Investigating the Role of Ammonia in Enhancing Secondary Organic Aerosol Formation from the Co-photooxidation of Anthropogenic and Biogenic VOCs

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Abstract. Ammonia (NH_3) plays a crucial role in the complex physicochemical processes occurring in the atmosphere, but the mechanisms governing secondary organic aerosol (SOA) formation from NH_3-involved interactions between mixed anthropogenic and biogenic organic compounds remain poorly understood, thereby limiting the predictive capacity for air quality and climate. Previous studies have demonstrated that NH_3 can alter the oxidation pathways of single aromatic hydrocarbon precursor, promoting particle formation and growth. However, its role in mixed organic precursor systems has not been systematically explored. This study aims to elucidate these mechanisms through photooxidation experiments conducted in a large outdoor photochemical smog chamber, investigating mixtures of n-heptylcyclohexane (anthropogenic) and α-pinene (biogenic) under varying NH_3 conditions. The results indicated that NH_3 obviously accelerated VOC degradation and significantly contributed to SOA enhancement through facilitating nucleation and participating in particle-phase reactions in the mixed system. The presence of NH_3 could not only promote the generation of intermediates such as aldehydes and ketones, but also lead to an increase in SOA mass and number concentration, particularly nitrogen-containing light-absorbing substances like imidazoles. This research can provide a scientific basis for systematically assessing how NH_3 affects the co-oxidation of ambient anthropogenic and biogenic gases, and deepen the understanding of its role in SOA generation, particularly light-absorbing aerosols, in the AVOC-BVOC mixed system.

1 Introduction

The atmospheric photochemical oxidation of anthropogenic and biogenic volatile organic compounds (AVOCs, BVOCs) can lead to the formation of secondary organic aerosols (SOA), which have been widely considered important for atmospheric chemistry, global climate, and human health (Ziemann and Atkinson, 2012; Shrivastava et al., 2017; Liu et al., 2022). Recent laboratory experiments have demonstrated that the contribution of specific VOC species to SOA varies under different conditions, including oxidant species and concentrations, seed particles, inorganic gas, temperature, relative humidity, and radiation intensity (Zhang et al., 2019; Palm et al., 2017; Zhang et al., 2023; Li et al., 2021a). Nevertheless, the evidence that current model predictions of SOA are generally lower than field observations suggests that significant nonlinear effects occur in the formation of SOA in the mixed VOCs systems (Hallquist et al., 2009; Xu et al., 2021). Hence, knowledge gaps still persist regarding the complex oxidation mechanisms of multiple coexisting gas- and particle-phase substances in the atmosphere, along with the properties, composition, and formation mechanisms of the resulting SOA, which poses challenges for precisely evaluating the global SOA budget, origins, and climatic implications.

It is well known that ammonia (NH_3) is a common primary alkaline pollutant in the atmosphere, primarily emitted from agricultural sources. Moreover, on-road mobile sources of NH_3 are becoming increasingly important with the rise in urban automobile ownership (Sun et al., 2017), significantly contributing to the pollution levels of fine particulate matter ($PM_{2.5}$) (Wen et al., 2023). Recent studies have revealed that NH_3 can influence the formation and chemical composition of single VOC-derived SOA (Du et al., 2023). NH_3 can promote new particle formation (NPF) and particulate growth during the photo-oxidation of aromatic hydrocarbons (e.g., toluene and xylene) (Liu et al., 2021a). Additionally, NH_3 directly contributes to SOA formation through acid-base reactions with organic compounds during the photo-oxidation of biogenic olefins (e.g., α-pinene) (Hao et al., 2020). Tunnel measurements show that NH_3 emitted by traffic rose from 21~225 ppb at the entrance to 40~2776 ppb at the exit (Liu et al., 2014). Therefore, investigating the role of high concentration NH_3 in the photochemical oxidation of mixed VOCs would benefit to deepen our understanding of the complex atmospheric oxidation mechanisms.

In recent years, the relative contribution of SOA to $PM_{2.5}$ mass concentration has significantly increased (Ming et al., 2017). Long chain alkanes have been found to not only significantly affect the SOA yield, but also play an important role in atmospheric oxidation (Donahue et al., 2009; Tang et al., 2019). Long chain alkanes in the atmosphere come from a wide range of sources, especially in the actual urban atmosphere, including volatile chemicals such as coatings and exhaust emissions from motor vehicles (Fang et al., 2021; Wang et al., 2021a; Qi et al., 2019; Deng et al., 2017b). Research has shown that the amount of SOA generated by long-chain alkanes is comparable to that of polycyclic aromatic hydrocarbons and monocyclic aromatic hydrocarbons, and even more significant in some cases (Luo et al., 2019; Agrawal et al., 2008; Siegl et al., 1999; Yuan et al., 2013; Deng et al., 2017a). The photochemical reactivity and SOA generation potential of long-chain alkanes are greatly influenced by their chemical structural characteristics. Cycloalkanes have the highest activity and SOA generation potential, followed by branched alkanes, and finally straight chain alkanes (Hu et al., 2022). As a mixed hydrocarbon compound with both cyclic and branched alkyl structures, n-heptylcyclohexane can serve as an important reference for studying anthropogenic SOA derived from long-chain alkanes. On a global scale, the BVOC emissions account for over 90% of the total VOCs worldwide (Shao et al., 2022; Ahlberg et al., 2017), making them the most important source of atmospheric organic compounds and a significant contributor to global SOA production (Chen and Jang, 2012). Under real atmospheric conditions, when BVOCs are mixed with anthropogenic emissions, their oxidation pathways and potential for generating SOA can be altered (Donahue et al., 2006; Emanuelsson et al., 2013; John H. Offenberg et al., 2007; Voliotis et al., 2021; Li et al., 2022b). Among them, α-pinene has the characteristics of high emissions, high reactivity, and high SOA contribution, making it a very important BVOCs species in the atmospheric environment (Wang et al., 2021b). At present, our understanding of the mixed oxidation mechanism of biogenic olefins and long-chain alkanes, as well as their derived SOA components and properties, is still limited. Moreover, there is less research on the impact of NH_3 on AVOC-BVOC mixed systems, and the mechanism of SOA formation in these systems is not yet clear.

Herein, a large outdoor photochemical smog chamber simulation was conducted to explore the SOA formation from the mixed system of n-heptylcyclohexane (representing AVOCs) and α-pinene (representing BVOCs) under the presence of NH_3. Then an in-depth analysis of the SOA composition was conducted, further clarifying the potential chemical mechanisms. This study aims to comprehensively reveal the important enhancing role of NH_3 on the co-photooxidation of anthropogenic-biogenic mixed system, and furtherly improve the understanding of the mechanisms and influencing factors of SOA in the system.

2 Materials and Methods

2.1 Experimental conditions

The experiments were conducted in a large outdoor photochemical smog chamber located on one rooftop of the building at the Chinese Research Academy of Environmental Sciences (CRAES). It was a 56 m^3 Teflon chamber covered with a well-controlled enclosure, inside where three fans were fixed to ensure uniform mixing (Li et al., 2021b). Before each experiment, the chamber was purged with zero air at a flow rate of 100 L min^{-1} for at least 24 hours to ensure cleanliness. Herein, all the experiments were performed from October to the ensuing January, and the initial conditions and experimental results could be found in Table S1. As significant organic precursors of SOA, the liquid-phase n-heptylcyclohexane, and/or α-pinene with known volumes were injected into a U-shaped tube and then blown into the chamber with zero air after heating. In all experiments, the initial concentration of n-heptylcyclohexane (TCI Development Co., Ltd, Shanghai) was in the range of 49.0~119.8 ppb, while α-pinene (Beijing Inno Chem Science & Technology Co., Ltd) was in the range of 43.7~86.7 ppb. With HONO as the precursor for OH radicals and NO, it was prepared by the dropwise addition of 0.2 mL 5 wt % $NaNO_2$ into 0.4 mL 30 wt % H_2SO_4, formed NO, NO_2, and HONO from which were blown into the chamber by zero air likewise. The measured initial NOx concentration in the chamber ranged from 89.9 to 157 ppb. NH_3 was introduced from a 500 ppm standard gas cylinder, the concentration of which was calculated based on the chamber volume and added volume of NH_3. The initial NH_3 concentration was in the range of 74.85~748.5 ppb. When the target species that introduced into the chamber were thoroughly mixed, the enclosure was opened, thus the photochemical reaction began. The entire photochemical reaction process of each experiment lasted about 7 h (usually from 10 a.m. to 17 p.m.), with a maximum temperature (T) of 14.4~40.7 ℃ and a maximum relative humidity (RH) of less than 15% inside the chamber. The sunlight was utilized as the natural light source at JNO_2 of $0.9\sim4.4\times10^{-3}$ s^{-1}. Sampling commenced immediately upon opening of the enclosure. The first filter collected samples continuously for 3.5 hours (i.e., the first half of the experiment, designated as "former") and was then replaced with a fresh one for an additional 3.5 hours of continuous collection (i.e., the second half of the experiment, designated as "latter"). Each set of experiments was conducted at least 2 times to verify reproducibility and ensure robust results. Under background conditions (i.e., blank measurements), the chamber air contained $SO_2 \leq 0.5$ ppb, NOx≤2 ppb, and $O_3 \leq 0.5$ ppb, while released or formed VOCs and particles were negligible (<0.01 μg m^{-3}).

