

The impact of CO on secondary organic aerosols formed from the mixture of α -pinene and n-dodecane

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Abstract. ~~Atmospheric simulation chambers are powerful tools for investigating~~ Secondary organic aerosol (SOA) formation is strongly influenced by atmospheric processes and form the basis for model parameterisations. Ensuring the conditions. Achieving atmospheric relevance of experimental conditions is crucial in chamber experiments is essential for understanding and predicting the impacts of ~~secondary organic aerosols (SOA)~~ on air quality and climate. However, many chamber studies are ~~often~~ conducted under simplified conditions, ~~which may limit their applicability to real-world scenarios. or with a single SOA precursor.~~ Here, we investigated the impact of CO on ~~the~~ SOA particle mass yields and chemical composition ~~of SOA particles formed~~ from α -pinene (a biogenic volatile organic compound (VOC, ~~α -pinene~~)), n-dodecane (an anthropogenic intermediate-volatility organic compound (IVOC, ~~n-dodecane~~)), and their mixture in the presence of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$ ~~+ NO~~) in the Manchester Aerosol Chamber (MAC). ~~This photochemical system better represents polluted atmospheric conditions) using online measurements.~~ The results show that the influence of CO differed between single- and mixed-precursor systems. In the single-precursor systems, CO significantly suppressed SOA particle mass yields, whereas no such suppression was observed in the mixture. Moreover, compared with the single-precursor systems, CO exerted a diminished impact on the organic peroxy (RO_2) radical reaction pathways in the mixture, with the extent of this change differing between α -pinene and n-dodecane. These findings ~~demonstrate that variations in reaction conditions can lead to different responses in SOA particle properties between the single and mixed precursor systems, highlighting~~ highlight the importance of ~~conducting~~ accounting for atmospheric complexity in laboratory ~~experiments under atmospherically relevant conditions~~ studies.

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1 Introduction

~~Organic aerosols (OA) account for 20 to 90% of the total atmospheric fine particulate matter mass. Secondary organic aerosol (SOA) constitutes a substantial fraction of ambient aerosol and can significantly influence climate, has significant impacts on air quality, climate and human health. A substantial fraction of OA consists of secondary organic aerosols (SOA), which are. It is formed through the vapour phase oxidation of gas-phase organic compounds and subsequent followed by gas-particle partitioning (Atkinson and Arey, 2003; Hallquist et al., 2009; Jimenez et al., 2009; Ramanathan et al., 2001; Robinson et al., 2007) into the condensed phase. These processes are complex and strongly influenced by atmospheric conditions (Hallquist et al., 2009; Kroll and Seinfeld, 2008; Xu et al., 2015). Comprehensive. Despite extensive research, achieving a comprehensive understanding and accurate prediction of SOA formation are critical for assessing the impacts of aerosols on global climate and regional air quality remain challenging (Kenagy et al., 2024; Shrivastava et al., 2017).~~

Laboratory studies and atmospheric modelling are two key approaches for investigating atmospheric SOA (Burkholder et al., 2017). Model parameterisations are largely derived from laboratory studies, and the accuracy of model predictions strongly depends on the atmospheric relevance of experimental conditions employed (Burkholder et al., 2017; Kanakidou et al., 2005; Kenagy et al., 2024). ~~The ambient atmosphere comprises a complex mixture of biogenic and anthropogenic emissions, including a wide range of gas-phase organic compounds and inorganic trace gases (Gu et al., 2021; Guenther et al., 1995). Field measurements have provided evidence that anthropogenic emissions can modulate SOA formed from biogenic precursors (Budisulistiorini et al., 2015; Shilling et al., 2013; Xu et al., 2015). However, many laboratory experiments are conducted under simplified rather than atmospherically relevant conditions for experimental reasons or with a single SOA precursor, which may introduce uncertainties in predicting SOA concentrations in when extrapolating these results to atmospheric models (Kenagy et al., 2024; Shrivastava et al., 2017; Tsigaridis et al., 2014).~~

