alcohols to form esters. This reaction may involve nucleophilic substitution, where sulfuric acid protonates the alcohol group, making water the leaving group (Surratt et al., 2007). Recent studies have shown that large amounts of organic acids formed during oxidation can drive such reactions (Du et al., 2023; Xu et al., 2021; Yang et al., 2021, 2023). It is speculated that C_{OH1} -OS-P2 (MW = 240) is formed via the reaction of $C_{OH1}\text{-}I5\text{-}P2$ with $\text{H}_2\text{SO}_4\text{.}$ The $C_{OH1}\text{-}I3$ \rightarrow $C_{OH1}\text{-}I3\text{-}P1$ reaction is highly exothermic by 70.8 kcal/mol. Similarly, $C_{OH1}\mbox{-}I3\mbox{-}P1$, which contains an unsaturated bond, is oxidized again to form a new RO2. The final fate of COH1-I3-I1 is COH1-I3-P2, which contains alcohol groups. COH1-OS-P3 (MW = 284) is then formed via the acid-catalyzed reaction.

Under high-NO₂ condition, OSs is mainly formed via ozonolysis. As shown in Fig. 9, RO (C_{032} -I7) releases CH₃ to form C_{032} -I7-P1, with the

barrier of 11.6 kcal/mol. C_{032} -I7-P1 contains an unsaturated bond and reacts with O₃ to form POZ, which rapidly decomposes to C_{032} -I7-I1 over the barrier of 22.1 kcal/mol. This decomposition is highly exothermic, with a predicted value of 54.7 kcal/mol. The reaction of C_{032} -I7-I1 with OH removes H₂O to form RO, which then reacts with HO₂ to form C_{032} -I7-P2, a compound containing alcohol groups. C_{032} -I7-P2 subsequently reacts with H₂SO₄ to form C_{032} -OS-P2 (MW = 256). Similarly, another RO₂ (C_{032} -I6) first converses the peroxy group to an alcohol group, forming C_{032} -I6-P1, which exothermicity is predicted to be 74.1 kcal/mol. The molecular structure of C_{032} -I6-P1 contains multiple alcohol groups, enabling it to react with sulfuric acid. Additionally, esterification crosslinking reaction may occur in the presence of polyols, leading to the formation of C_{032} -OS-P4 (MW = 414), with the exosthermicity of 9.2 kcal/mol. The formation mechanism of C_{032} -I9-P1 is detailed in Fig. S11.

4. Conclusions and atmospheric implications

This study represents the first systematic investigation of anthropogenic-biogenic interactions between Δ^3 -carene and these two pollutants. Although the initial concentrations of Δ^3 -carene in this study are higher than those in the atmosphere and the SOA mass loading may be overestimated, this work provides new insights into the nonlinear relationship between NO_x and SOA yields, potentially informing future studies on atmosphere-relevant reactant concentrations. A notable finding is that the oxidants reacting with VOC vary depending on NO₂ concentrations: OH is the dominant oxidant at low-NO₂ conditions, while O₃ becomes the primary oxidant at high-NO₂ conditions. Interestingly, the response of mixed pollutants $(NO_2 + SO_2)$ significantly differs under varying NO₂ concentrations. This suggests that considering only the effects of pollutants at "extremely" low or high concentrations may lead to the biased predictions of SOA generation, increasing uncertainty regarding the impacts of aerosol particles on air quality, climate, and human health (Henze et al., 2008; Lane et al., 2008). The results of this work may hold significant implications for accurately simulating air quality models influenced by SOA formation.

Characterization of the SOA composition in the laboratory confirms the formation of POs, ONs and OSs, with a higher proportion of SV-OOA as compared to those observed in the atmosphere. This indicates that the influence of multiple physical environmental parameters in the atmosphere, such as acid-catalyzed polyphase and liquid-phase reactions, is more pronounced in the SOA formation than that in the laboratory studies. VUV-FEL photoionization mass spectra provide experimental evidence for the formation of new organic peroxides at MW = 220, 232, 260, 304, 306 and 308, new organic nitrates at MW = 223 and 245, and new organosulfates at MW = 212, 240, 256, 284, 400 and 414, respectively. A series of contrast experiments in this work distinguish whether the formation of these products is dominated by OH or O₃, which is critical for identifying and analyzing the sources of SOA in the atmospheric environment. These newly-observed compounds have significant implications for atmospheric chemistry, and their identification in the particle phase enhances our understanding of the SOA formation processes. This study has proposed the possible formation mechanisms and energetic information of new compounds generated from the Δ^3 carene photooxidation, which contribute to comprehensive understanding of the aerosol formation mechanisms in regions influenced by both anthropogenic and biogenic sources.

CRediT authorship contribution statement

Ya Zhao: Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Chong Wang: Investigation, Formal analysis, Data curation. Yingqi Zhao: Validation, Investigation, Formal analysis, Data curation. Yufeng Shao: Investigation, Formal analysis, Data curation. Hua Xie: Visualization, Software, Investigation, Funding acquisition. Jiayue Yang: Validation, Resources, Methodology. Weiqing Zhang: Validation, Resources, Methodology. Guorong Wu: Validation, Resources, Methodology. Gang Li: Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. Ling Jiang: Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. Xueming Yang: Validation, Supervision, Resources, Project administration.

Declaration of competing interest

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.

Acknowledgments

The authors gratefully acknowledge the staff members of the Dalian Coherent Light Source (31127.02. DCLS) for technical support and assistance in data collection. This work was supported by the National Natural Science Foundation of China (Nos. 22125303, 92361302, 22103082, 22273101, 22288201, and 21327901), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB0970100), the National Key Research and Development Program of China (No. 2021YFA1400501), the Innovation Program for Quantum Science and Technology (No. 2021ZD0303304), Dalian Institute of Chemical Physics (DICP I202437), Chinese Academy of Sciences (No. GJJSTD20220001), International Partnership Program CAS and the of (121421KYSB20170012).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2025.121313.

Data availability

Data will be made available on request.

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