2.2 Instrumentation

The collected precursor samples (n-heptylcyclohexane and α-pinene) in the Tenax TA tube underwent quantitative analysis using thermal desorption gas chromatography (TD-GC, GC, 8890, Agilent, USA; TD, UNITY-xr, Germany) to obtain precursor concentrations and consumption rates within the chamber. The mass concentration, number concentration, surface mean diameter, and volume concentration of formed particles were monitored with a scanning mobility particle sizer (SMPS, model 3080, model 3081, and model 3772, TSI Inc., USA). Additionally, the qualitative analysis of organic chemical compounds, which were subjected to ultrasonic extraction from quartz films using 10 mL of methanol (20 minutes), was performed using an electrospray ionization quadrupole time-of-flight mass spectrometer (ESI-Q-ToF-MS, Bruker, Germany). Furthermore, an FTIR spectrometer (Bruker, Germany) equipped with a RTDLaTGs detector and a UV-Vis light spectrometer (Hitachi, U-3900) were applied to the qualitative detection of potential functional groups in the organic components. The qualitative and quantitative analysis of eluted aldehyde-ketones from collected samples were carried out using an HPLC-UV/MS (Shimadzu, Japan). The T and RH inside the chamber were monitored using the temperature and humidity sensors (Beijing Star Sensor Technology Co., Ltd.), while the irradiance was detected with a JNO_2 filter radiometer (Metcon, Germany). The consumption and generation of gaseous SO_2, NOx and O_3 inside the chamber were monitored in real-time by online SO_2 (EC 9850, Ecotech, Australia), NOx (EC 9841, Ecotech, Australia) and O_3 analyzers (EC 9830, Ecotech, Australia).

2.3 Calculation

In this work, the OH exposure during the photo-oxidation process of precursor compounds were quantified by utilizing TD-GC, as illustrated by Eq. (S1) (Mao et al., 2009):

$$OH\ exposure = \frac{ln\frac{[tracer]_0}{[tracer]_t}}{k}, \qquad \text{(S1)}$$

where k denoted the rate constant for the reaction of the tracer and the OH radical.

Here, the tracer referred to a precursor compound capable of reacting with OH radicals. Given the rapid photo-oxidation rate of α-pinene, n-heptylcyclohexane was appointed as the trace. In experiments without n-heptylcyclohexane, α-pinene served as the tracer. At the standard temperature (298 K), the reaction rate constant for OH radical with n-heptylcyclohexane was 1.91×10^{-11} cm^3 $molecules^{-1}$ s^{-1}, and with α-pinene was 5.23×10^{-11} cm^3 $molecules^{-1}$ s^{-1} (Atkinson and Arey, 2003). Furthermore, the physical significance of OH exposure was the total OH concentration from the onset to the detection period; hence, the cumulative time was employed in the calculation of OH exposure.

The SOA yield (Y) was defined as the fraction of reactive organic gases (ROG, μg m^{-3}) converted into aerosols, and it could be calculated by Eq. (S2):

$$Y = \frac{\Delta Mo}{\Delta ROG}, \qquad \text{(S2)}$$

where ΔMo (μg m^{-3}) was the maximum mass concentration of SOA, obtained by deriving the data from the Scanning Mobility Particle Sizer (SMPS); ΔROG is the amount of precursor substances involved in the reaction.

The absorption of SOA generated in the experiment across the 300 to 700 nm was measured using a UV-Vis absorption spectrophotometer. The specific absorption coefficient, denoted as Abs_λ, was calculated based on Eq. (S3) (Liu et al., 2021b):

$$Abs_\lambda = (A_\lambda - A_{700}) \cdot \frac{V_1}{V_a \cdot L} \cdot ln10, \qquad \text{(S3)}$$

where A_λ was the light absorption coefficient of SOA at the λ wavelength, A_{700} was the light absorption intensity background value, V_l was the volume of methanol with dissolved aerosols, V_a was the volume of the sampled air, and L (1 cm) was the optical path length.

Based on the UV-Vis absorption spectra, the mass absorption efficiency (MAE_λ; m^2 g^{-1}) was characterized the ultraviolet absorption intensity of SOA, which was calculated according to Eq. (S4) (Liu et al., 2021b):

$$MAE_\lambda = \frac{Abs_\lambda}{\mathrm{M}}, \qquad \text{(S4)}$$

where Abs_λ (m^{-1}) was the light absorption coefficient of SOA at the λ wavelength, and M (μg m^{-3}) was the mass concentration of methanol-soluble organic matter.

Mass defect was defined as the difference between exact mass and nominal mass of a certain compound (Roach et al., 2011).

3 Results and discussion

3.1 General results

The experiments were carried out according to the scheme of n-heptylcyclohexane + HONO (AL), n-heptylcyclohexane + HONO + NH_3 (AL-N), α-pinene + HONO (AP), α-pinene + HONO + NH_3 (AP-N), n-heptylcyclohexane + α-pinene + HONO (MIX) and n-heptylcyclohexane + α-pinene + HONO + NH_3 (MIX-N), and the initial conditions and results were summarized in Table S1. Since consistent results from replicate experiments effectively ruled out interference from random uncertainties, herein selected one representative dataset for presentation. In the background experiment, the mass concentration of inorganic particles formed from the photochemical reaction of NH_3 with NOx was below 10 μg m^{-3}, and the number concentration was < 2000 # cm^{-3} (Fig. S1(a)). This is approximately 1~2 orders of magnitude lower than the total particle concentration in the organic reaction system. Therefore, the contribution of inorganic particle formation in the organic precursor system is considered negligible. By the conclusion of the reaction, the maximum particle diameters at varying NH_3 concentration converged to statistically similar values (Fig. S1(b)). As showed in Fig.1(a), the maximum of OH exposure was in the range of (5.6~7.9) × 10^{10} molecules cm^{-3} s corresponding to 10.4~14.6 simulated hours, assuming a diurnal average OH concentration of 1.5×10^6 molecules cm^{-3} (Mao et al., 2009; Li et al., 2024). The OH exposure continuously increased over time, leading to an enhanced atmospheric oxidation capacity. The reaction commenced with a decline in the concentration of reactants, and the consumption rate of which seemed to be accelerated by the addition of NH_3 (Fig. 1(b)). Upon illumination, the SOA mass concentration rose rapidly while NOx levels declined. Compared with the NH_3-free system, the NH_3-containing system produced significantly higher SOA mass concentrations; moreover, the mixed organic system yielded higher SOA mass concentrations than the single one.