~~Organic peroxy radicals (RO_2) play a central role in SOA formation (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). They can undergo bimolecular termination reactions with hydroperoxyl radicals (HO_2), other RO_2 radicals, or nitrogen oxides ($NO_x = NO + NO_2$), as well as unimolecular termination (Atkinson, 2000; Goldman et al., 2021; Molteni et al., 2019; Ziemann and Atkinson, 2012). Recent studies have focused on the autoxidation pathways of RO_2 radicals that produce highly oxygenated molecules (HOMs), which are considered potentially important contributors to SOA formation owing to their extremely low volatility (Bianchi et al., 2019; Ehn et al., 2014; Pospisilova et al., 2020). In real atmospheric environments, the coexistence of multiple SOA precursors and various inorganic trace gases introduces additional chemical complexity into the system (McFiggans et al., 2019; Xu et al., 2015). The ambient atmosphere comprises a complex mixture of biogenic and anthropogenic gas phase organic compounds. However, laboratory studies often focus on single precursors. Increasing evidence indicates that interactions among oxidation products from different sources can influence the formation of SOA, observed enhanced SOA production when anthropogenic emissions from Sacramento mixed with isoprene rich air from the foothills. Such complexity can substantially modify RO_2 reaction pathways, thereby influencing product distributions and yields.~~

An increasing number of studies have focused on mixtures of multiple precursors. McFiggans et al. (2019) demonstrated that the presence of isoprene can suppress the particle mass yield of SOA formed from α -pinene. In mixing α -pinene with isoprene substantially suppresses SOA formation from α -pinene, reducing SOA mass formation by about 60 % and SOA yield by 40 %. This suppression was attributed to two main mechanisms. First, isoprene, which exhibits a relatively low yield, efficiently competes with α -pinene for available OH, thereby suppressing the formation of α -pinene-derived RO₂ radicals. Second, isoprene-derived RO₂ radicals can scavenge HOM-RO₂ derived from α -pinene, leading to the formation of products with higher volatility. More broadly, mixing effects on SOA particle mass yields have also been observed for other precursor combinations. For example, in multi-precursor systems consisting of two monoterpenes (α -pinene and limonene), SOA formation from α -pinene was enhanced by approximately 50 %, while that from limonene was reduced by about 20 % (Takeuchi et al., 2022). More recent studies have extended such investigations to ternary mixtures comprising biogenic (α -pinene and isoprene) and anthropogenic (o-cresol) precursors, and have also shown that the overall SOA particle mass yields in the mixture deviate from those predicted by additive calculations (Voliotis et al., 2022a). These findings suggest that simple linear combinations addition of SOA particle mass yields from individual components may lead to inaccurate estimates of total SOA formation in mixed-precursor systems.

Atmospheric inorganic trace gases, such as CO and nitrogen oxides (NO_x = NO₂ + NO), can influence the alter oxidant levels and alter the RO₂ reaction pathways (Atkinson, 2000; Baker et al., 2024; Chen et al., 2022; Kang et al., 2025; Kroll and Seinfeld, 2008; Lane et al., 2008; Pullinen et al., 2020; Pye et al., 2019; Sarrafzadeh et al., 2016) of organic peroxy (RO₂) radicals, which play a central role in the formation of SOA. In laboratory studies, without adequately considering the effects of these trace gases, the fate of RO₂ radicals may differ substantially from that in the real experiments, SOA precursor concentrations are often higher than those typically observed in the ambient atmosphere for practical reasons (Ziemann and Atkinson, 2012). This can lead to relatively low HO₂/RO₂ ratios compared with atmospheric conditions, favouring RO₂ + RO₂ reactions over RO₂ + HO₂ reactions (Ziemann and Atkinson, 2012). The former forms accretion products, which may have extremely low volatility and are expected to contribute to SOA formation, potentially leading to an overestimation of SOA particle mass yields (Kenagy et al., 2024; Peräkylä et al., 2023; Ziemann and Atkinson, 2012). The presence of CO can directly consume OH and shift produce HO₂ radicals, thereby shifting the hydroperoxy (HO₂) radical/RO₂ ratio, thereby favouring and increasing the importance of the RO₂ termination of RO₂ + HO₂ over RO₂ + RO₂ reactions via HO₂ (Lu and Khalil, 1993). Previous studies have quantified the effect of CO on SOA production. McFiggans et al. (2019) showed that CO suppressed α -pinene dimer (containing 17 to 20 carbon atoms) formation by a factor of two. Similarly, while the amounts of HOMs were suppressed by factors of 4 to 5. Baker et al. (2024) introduced CO into the α -pinene oxidation system and further demonstrated that unrealistically low HO₂/RO₂ ratios can lead to significant overestimation of SOA mass yields. Under elevated HO₂/RO₂, under constant OH conditions, the formation of highly oxygenated molecule (HOM) addition of CO increased the HO₂/RO₂ ratio from approximately 1/100 to about 1/1, leading to a ~ 60 % reduction in the abundance of HOM-accretion products decreased by about 60 % and a ~ 30 % decrease in the SOA formation potential of HOMs. However, these studies were conducted under NO_x-free conditions. In the ambient atmosphere, CO is high concentrations of CO are often co-emitted with other anthropogenic pollutants, such as NO_x, and the termination of RO₂ radicals involves complex interactions among RO₂s. NO_x can react with RO_x radicals (RO_x = OH + HO₂ + RO₂), thereby influencing RO_x cycling and, consequently, the formation of SOA and O₃