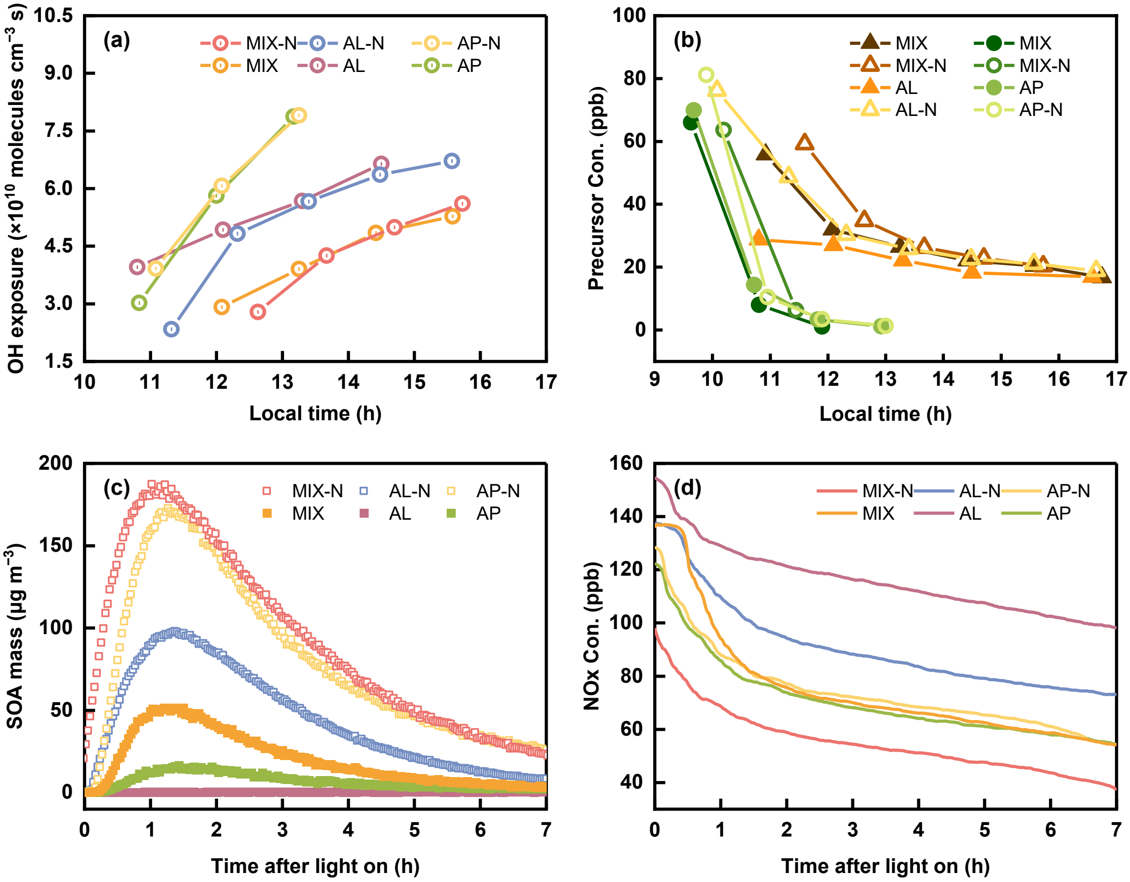


Figure 1: (a) The OH exposure (b) Precursor concentration (c) SOA mass concentration and (d) NOx concentration in the MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, MIX (n-heptylcyclohexane + α-pinene + HONO) experiment, AL-N (n-heptylcyclohexane + HONO + NH_3) , AL (n-heptylcyclohexane + HONO) experiment, AP-N (α-pinene + HONO + NH_3) experiment and AP (α-pinene + HONO) experiment. In Fig.1(b), the triangle represented n-heptylcyclohexane, and the circle referred to α-pinene. In Fig(b) and (c), the solid and hollow symbols denoted NH_3-free and NH_3-containing experimental systems, respectively.

In terms of particle size, the average SOA diameter in the MIX-N experiment was distinctly larger than that in the AL-N experiment but almost identical to that in the AP-N experiment, implying that the disparity stemmed primarily from precursor type rather than NH_3. Previous work likewise indicated that the average SOA diameter in mixed systems was governed by the highly reactive BVOC precursors (Cui et al., 2024). As showed in Fig.2, the average diameter of particles from photochemical oxidation ranged from 300 to 450 nm in the MIX-N and MIX experiment, ranged from 200 to 300 nm in the AL-N and AL experiment, and ranged from 250 to 450 nm in the AP-N and AP experiment. Obviously, the absence of any appreciable shift in average diameter between NH_3-present and NH_3-free conditions further corroborated that NH_3 exerted no significant enhancement on particle size. However, Li et al. (2018) reported that NH_3 could increase SOA size-growth potential; this discrepancy was attributable to their lower reactive organic compounds-to-primary NOx concentration ratio (VOC/NOx) (1.6~4.9 ppbC ppb^{-1}). Under such high-NOx conditions, the photo-oxidation of organics preferentially drove post-nucleation growth, an effect that was largely muted in our experiments with higher VOC/NOx (3.1~16.2 ppbC ppb^{-1}) (Li et al., 2018; Li et al., 2022c).

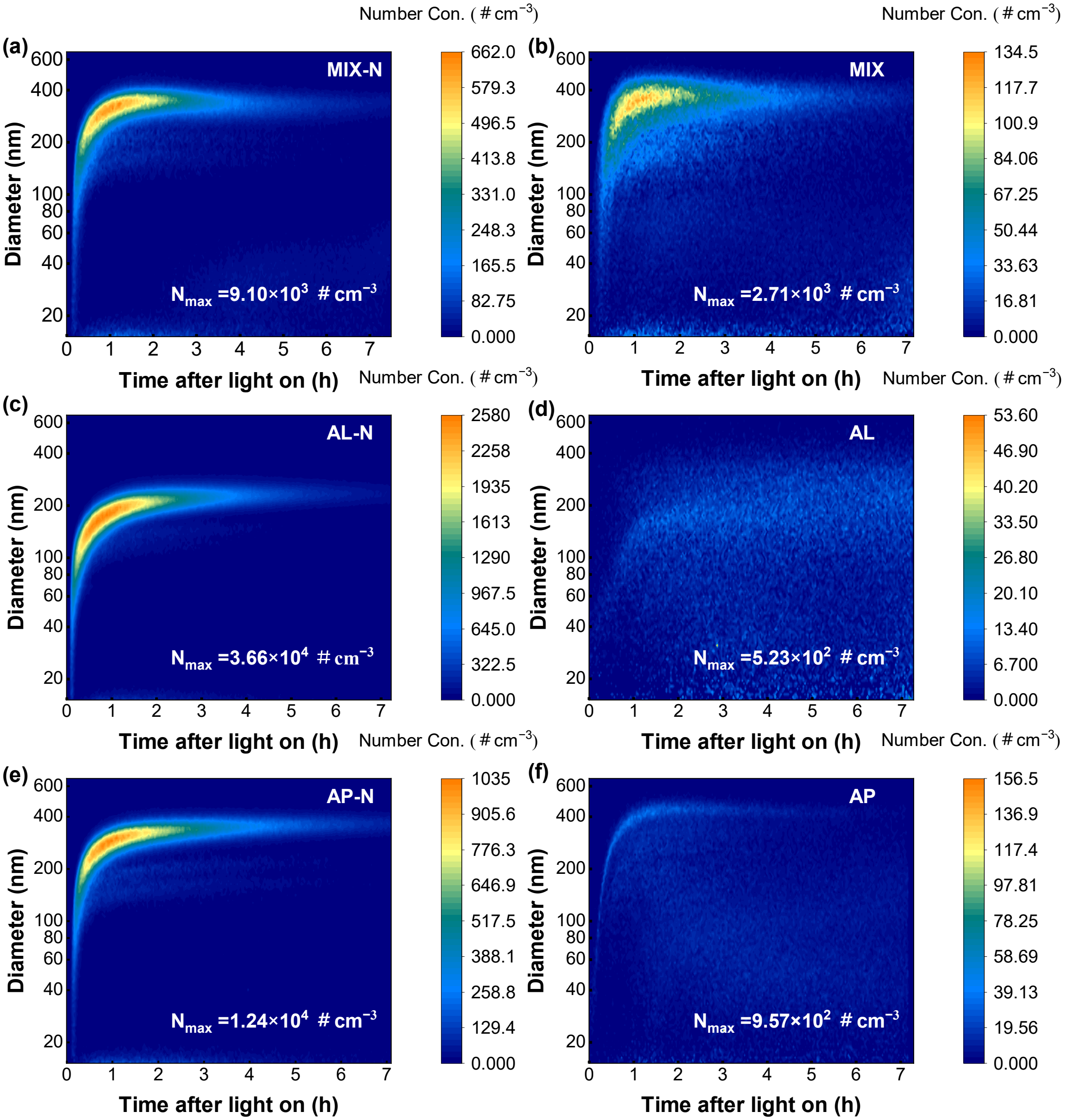


Figure 2: The number concentration distributions of particles at different diameters in the (a) MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, (b) MIX (n-heptylcyclohexane + α-pinene + HONO) experiment, (c) AL-N (n-

heptylcyclohexane + HONO + NH_3) , (d) AL (n-heptylcyclohexane + HONO) experiment, (e) AP-N (α-pinene + HONO + NH_3) experiment and (f) AP (α-pinene + HONO) experiment.

In the process of each experiment, particles were generated rapidly within the first hour of the reaction (Fig. 2). When the maximum number concentration reached approximately 10^4 # cm^{-3}, strong particle growth appeared as a clear banana shape. Compared to the NH_3-free experiments, the maximum SOA yield of the mixed organic system rose from 14.3 % to 40 % when NH_3 was present, indicating that the introduction of NH_3 led to a marked escalation in SOA production (Fig. 3(a)). Although temperature could significantly affect the partitioning process of organic compounds and lower temperatures could sensibly facilitated the formation of particles (Li et al., 2022d), the particle mass concentration exhibited a pronounced enhancement in the NH_3-present systems under identical organic precursor as well as comparable temperature and VOC/NOx ratio, suggesting that NH_3 played a facilitative role in the particle formation aligned with other research (Xu et al., 2021). It was probably because NH_3 could react with certain compounds found in SOA, contributing to convert itself into nitrogen-containing organic compounds (NOC) that remained in particles (Laskin et al., 2015), such as imines and (O'brien et al., 2013). On the other hand, both nuclei coagulation and condensation caused by acid–base reactions between NH_3 and organic acids (such as pinic acid and pinonic acid) were responsible for the SOA growth (Xu et al., 2021).

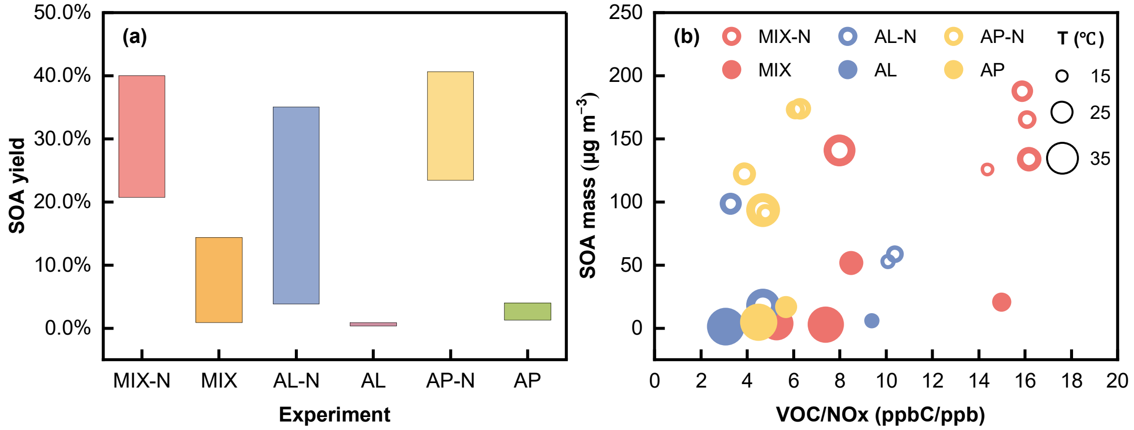


Figure 3. The (a) SOA yield and (b) relationship between SOA formation and NH_3, VOC/NOx ratio, as well as temperature (T) in the MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, MIX (n-heptylcyclohexane + α-pinene + HONO) experiment, AL-N (n-heptylcyclohexane + HONO + NH_3), AL (n-heptylcyclohexane + HONO) experiment, AP-N (α-pinene + HONO + NH_3) experiment and AP (α-pinene + HONO) experiment. In Fig. 3(b), the temperature and SOA mass concentration here referred to the maximum value during the reaction process. The red circles referred to MIX-N experiments, and the red filled circles referred to MIX experiments. The blue circles referred to AL-N experiments, and the blue filled circles referred to AL experiments. The yellow circles referred to AP-N experiments, and the yellow filled circles referred to AP experiments. The size of the circle represented the level of temperature. The larger the circle, the higher the experimental temperature.

3.2 Light absorption of SOA

Identifying the chemical class of SOA was essential to elucidating how NH_3 influences the photo-oxidation of binary organic mixtures; to this end, we derived functional group information of the SOA by resolving the absorption spectrum. The infrared absorption spectrum featured peaks that correspond to the functional groups of organic matter in the SOA. Various characteristic functional groups of the main products could be differentiated by identifying the positions of these peaks (Fig. 4). The peak observed at 2923 cm^{-1} and 2855 cm^{-1} originated from the O–H stretching vibration. The characteristic peak at 1645 cm^{-1} corresponded to the C=O stretching vibrations of the carbonyl group in either aldehyde or amide. The peak around 1054 cm^{-1} was considered as the O—H bending vibration or C—O stretching vibration, while the distinctive peak at 1382 cm^{-1} represented the —NO_2 stretching vibration of the nitro group (Babar et al., 2017; Huang et al., 2018). These peaks were consistently found in both MIX-N, AL-N and AP-N experiments, indicating that the predominant products from the NH_3-containing systems were compounds with carbonyl functionalities, along with certain NOC (Liu et al., 2015). Especially in systems containing NH_3, the enhanced peak at 1382 cm^{-1} suggested that the introduction of NH_3 led to an increased light absorption of SOA, resulting from the enhancement of NOC formation (Wang et al., 2022).

In the UV absorption profiles, the peak at 300 nm was found when NH_3 participating in the reaction, which suggested the formation of carbonyl groups (Martinez et al., 1992). However, the MAE in each system were relatively small, and the light absorption within the UV-visible spectrum were weak. This could be attributed to the absence of conjugated double bonds in the SOA derived from n-heptylcyclohexane and α-pinene (Lambe et al., 2012). Notably, the latter phase of each experiment showed a more pronounced light absorption than the former phase. The MAE at 300 nm during the former half of the experiments followed the sequence MIX-N > AL-N > AP-N, whereas followed MIX-N ≈ AP-N > AL-N in the latter half. These observations implied that more light-absorbing substances generated as the reaction progressed. Furthermore, the relative magnitude of SOA mass concentrations can be inferred based on the MAE values. The SOA generated from the n-heptylcyclohexane and α-pinene mixture contained a higher concentration of light-absorbing substances per unit mass.

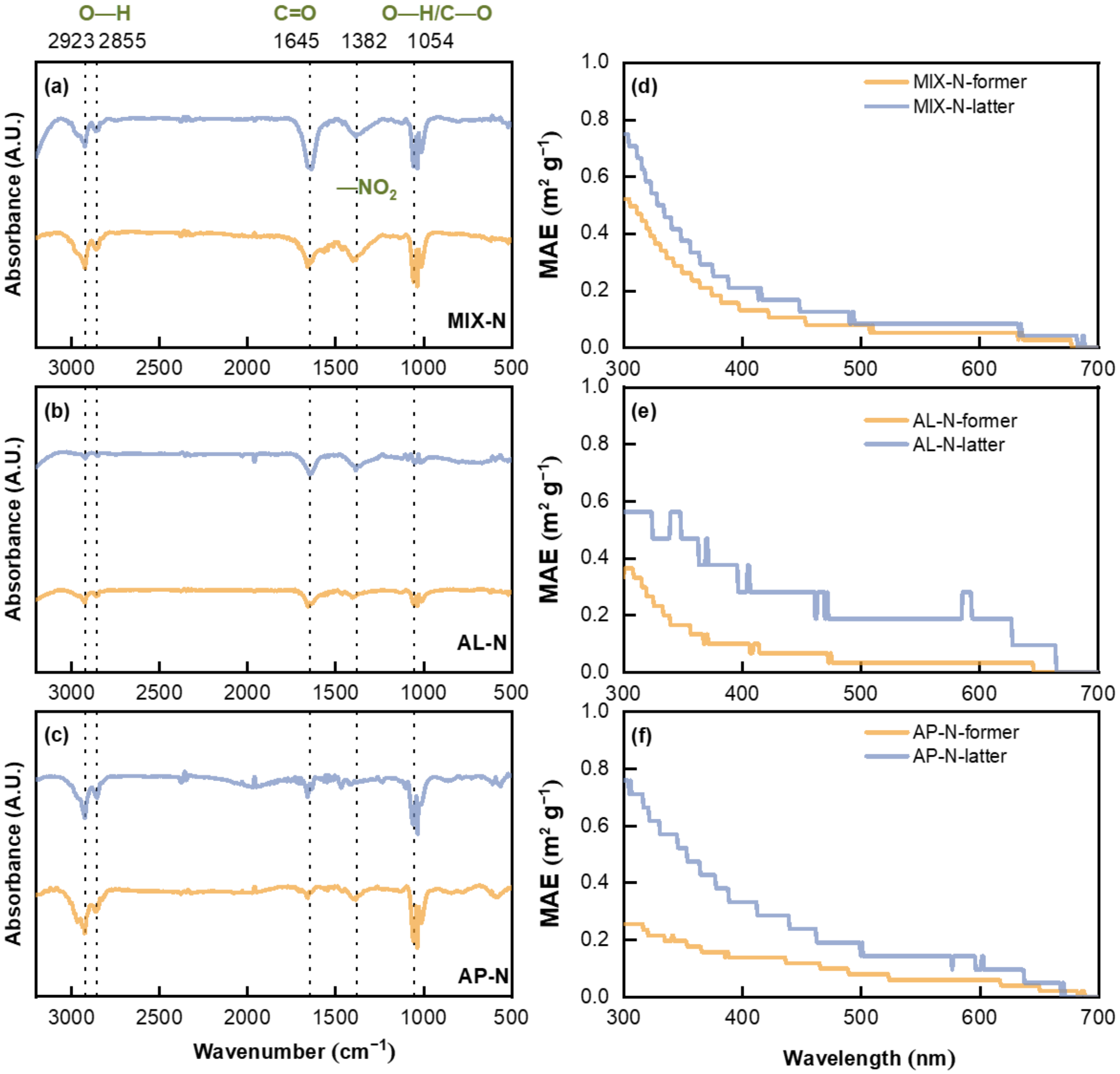


Figure 4. Infrared absorption spectrogram of generated particles in the (a) MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, (b) AL-N (n-heptylcyclohexane + HONO + NH_3), (c) AP-N (α-pinene + HONO + NH_3) experiment and ultraviolet absorption spectrogram of generated particles in the (d) MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, (e) AL-N (n-heptylcyclohexane + HONO + NH_3), (f) AP-N (α-pinene + HONO + NH_3) experiment. "Former" referred to the former half of the reaction process, and "Latter" referred to the latter half of the reaction process.

3.3 Chemical compositions of SOA

3.3.1 Molecular composition

For a deeper examination on the characteristics of organic compounds within the particulate phase, mass spectrometry was utilized to analyse the particulate matter under both positive and negative ionization modes, as shown in Fig. 5. Under positive mode, a notable formation of trimer was observed in both NH_3-containing and NH_3-free mixed system, with m/z spanning ranges of 0~300 Da, 300~450 Da, and 500~550 Da. However, the signal intensity of SOA polymeric products slightly decreased in the NH_3-containing mixed system, indicating that participation of NH_3 in photochemical reactions may have competitively interrupted the cross-reactions between n-heptylcyclohexane and α-pinene and their intermediates, thereby suppressing the formation of high-molecular-weight organics to some extent.