(Chen et al., 2022; Clapp and Jenkin, 2001; Pusede et al., 2015), and HO_2 . It is therefore important to consider the effects of CO and NO_x in conjunction. NO_x governs O_3 concentrations through the photostationary state, thereby indirectly modulating OH via O_3 photolysis. Under NO_x -free conditions, $\text{RO}_2 + \text{RO}_2$ and/or $\text{RO}_2 + \text{HO}_2$ reactions dominate over $\text{RO}_2 + \text{NO}$ reactions, whereas in the presence of NO_x , RO_2 radicals can react rapidly with NO to form alkoxy (RO) radicals (RO) or organic nitrates (Atkinson, 2000; Chen et al., 2022; Kang et al., 2025; Ziemann and Atkinson, 2012) (RONO_2). RO_2 can also react with NO_2 to form peroxy nitrates; however, these species are generally thermally unstable, except at very low temperatures or when derived from acylperoxy radicals (Atkinson, 2000; Goldman et al., 2021; Ziemann and Atkinson, 2012). The effects of NO_x on SOA particle mass yields have been extensively studied. Sarrafzadeh et al. (2016) reported that, in β -pinene photooxidation experiments under low- NO_x conditions, SOA particle mass yields increased with rising NO_x concentrations, which they attributed to enhanced OH concentrations. However, after removing the effect of OH, the yields decreased with increasing NO_x . Pullinen et al. (2020) revealed that increasing higher NO_x concentrations led to a decrease in reduced the fraction formation of gas-phase α -pinene HOM-accretion products, leading to a lower SOA particle mass yield. When CO and NO_x coexist, oxidant levels and RO_2 reaction pathways are influenced by multiple interacting processes. These findings highlight interactions contribute to the need for laboratory studies to account for complexity of the full range of atmospherically relevant conditions ambient atmosphere. It is therefore important to investigate SOA formation in systems containing multiple trace gases.

In this study, we employed a photochemical system incorporating mixtures of biogenic and anthropogenic SOA precursors together with multiple inorganic trace gases commonly associated with anthropogenic emissions. Within this framework, we investigated the impact of CO on the SOA particle mass yields and chemical composition of SOA particles formed from a biogenic volatile organic compound (VOC, α -pinene), an anthropogenic intermediate volatility organic compound (IVOC, n-dodecane), and their mixture, in the presence of NO_x . Based on changes in chemical composition, we inferred shifts in RO_2 reaction pathways and their potential influence on yields. α -Pinene ($\text{C}_{10}\text{H}_{16}$) is the most abundant monoterpene in the troposphere and contributes significantly to the global SOA budget (Andreae and Crutzen, 1997; Lee et al., 2006). n-Dodecane ($\text{C}_{12}\text{H}_{26}$) serves as a proxy for anthropogenic IVOCs, intermediate-volatility organic compounds (IVOCs), being widely present in fuels and emitted primarily as a non-combusted hydrocarbon (Zhao et al., 2015). CO and NO_x are ubiquitous atmospheric trace gases with substantial anthropogenic sources. Experiments were conducted in the Manchester Aerosol Chamber (MAC), using a combination of online and offline instruments to characterise particle- and gas-phase compounds. This work provides new insights into SOA particle properties under polluted conditions more representative of the atmosphere.

Table 1. Summary of experimental conditions.

Experiment No.	Experiment Type	[n-dodecane] ₀ ^a (ppb)	[α -pinene] ₀ ^a (ppb)	[NO _x] ₀ ^a (ppb)	[precursor] ₀ ^a /[NO _x] ₀	[CO] ₀ ^a (ppb)	[Seed] ₀ ^a ($\mu\text{g m}^{-3}$)	[O ₃] _{max} (ppb)	SOA ($\mu\text{g m}^{-3}$)	SOA particle mass yields
α-Pinene experiments										
1	α -pinene	-	59.4	57	1.0	171	31.0	37.9	39.9	0.12
2	α -pinene	-	48.9	54	0.9	185	56.1	39.0	42.1	0.16
3	α -pinene + CO	-	42.7	68	0.6	8360	35.9	60.7	17.8	0.08
n-Dodecane experiments										
4	n-dodecane	160	-	281	0.6	160	37.8	103.1	177.5	N.A. ^b
5	n-dodecane	160	-	156	1.0	195	31.2	98.4	122.9	0.17
6	n-dodecane + CO	160	-	133	1.2	9261	48.2	99.1	26.3	0.05
7	n-dodecane + CO	160	-	204	0.8	9473	47.1	98.5	14.7	0.02
Mixed-precursor experiments										
8	mixture	80	24.8	160	0.9	139	34.5	85.9	71.4	N.A. ^b
9	mixture	80	27.4	121	0.6	168	36.9	76.2	63.9	0.11
10	mixture + CO	80	22.1	109	0.6	10000	45.6	93.8	67.1	0.18
11	mixture + CO	80	14.3	161	0.9	10668	37.8	109.4	50.5	0.14

^aThe subscript "0" indicates the initial concentration.

^bN.A.: no available data.

2 Methodology

2.1 Generic peroxy radical chemistry

140 The analysis has been informed by the prevailing generic peroxy radical chemistry. RO₂ radicals can undergo bimolecular termination reactions with HO₂ radicals, other RO₂ radicals, or NO_x, leading to the formation of closed-shell products (Atkinson, 2000; Ziemann and Atkinson, 2012).

Hydroperoxides:



Carbonyls and alcohols:



Organic nitrates:



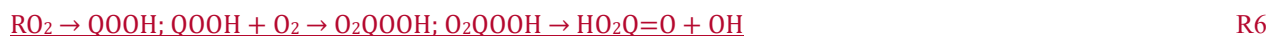
145 Peroxy nitrates:



Accretion products:

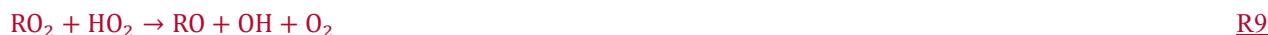


RO₂ radicals can also undergo unimolecular reactions that lead to the formation of carbonyls (Goldman et al., 2021; Molteni et al., 2019).



150 QOOH is a key oxidation intermediate formed via intramolecular hydrogen abstraction by RO₂ radicals.

Besides closed-shell products, RO₂ radicals can also form RO radicals (Orlando et al., 2003).



HOMs are formed via autoxidation pathways of RO₂ radicals (Bianchi et al., 2019; Goldman et al., 2021).



155 These reaction pathways compete with one another, thereby influencing the distribution of products.

160 α -Pinene photooxidation is expected to produce C₁₀H₁₅O_x and C₁₀H₁₇O_x as major RO₂ families. The C₁₀H₁₇O_x family is initiated via OH addition to α -pinene (Berndt et al., 2016; Jenkin et al., 1997; Kang et al., 2025; Vereecken and Peeters, 2004). RO₂ + HO₂ termination (R1) of C₁₀H₁₇O_x forms C₁₀H₁₈O_n hydroperoxides, and RO₂ + RO₂ termination (R2) yields C₁₀H₁₆O_n carbonyls and C₁₀H₁₈O_n alcohols. Unimolecular termination (R6) of C₁₀H₁₇O_x generates C₁₀H₁₆O_n carbonyls. The C₁₀H₁₅O_x family is formed via hydrogen abstraction from α -pinene or from first-generation oxidation products (e.g., pinonaldehyde), as

165 well as directly from ozonolysis through the vinyl hydroperoxide pathway (Jenkin et al., 1997; Johnson and Marston, 2008; Kang et al., 2025). RO₂ + HO₂ termination (R1) of C₁₀H₁₅O_x forms C₁₀H₁₆O_n hydroperoxides, whereas RO₂ + RO₂ termination (R2) produces C₁₀H₁₄O_n carbonyls and C₁₀H₁₆O_n alcohols. Unimolecular termination (R6) of C₁₀H₁₅O_x generates C₁₀H₁₄O_n carbonyls. RO₂ + RO₂ reactions (R2) between C₁₀H₁₅O_x and C₁₀H₁₇O_x radicals lead to the formation of C₁₀H₁₄O_n carbonyls and C₁₀H₁₈O_n alcohols, and/or C₁₀H₁₆O_n carbonyls and alcohols.

170 The main RO₂ radicals expected from n-dodecane photooxidation are C₁₂H₂₅O_x family (Zhang et al., 2014). RO₂ + HO₂ termination (R1) yields C₁₂H₂₆O_n hydroperoxides, while RO₂ + RO₂ termination (R2) produces C₁₂H₂₄O_n carbonyls and C₁₂H₂₆O_n alcohols. Unimolecular termination (R6) of C₁₂H₂₅O_x generates C₁₂H₂₄O_n carbonyls.