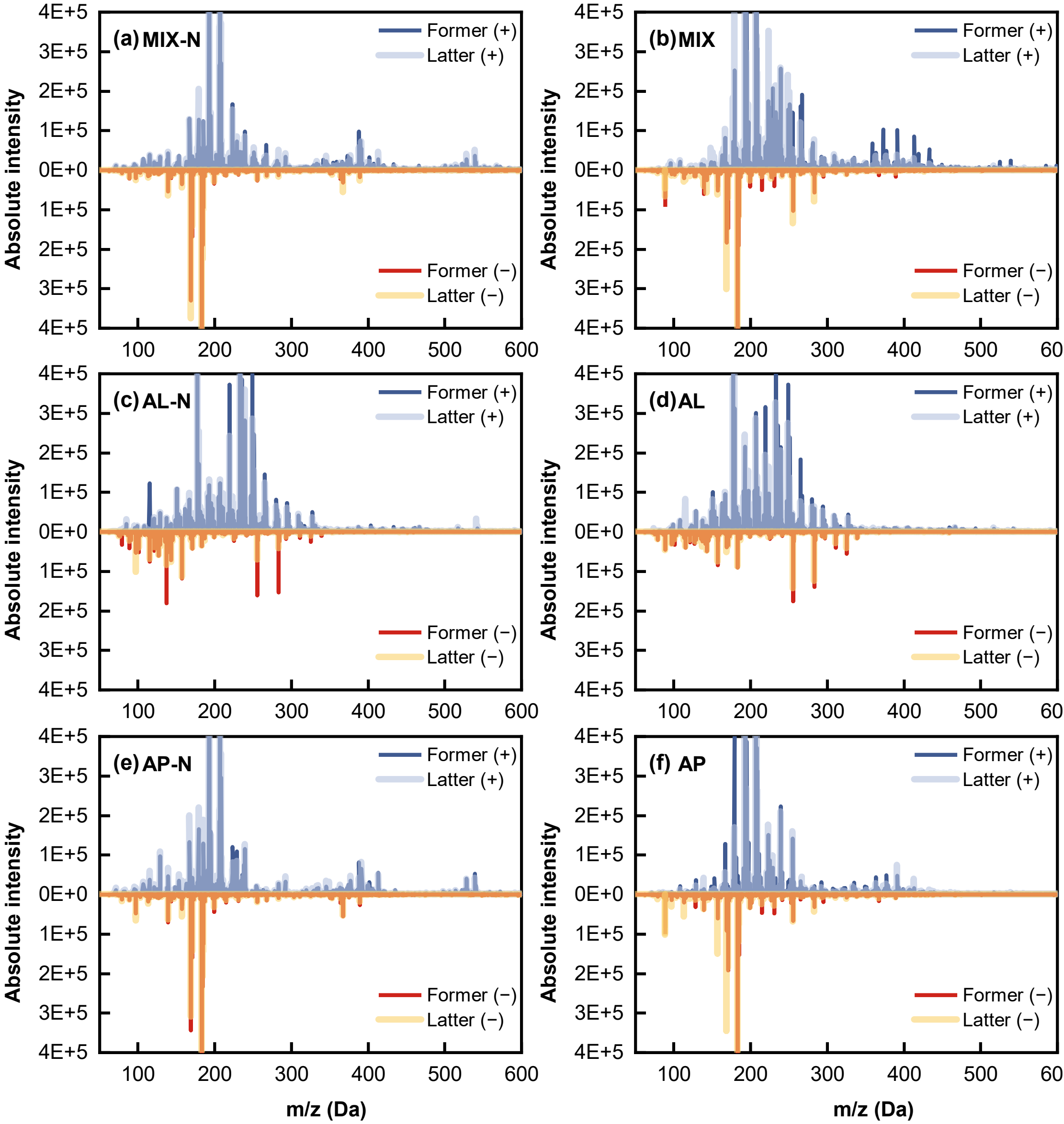
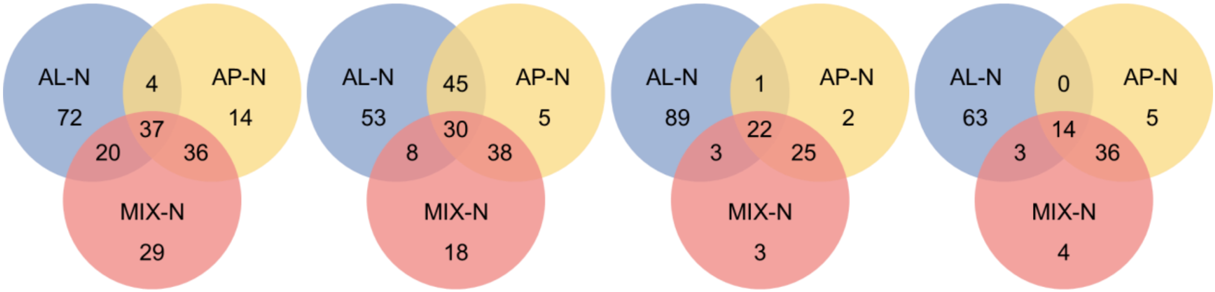
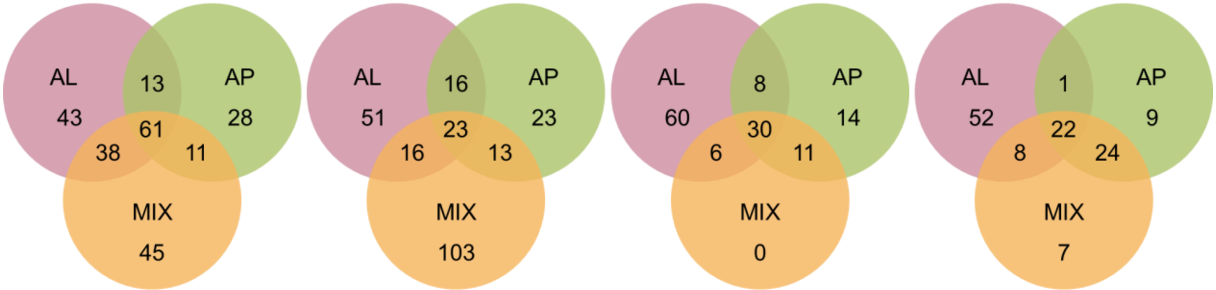


Figure 5. Mass spectra of generated SOA under positive (+) / negative (−) mode in the (a) MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, (b) MIX (n-heptylcyclohexane + α-pinene + HONO) experiment, (c) AL-N (n-heptylcyclohexane + HONO + NH_3), (d) AL (n-heptylcyclohexane + HONO) experiment, (e) AP-N (α-pinene + HONO + NH_3) experiment and (f) AP (α-pinene + HONO) experiment.

As Venn diagram displayed in the Fig. 6, the positive mode revealed a higher detection of compounds with mass spectrometry signal relative intensities exceeding 0.05 compared to the negative mode, with a limited overlap in compound detection between the two modes. This indicated a prevalence of compounds with protonatable functional groups (such as —NH—, —O—, —CH_2, C=O, etc.) in the reaction systems involving n-heptylcyclohexane and α-pinene, while compounds with alcoholic and carboxylic acid functionalities were relatively less abundant (Glasius, 1999, J. Chromatogr. A; Steckel and Schlosser, 2019, Molecules). In positive mode, 414 compounds were totally detected, with 234 compounds consistently present across both former and latter half of the reaction, representing over 56% of the total compounds identified (Table S2). In negative mode, 182 compounds were totally identified, with 74% of these compounds being consistently detected throughout the reaction phases. The presence of unique compounds in each stage, observed in both ionization modes, was likely due to the cross-reactions of intermediates thus the generation of new substances (Shao et al., 2022).



(a) Latter (+) (b) Former (+) (c) Latter (−) (d) Former (−)



(e) Latter (+) (f) Former (+) (g) Latter (−) (h) Former (−)

Figure 6. Number of common discrete compounds and unique compounds in single and mixed experiments detected under positive (+) and negative (−) mode, the signal relative intensity of which were greater than 0.05. A relative intensity of 1 was assigned to the most intense peak that was non-impurity in each sample group.

In the presence of NH_3 within the reaction system, the species common to both the MIX experiments and the AP experiments were 1.8 to 12 times more abundant than those common to the MIX experiments and the AL experiments. This finding was similar to the 16-fold increase reported by Shao et al. (2022) in their experiments with mixed α-pinene and o-cresol, underscoring the prominence of α-pinene oxidation in mixed systems of AVOC and BVOC. Conversely, in the absence of NH_3, a higher number of shared compounds between the AL and MIX experiments were noted in positive mode, whereas a greater overlap was observed between the AP and MIX experiments in negative mode, indicating that the participation of NH_3 could promote the formation of a greater number of compounds bearing readily protonatable functional groups.