175 In the mixture, RO₂ radicals originating from different precursors can undergo cross-reactions. Reactions (R2) between C₁₀H₁₅O_x and C₁₂H₂₅O_x yield C₁₀H₁₄O_n carbonyls and C₁₂H₂₆O_n alcohols or C₁₂H₂₄O_n carbonyls and C₁₀H₁₆O_n alcohols. Similarly, reactions (R2) between C₁₀H₁₇O_x and C₁₂H₂₅O_x lead to the formation of C₁₀H₁₆O_n carbonyls and C₁₂H₂₆O_n alcohols, or C₁₂H₂₄O_n carbonyls and C₁₀H₁₈O_n alcohols.

RO radicals formed via reactions R7–R9 can subsequently undergo unimolecular decomposition, isomerisation, or react with O₂ (Orlando et al., 2003). Reaction of RO radicals with O₂ leads to the formation of carbonyl compounds and HO₂ radicals:



180 RO radicals derived from C₁₀H₁₅O_x can form C₁₀H₁₄O_n carbonyls via this pathway, whereas RO radicals derived from C₁₂H₂₅O_x yield C₁₂H₂₄O_n carbonyls.

185 Theoretically, C₁₀H₁₄O_n and C₁₂H₂₄O_n carbonyls can be formed via multiple pathways, including RO₂ + RO₂ reactions (R2), unimolecular termination of RO₂ radicals (R6), and reaction of RO radicals with O₂ (R11). However, previous studies have demonstrated that, under ambient-temperature conditions and in the presence of NO_x, unimolecular termination pathways are not expected to be dominant in RO₂ chemistry (Goldman et al., 2021; Goss et al., 2025). In addition, RO radicals derived from α -pinene generally favour fragmentation owing to the low energy barrier for C-C bond scission (Dibble, 2001). For linear RO radicals formed from long-chain alkanes, isomerisation dominates over reactions with O₂ (Atkinson, 2007; Ziemann and Atkinson, 2012)2-1. On this basis, both unimolecular termination and RO + O₂ reactions are expected to make only minor contributions and are therefore not explicitly considered in this study.

195 Therefore, C₁₀H₁₄O_n and C₁₂H₂₄O_n carbonyls are expected to be formed predominantly via RO₂ + RO₂ reactions (R2). In contrast, C₁₀H₁₆O_n, C₁₀H₁₈O_n, and C₁₂H₂₆O_n species can be produced not only through reactions (R2) but also via RO₂ + HO₂ pathways (R1). Accordingly, changes in the relative abundances of C₁₀H₁₄O_n and C₁₂H₂₄O_n compounds are used as indicators to assess the influence of CO on RO₂ chemistry. In general, the presence of CO is expected to reduce the relative contribution of RO₂ + RO₂ termination, which would be reflected in decreased relative abundances of C₁₀H₁₄O_n and C₁₂H₂₄O_n species.

2.2 Experimental setup and procedure

The experiments were conducted in the 18 m³ MAC at the University of Manchester. The chamber comprises a fluorinated ethylene propylene (FEP) Teflon bag supported by three rectangular frames. Further details of the chamber are provided in Shao et al. (2022). ~~illumination was provided by a series of halogen lamps (50W/4700K MR16, Solux).~~ The irradiation source, consisting of two xenon arc lamps (XBO 6000W/HSLA OFR, Osram), and a series of halogen lamps (50W/4700K MR16, Solux), is mounted inside the chamber and generates irradiation over the wavelength range of 290–800 nm to mimic the atmospheric radiation spectrum. The corresponding actinic flux spectrum is presented in Shao et al. (2022). The photolysis rate of NO₂ (J_{NO_2}) was $1.38 \times 10^{-3} \text{ s}^{-1}$. To promote OH radical production, an additional UVC lamp operating at 254 nm (TUV 130W XPT SE UNP/20, Philips) was installed, with more than 90 % of its length masked to prevent excessive irradiation. The liquid precursors (α -pinene, ~~analytical~~ analytical standard, Sigma-Aldrich; n-dodecane, anhydrous, ≥ 99.0 %, Sigma-Aldrich) were initially injected via syringe into a heated glass bulb to facilitate vaporisation. ~~The resulting, after which the~~ vapours were ~~subsequently~~ carried into the chamber by electronic capture device-grade nitrogen (ECD N₂). NO_x was introduced from a custom-made cylinder using ECD N₂ as the carrier gas. ~~They~~ NO₂ served as ~~at the~~ the source of ~~OH via O₃, and the subsequent O₃~~ photolysis generated OH radicals, thereby initiating ~~the~~ photochemical oxidation. The initial precursor/NO_x ratios were controlled within the range of 0.6 ~~to 1~~ to 1.2, while the initial NO₂/NO ratios ~~were maintained~~ dranged between 1.5 and 2.5. Seed particles with a mass concentration of $40.2 \pm 8.0 \mu\text{g m}^{-3}$ were generated by nebulising aqueous ammonium sulfate solutions ((NH₄)₂SO₄, ACS reagent, ≥ 99.0 %, Sigma-Aldrich) using an aerosol generator. ~~(ATM 230, Topas). During seed injection, the carrier air was passed through the humidifier, ensuring the deliquescence of the seeds as they were generated.~~ These particles provided a condensation surface for the oxidation products, thereby reducing wall losses and suppressing nucleation (Nah et al., 2017).