3.3.2 Elementary composition

An in-depth analysis of the SOA chemical composition across the systems was performed by categorizing the detected molecular formulas according to their elemental makeup, primarily into CHO and CHON groups (with C, H, O, N corresponding to the constituent atoms in the molecules), and further divided into six classes based on carbon count. The observed peak area for each compound was normalized against the total peak area of the sample, as illustrated in Fig. 7. Among molecules containing solely C, H, and O, C_3~C_5 exhibited lower signal intensities. The MIX-N experiment predominantly comprised C_6~C_{10}, whereas the MIX experiment was enriched with C_{11}~C_{15} molecules. This served as compelling evidence that the presence of NH_3 strongly promoted the termination of cross-reactions or self-oxidation of organic precursors and their intermediates, thereby suppressing the formation of high-molecular-weight compounds. For molecules that include C, H, O, and N, the majority in each system were composed of compounds with 9 to 10 carbon atoms.

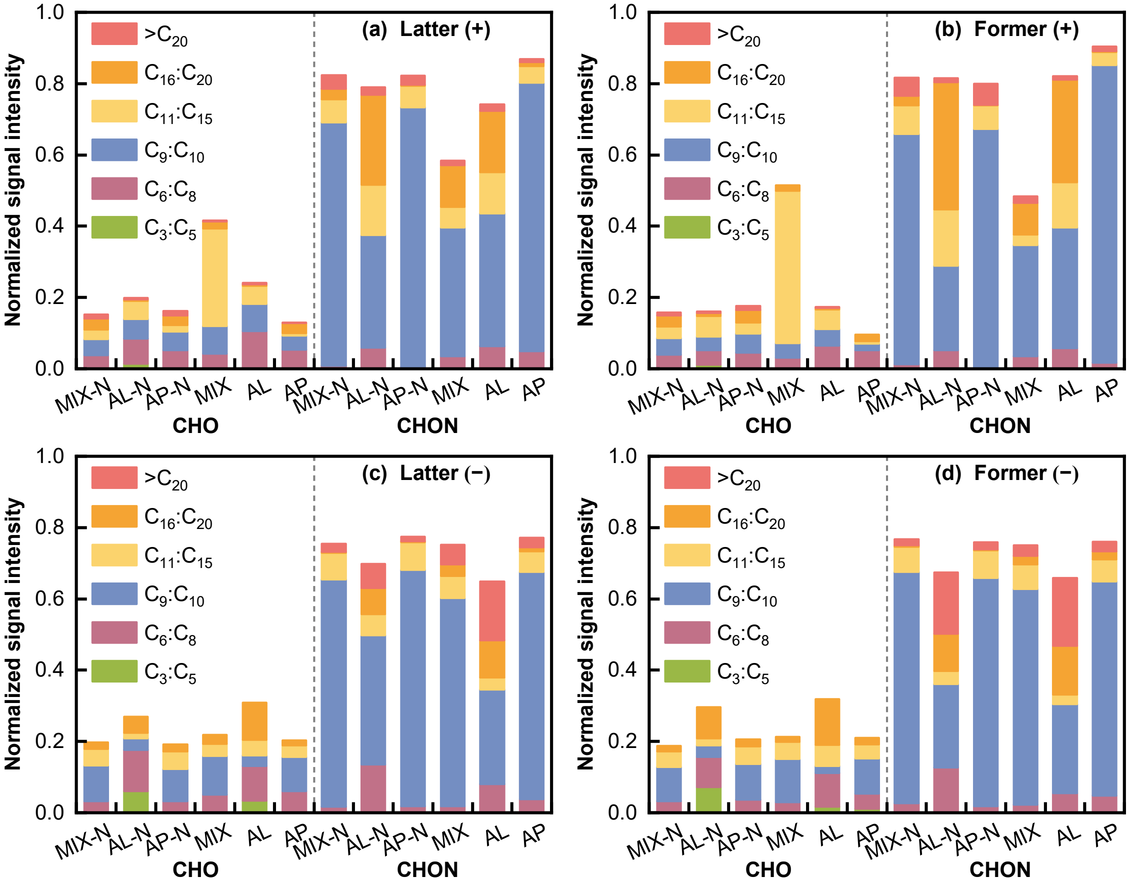


Figure 7. The normalized signal intensity distribution of different compound categories (CHO and CHON) for various single and mixed precursor systems in positive and negative mode.

C_6~C_{10} compounds included those produced through both functionalization (addition oxygenated function group) and fragmentation (cleavage of C—C bond) pathways during α-pinene oxidation (Eddingsaas et al, 2012). The main routes of the α-pinene degradation were the OH addition channel and an H-abstraction channel (Capouet et al., 2004), via which particle-phase dimerization and oligomerization reactions finally occurred (e.g. alcohol + carbonyl to form hemiacetals and acetals, hydroperoxide + carbonyl to form peroxyhemiacetals and peroxyacetals, carboxylic acid + alcohol to form esters, and aldehyde self-reactions to form aldols) (Ziemann and Atkinson, 2012; Gao et al., 2004a, b), resulting in formation of large molecules (>C_{10}) and potentially accounting for the C_{16}~C_{20} abundance. Additionally, the gas-phase autoxidation of α-pinene might contribute to the formation of CHO products with 16~20 carbon atoms (Berndt, 2021; Ehn et al., 2014).

In general, the heptyl-chain of n-heptylcyclohexane could afford it many sites of reaction without the potential of disrupting the stability of the C_6 ring, and continued oxidation of branch chain would tend to eventually cause fragmentation (Capouet et al., 2004). This could account for the predominant presence of C_3~C_5 in AL experiments, which was likely associated with the oxidation of the branched structure of n- heptylcyclohexane. Obviously, the presence of NH3 led to a significant enhancement in the abundance of C_3~C_5 molecules, as NH_3 could promote the partitioning of these small molecules from the gas phase into the particulate phase (Li et al., 2022a).

In the MIX experiments, products containing only CHO elements exhibited a higher abundance of C_{11} to C_{15} compounds, which could be attributed to the cross-products of n-heptylcyclohexane and α-pinene oxidation and their intermediates, leading to the formation of high carbon number compounds. However, upon the addition of NH_3, it promoted the transformation of high molecular weight products into smaller ones, resulting in a decrease in the abundance of C_{11} to C_{15}. This was consistent with the previous conclusion.

3.3.3 Compounds composition

Furthermore, we identify SOA compounds by dividing regions based on different O/C, H/C, and OSC values. (Fig. 8). The nitrogen-number scaling was intentionally applied to visually distinguish how molecular species distributions vary across different nitrogen -number ranges, thereby potentially offering preliminary clues for subsequent analysis of NH_3-involved reaction pathways in mixed organic oxidation systems. Given that the reaction precursors did not contain aromatic compounds, naturally no aromatic hydrocarbons were formed in region A1. Clearly under the positive mode, the products of n-heptylcyclohexane and α-pinene were mainly found in region A2 and B1, suggesting that the products from both single and mixed systems were primarily composed of aliphatic compounds and oxygenated organic molecules (OOMs) with more reducing functional groups. Scaling by nitrogen number allows for a more intuitive view of the NOC species distribution. Since the SOA collected in this experiment covered entire reaction period, it might contain some intermediates with unstable structures. Furthermore, the oxidation conditions in our photochemical experiments were significantly more complex than those in the ozonolysis of single α-pinene. Consequently, the average H:C ratio was likely to be slightly higher than reference values (Putman et al., 2012). In the presence of NH_3, there were fewer compounds in B2 than in the experiments without NH_3 (Fig. S2) presenting fewer OOMs with more oxidizing functional groups (alcohols, ethers, peroxides, carbonyls) in the products. This could be attributed to the suppression effect of OOMs formation by NH_3. As for the negative mode, the products of n-heptylcyclohexane and α-pinene were major detected as aliphatic compounds (Fig. S3 and S4). Furthermore, the mass defect plot revealed that products bearing a higher oxygen content were clearly detected in the absence of NH_3, whereas the maximum oxygen content of the products was markedly lower when NH_3 was present, implying that NH_3 could terminate the multistep oxidation of oligomeric intermediates during the reaction (Fig. S5 and S6). This also suggested that the presence of NH_3 inhibited the formation of OOMs. In summary, the photo-oxidation reaction of the n-heptylcyclohexane and α-pinene single / mixed systems yielded aliphatic compounds and OOMs, and the participation of NH_3 in the reaction could suppress the formation of OOMs.

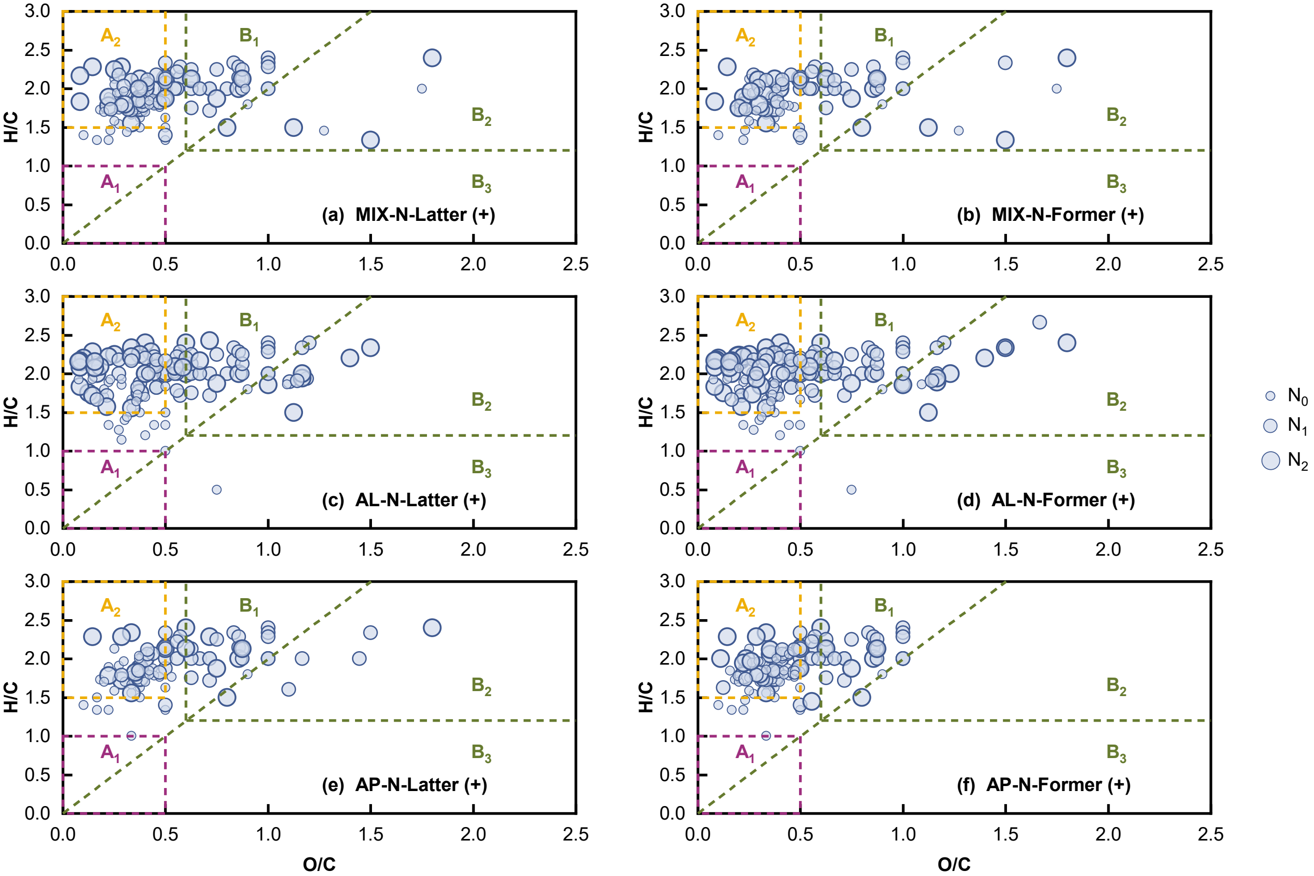


Figure 8. Van Krevelen diagram of compounds detected single / mixed experiments of n-heptylcyclohexane and α-pinene under positive mode. The lower left region (Al) with low H/C and low O/C region (O/C ≤ 0.5, H/C ≤ 1.0) indicated the low oxygen aromatic hydrocarbons. The region A2 with high H/C and low O/C region (O/C ≤ 0.5, H/C ≥ 1.5) represented aliphatic compounds (Mazzoleni et al.,2010; Mazzoleni et.al,.2012). OOMs contained a great fraction of reducing functional groups in the Bl region (O/C ≥ 0.6, H/C > 1.2, OSc < 0), oxidizing functional groups in the B2 region (O/C ≥ 0.6, H/C > 1.2, OSc > 0). The moderate oxidation level OOMs were in B3 region (OSc ≥ 0, H/C ≤ 1.2) (Tu et.al.,.2016)

3.4 Generation of OVOCs Intermediates

To gain a more comprehensive understanding of the mechanisms of SOA formation, we conducted an analysis of oxygenated VOCs (OVOCs) intermediates, key carbonyl compounds identified in the reaction products (Fig. 9). In the MIX experiment, hexanal peaked at 1.1 μg m^{-3} during the former half of the reaction, and was subsequently consumed by fragmentation or further oxidation. The highest concentration in the latter half of the reaction was heptanal (2.3 μg m^{-3}), which could be attributed to the fact that the heptane branch was first broken and further oxidation was required to break into smaller branches, but sufficient oxidation environment cannot be provided by largely consumed oxidants in the later stage of the reaction. In this system, the total amount of aldehydes and ketones was relatively small, presumably because the aldehydes/ketones reacted with intermediates or products and were transferred to the particle phase. When NH_3 was present, the mass concentrations of all carbonyls rose sharply, indicating that NH_3 either initiated cross reactions and side-reactions within the mixture or reacted with specific intermediates, driving more oxidation/fragmentation of the intermediates into aldehydes and ketones.

In the AL experiment, every carbonyl except crotonaldehyde and heptanal was more abundant in the latter half of the reaction. This might be due to the unstable structure of these two compounds, which caused their rapid oxidation to other substances. Moreover, relative to the NH_3-free case, the NH_3-present system produced substantially more aldehydes and ketones with ≤4 carbon atoms, demonstrating that NH_3 enhanced carbonyl compounds formation in the system, especially that with small molecule.

In the AP experiment, compared with the NH_3-free system, every carbonyl except acetaldehyde increased when NH_3 was present. The decrease of acetaldehyde presumably because NH_3 reacted directly with it to form nitrogen-containing products that partitioned into the particle phase, lowering its gas-phase concentration.

In summary, NH_3 redirected the oxidation pathway through competitive reactions, yielding a larger fraction of lower molecular weight products and small carbonyls.

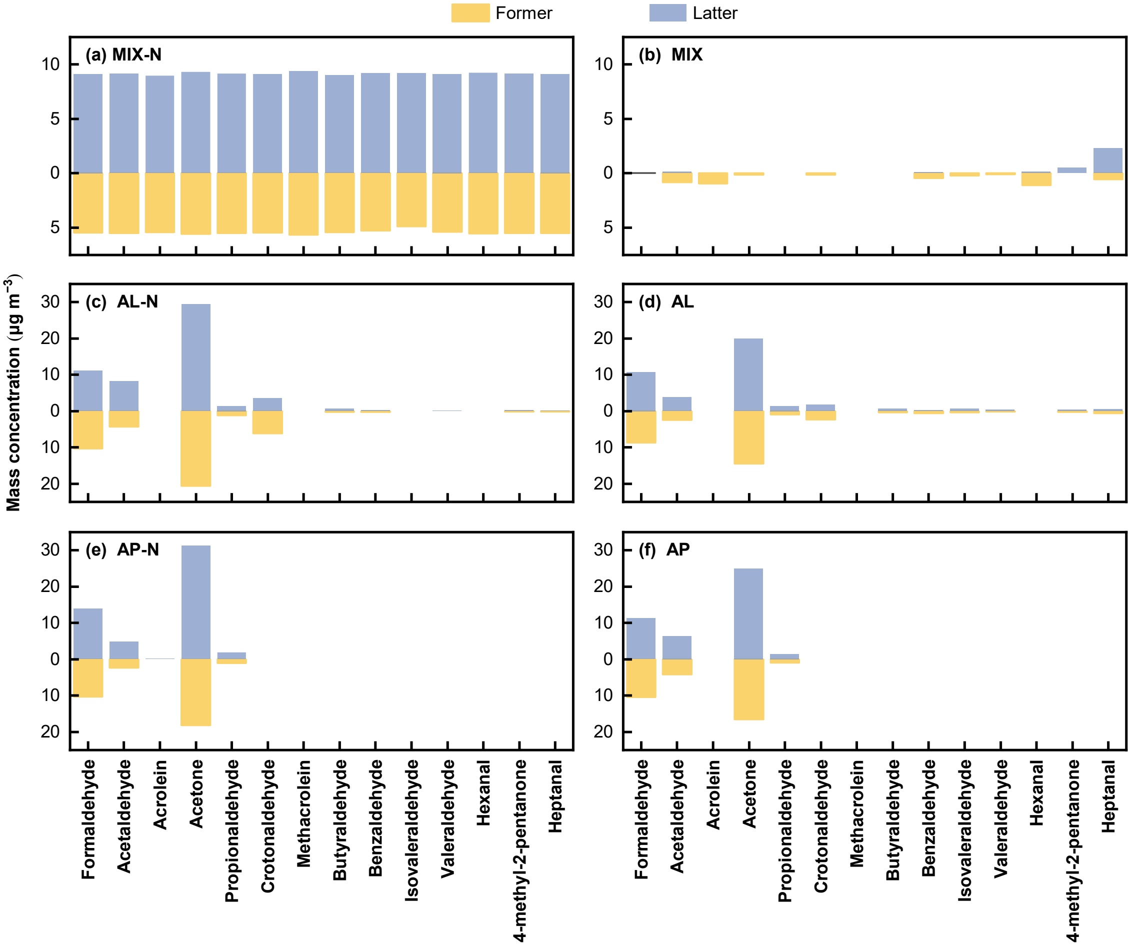


Figure 9. Mass concentration of aldehydes and ketones generated by photo oxidation in the (a) MIX-N (n-heptylcyclohexane + α-pinene + HONO + NH_3) experiment, (b) MIX (n-heptylcyclohexane + α-pinene + HONO) experiment, (c) AL-N (n-heptylcyclohexane + HONO + NH_3), (d) AL (n-heptylcyclohexane + HONO) experiment, (e) AP-N (α-pinene + HONO + NH_3) experiment and (f) AP (α-pinene + HONO) experiment.