The initial experimental conditions are summarised in Table 1. Each experiment typically consisted of four steps ~~(Fig. S1)~~:

- (i) Pre-experiment: ~~Prior to each run, a series of preparation steps Repeated flush-fill cycles~~ were conducted, ~~including cyclic flushing~~ to achieve a low-background condition. During these cycles, the chamber was flushed for approximately 7 min and filling then refilled with clean air at a high the same flow rate, with this procedure repeated for approximately about 1.5 h, preheating the precursor injection bulb, introducing all reactants. Subsequently, SOA precursors, NO_x, CO, and seed aerosols, and adjusting were introduced into the chamber. The temperature and relative humidity were adjusted to the target values (approximately 25 °C and 50 \pm 5 %, respectively).
- (ii) Stabilisation: The chamber was kept in the dark for 20 to 30 min ~~with all the reactants and seed aerosols, allowing their concentrations to stabilise.~~ initial conditions prior to illumination.
- (iii) Experiment: ~~Each photochemical experiment lasted for approximately 5 h, corresponding to four cycles of the Filter Inlet for Gases and Aerosols coupled to a Chemical Ionisation Time-of-Flight Mass Spectrometer (FIGAERO-CIMS). Each cycle spanned 1.5 h, with the first 30 min allocated to gas and particle sampling and gas phase analysis, followed by 1 h of particle phase analysis (described in Sect. 2.3.1). In the final cycle, the photochemical reaction was terminated after the completion of particle sampling.~~ When the lights were turned on, photooxidation and subsequent SOA formation were initiated. Each “experiment” phase lasted for approximately 5 h.

(iv) Post-experiment: After the ~~light sources~~lights were ~~switched~~turned off, the chamber underwent ~~cyclic flushing and filling with clean air~~repeated flush-fill cycles for approximately 1 h. It was then filled with ~~ozone~~O₃ at a high concentration (≥ 1 ppm) and left to soak overnight to oxidise and remove residual O₃-~~reacting~~reactive organic species.

~~Table 1 summarises the key experimental conditions and results. Repeat experiments were conducted to enhance the reliability of the results and to address data gaps caused by instrument failures. Instrument availability for each experiment is listed in Table S1. Unless otherwise stated, the figures in this paper show mean values from the available repeat experiments.~~

2.23 Iso-reactivity conditions

OH radicals served as the primary oxidant in our experiments. ~~To ensure comparability across systems, all~~All experiments were initiated ~~with~~under iso-reactivity ~~towards OH radicals~~conditions with respect to OH (Voliotis et al., 2022b; Voliotis et al., 2021). Specifically, the total OH reactivity was kept constant between single- and mixed-precursor systems. In the ~~mixture, the mixed-precursor system, SOA~~ precursor concentrations were ~~adjusted to contribute~~set such that each contributed equally to the ~~overall~~total OH reactivity. ~~This approach ensured that both precursors~~Under these conditions, each precursor had an equal ~~initial~~probability of reacting with OH and producing first-generation oxidation products (Voliotis et al., 2022b; Voliotis et al., 2021). The initial reactivity was calculated using the following equation:

$$\text{Initial reactivity (s}^{-1}\text{)} = \sum C_{\text{precursor},i} \times K_{\text{OH},i} \quad (1)$$

where $C_{\text{precursor},i}$ is the concentration of precursor i (molecule cm^{-3}), and $K_{\text{OH},i}$ is the reaction rate coefficient of precursor i with OH ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The reaction rate coefficients for α -pinene and n-dodecane with OH are 5.33×10^{-11} and 1.32×10^{-11} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Atkinson, 2003; Dash et al., 2014). As α -pinene exhibits greater reactivity towards OH than n-dodecane, a higher initial concentration of n-dodecane was used to achieve iso-reactivity in the experiments. ~~The target mixing ratios of α -pinene were 40 ppb in the single-precursor system and 20 ppb in the mixed-precursor system, while those of n-dodecane were 160 ppb and 80 ppb, respectively. The ratio of α -pinene to n-dodecane falls within the range observed in urban and roadside environments~~ (Okada et al., 2012). The initial CO concentration was also determined according to the principle of iso-reactivity. The reaction rate coefficient of CO with OH is $2.50 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Amedro et al., 2012).