3.5 Possible photochemical oxidation paths

Under high-NOx conditions, the photo-oxidation reaction of n-heptylcyclohexane and α-pinene mixture began with H-abstraction by OH radical and thus reaction with O_2 to form an alkyl peroxy radical (RO_2). When NH_3 co-existed with n-heptylcyclohexane, α-pinene and NOx, it markedly enhanced SOA production from the photochemical oxidation of the binary mixture. Cross-reactions between n-heptylcyclohexane, α-pinene and their organic intermediates promoted nucleation and growth of high-molecular-weight oligomers; in particular, peroxy radicals derived from n-heptylcyclohexane added across the double bond of α-pinene, yielding mixed oxidation products such as alkylated terpene oxides. Concurrently, NH_3 neutralised organic acids to form low-volatility ammonium salts, strongly depressing their saturation vapour pressures. NH_3 also reacted with OH radicals or organic radicals to generate nitrogen-containing radicals that further evolved into N-containing molecules, again lowering volatility. Moreover, NH_3 participated in Maillard chemistry with carbonyls, producing N-heterocycles (e.g. imidazoles, Fig. 10) that subsequently fragmented into smaller N-heterocycles and organic acids. Existing observational evidence had indicated that the presence of NH_3 could substantially enhance the formation of imidazole compounds (Liu et al., 2023). These low-volatility products underwent further multigenerational oxidation, giving highly oxygenated and nitrated species. Through these intertwined pathways NH_3 substantially reduced the overall volatility of the photo-oxidation products from the n-heptylcyclohexane and α-pinene mixture, efficiently enhancing SOA formation. By reacting with organic peroxy radicals formed during oxidation, NH_3 produced low volatility compounds that partitioned directly into the particle phase. This partitioning interrupted self-/cross-reactions of $RO_2\cdot$ and suppressed the formation of large OOMs. Meanwhile, multi-step oxidation initiated by NH_3 reacting with carbonyls additionally generated aldehydic and ketonic intermediates, further enriching the gas-phase carbonyl compounds.

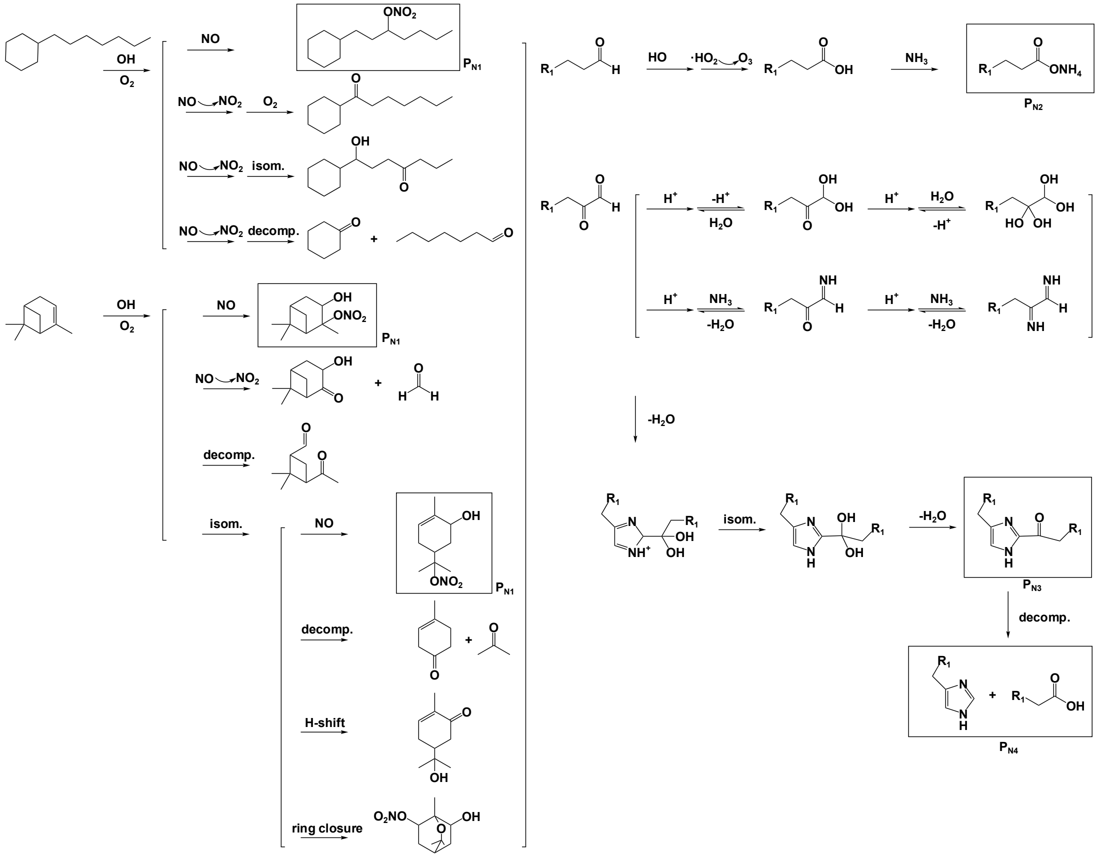


Figure 10. Proposed possible reactions of the mixture experiment in the presence of NH_3 (R_1 was alkyl groups, P_{N1} was organic nitrate esters, P_{N2} was organic ammonium salt, P_{N3} was imidazole compounds, P_{N4} was multi-generational compounds of imidazole cleavage).

4 Conclusions

In the present work, a large-scale outdoor photochemical smog chamber was utilized to study the effect of inorganic gases (NH_3) on the photochemical process of mixed AVOC (n-heptylcyclohexane) and BVOC (α-pinene). After the reaction begins, NH_3 promoted nucleation and participated in particle-phase reactions, leading to the rapid formation and growth of SOA particles within one hour, consequently accelerating precursor consumption. In contrast to previous findings, the influence of NH_3 on the surface mean particle size of precursor-derived SOA was relatively small, primarily because a higher VOC/NOx ratio could weaken the enhancement of new particle growth under high-NOx conditions. The primary products from experiments with mixed n-heptylcyclohexane and α-pinene were gas-phase carbonyl compounds, as well as particle-phase aliphatic compounds, NOCs including imidazoles, and oxygenated organic molecules (OOMs). Reactions between NH_3 and carbonyls enhanced the production of aldehydes and ketones, while its acid-base reactions with organic acids, its radical reactions, and its Maillard reactions with carbonyls promoted SOA formation in the binary system. Furthermore, reactions between NH_3 and organic radicals terminated the cross-reactions and autoxidation of RO_2, thereby suppressing OOMs formation.

This study explored the influence of NH_3 on photochemical oxidation reactions and products in mixed systems of cyclic branched alkanes and biogenic alkenes under high-NOx conditions, improving upon previous studies of single organic systems by better simulating real atmospheric conditions. The findings can deepen the understanding of SOA formation in regions impacted by complex emissions and further clarify the mechanisms through which NH_3 affects mixed oxidation reactions. This study reveals potential pathways for NH_3 participation in mixed oxidation reactions. Future research should conduct in-depth analyses and quantification of product characteristics to elucidate definite pathways, thereby achieving a comprehensive understanding of chem-physical processes in the real atmosphere.

In recent years, global NH_3 emissions have shown an overall upward trend, with agricultural emissions remaining dominant. South and East Asia (e.g., India, Bangladesh, and China) are regions with the highest global NH_3 concentrations, while significant concentrations have also been observed in biomass burning areas of North Africa, Central Africa, and South America (Khan et al., 2020). Because NH_3 influences aerosol formation and evolution in multiple ways, investigating its atmospheric behavior and accurately identifying its chemical evolution mechanisms in complex atmospheric environments can help to mitigate aerosol impacts on climate and improve the accuracy of regional air quality forecasting.

Data availability

The data used in this study are available upon request from the corresponding author.

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Author contributions

J.L. conceived the study. Y.Y. performed the experiments and conducted the data analyses. Y.Y. and J.L. interpreted and discussed the data results. Y.Y. wrote the manuscript. J.L. and H.L. revised the manuscript. All authors contributed to the final paper.

Competing interests

The authors declare no competing interests.

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