2.34 Instrumentation

Near-real-time gas- and particle-~~phase~~ composition was measured using ~~a Filter Inlet for Gases and Aerosols coupled to a Chemical Ionisation Time-of-Flight Mass Spectrometer~~ (FIGAERO-CIMS (Aerodyne Research Inc.). ~~Precursors (α -pinene and n-dodecane)~~SOA precursors were measured in real time using a Vocus Proton-Transfer Reaction Time-of-Flight Mass ~~Spectrometry~~Spectrometer (Vocus PTR-ToF-MS, ToFwerk). The non-refractory submicron aerosol particle composition, including ~~aerosol~~ sulfate, nitrate, ammonium, chloride, and organics, was measured in real time using a Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS, Aerodyne Research Inc.). NO and NO₂ were measured using a chemiluminescence NO-NO₂-NO_x analyser (Model 42i, Thermo Fisher Scientific Inc.). O₃ and CO were measured using a UV absorption O₃ analyser (Model 49C, Thermo Fisher Scientific Inc.) and a CO analyser (Model 48i, Thermo Fisher Scientific

Inc.), respectively. ~~Particle~~The mass concentration of seed aerosols in the 20–500 nm size range was measured ~~with~~ using a Differential Mobility Particle Sizer (DMPS), consisting of a Vienna-design differential mobility analyser (DMA) coupled to a Condensation Particle Counter (CPC, model 3775, TSI Inc.) (Alfarra et al., 2012). ~~The availability of instruments for each experiment is listed in Table S1.~~

2.34.1 FIGAERO-CIMS

The FIGAERO system enables simultaneous characterisation of gas- and particle-phase species by sampling gases through one inlet while collecting particulate matter on a filter via a separate sampling port (Bannan et al., 2019; Lopez-Hilfiker et al., 2014). The instrument was operated in negative-ion mode using I⁻ as the reagent ion, generated by passing CH₃I and N₂ over a ²¹⁰Po radioactive source. It was run in a cyclic mode consisting of the following procedure:

- (i) 30 min of gas-phase sampling and simultaneous particle collection onto a PTFE filter (2.0 μm pore size, Zefluor; ~~filters were pre-heated to 200 °C to remove potential contaminants~~) both at 1 L min⁻¹. During this step, the instrument was flushed with N₂ for 0.5 min every 4.5 min to obtain the ~~gas-phase instrument~~ background signal.
- (ii) 25 min of temperature-programmed thermal desorption of the collected particles, with the temperature ramped from ambient to ~~340 °C~~ 200 °C.
- (iii) 15 min of isothermal soaking at ~~340 °C~~ 200 °C.
- (iv) 20 min of cooling from ~~340 °C~~ 200 °C to ambient temperature.
- (v) 2 min of N₂ flushing to clean the instrument.

~~An “instrument background”~~ Each cycle spanned approximately 1.5 h, and each experiment comprised four such cycles. In the final cycle, the photochemical reaction was terminated after procedure ~~was~~ (i), corresponding to the completion of particle sampling (Fig. S1).

To account for background species in the chamber, background measurements were conducted weekly ~~to correct for the~~. During these measurements, all components (SOA precursors, seed particles, CO, and NO_x) were injected under the same conditions as in the regular experiments, while the chamber was kept in the dark. Data obtained during these background measurements were subtracted from the corresponding gas- and particle-phase ~~background~~ data acquired during the “experiment” phase.

The FIGAERO-CIMS data were analysed using the Tofware package (v4.0.0) in Igor Pro 7.0.8 (WaveMetrics©). ~~Peak~~ I⁻, H₂OI⁻, CH₂O₂I⁻, and I₃⁻ were used for mass-to-charge calibration (calibration error ≤ 3 ppm). High-resolution peak identification and fitting ~~was~~ were performed ~~over~~ in the m/z range of 200–550 (iodide adducts), which contained the vast majority of the total signal. Owing to the lack of available calibration standards and potential variability in instrument sensitivity across different oxygenated organic compounds, quantitative analysis using I-CIMS remains challenging (Lee et al., 2014) ~~to 550 Da~~. As a result, a uniform instrument sensitivity was assumed for all detected products. Additional uncertainties arise from the thermal decomposition in the FIGAERO. As shown in Fig. S2, several compounds with relatively low carbon numbers exhibited comparatively high average carbon oxidation state (\overline{OSc}) values and elevated maximum desorption temperature (T_{max}).

However, these species together accounted for less than 10 % of the total signal, indicating that the impact of thermal decomposition on the chemical composition was limited.

2.34.2 Vocus PTR-ToF-MS

The Vocus PTR-ToF-MS provides high-sensitivity and fast-response measurements of organic compounds without the need for pre-concentration or chromatographic separation. Compared to traditional PTR-MS, the Vocus employs a focusing ion-molecule reactor (IMR) ~~equipped with consisting of a glass tube that is mounted inside~~ a radio frequency (RF) quadrupole, ~~which focuses ions with an axial electric field applied~~ along the ~~central axis of the reactor and thereby improve~~ tube. ~~This design enhances~~ ion transmission efficiency ~~and suppresses the clustering of ions with water molecules, thereby improving sensitivity and lowering the limit of detection~~ (Jensen et al., 2023; Krechmer et al., 2018; Yuan et al., 2017). ~~An axial electric field is applied within the IMR to increase ion collision energies and suppress the clustering of ions with water molecules.~~

In our experiments, the ion source was supplied with a 20 sccm flow of water vapor. The IMR was operated at 60 °C and 2.0 mbar, with an axial voltage of approximately 568 V and an RF amplitude of 450 V at 1.3 MHz. The reduced electric field strength (E/N) was 141 Td. Measurements were ~~made conducted~~ on a 5 min cycle, consisting of ~~a 4 min chromatography cycle and a of sampling followed by~~ 1 min ~~of~~ instrumental background ~~measurement~~. Instrument calibration was conducted daily. The calibration curve for α -pinene is presented in Fig. ~~S2S3~~. Owing to the absence of an n-dodecane ~~gas calibration~~ standard, direct quantification was not feasible. Moreover, n-dodecane undergoes extensive fragmentation during ionisation, and its ~~protonated~~ molecular ion signal is ~~subjected subject~~ to interference ~~by from~~ overlapping ~~fragments species~~. Therefore, alternative approaches were adopted for its quantification: (i) the initial ~~concentrations mixing ratios~~ were taken as the ~~set target~~ values (160 ppb in the single-precursor system and 80 ppb in the mixed-precursor system), and (ii) the relative consumption of n-dodecane was inferred from the ~~signal change temporal evolution~~ of ~~representative the~~ $C_{10}H_{21}^+$ fragment ions. ~~In this study, the ion $C_{10}H_{21}^+$ was selected as a marker ion of n-dodecane to track its temporal behaviour (Fig. S3S4).~~ However, ~~this ion may still be influenced by contributions interference~~ from other oxidation products, ~~which could result in or fragments cannot be fully excluded and may have led to~~ an overestimation of SOA particle mass yields. Nevertheless, this uncertainty ~~does not is unlikely to~~ affect the ~~observed effects of CO on the~~ overall trends ~~and/or~~ relative differences in yields.

2.34.3 C-ToF-AMS

A detailed description of the C-ToF-AMS can be found in Drewnick et al. (2009). Ionization efficiency (IE) and relative ionization efficiency (RIE) calibrations were carried out using size-selected NH_4NO_3 and $(NH_4)_2SO_4$ particles. The average IE of NH_4NO_3 was determined to be 2.75×10^{-7} ions molecule⁻¹, while the RIE for NH_4^+ and SO_4^{2-} were 4.71 ± 0.24 and 1.13 ± 0.01 , respectively. These values are comparable to those reported in the literature (Canagaratna et al., 2007; Lannuque et al., 2023).

In this study, the organic aerosol (OA)/sulfate correction method was applied to ~~calibrate correct for chamber wall losses in~~ the SOA particle mass ~~concentration derived from concentrations measured by AMS measurements~~ (Wang et al., 2018). This

335 method assumes that the loss rate constants of OA and seed aerosols are identical, and that seed concentrations are affected solely by wall loss. The corrected particle mass concentration is given by:

$$C_{OA}(t) = \frac{C_{OA}^{SUS}(t)}{C_{seed}^{SUS}(t)} C_{seed} \frac{C_{OA}(t)}{C_{seed}(t)} C_{seed}(0) \quad (2)$$

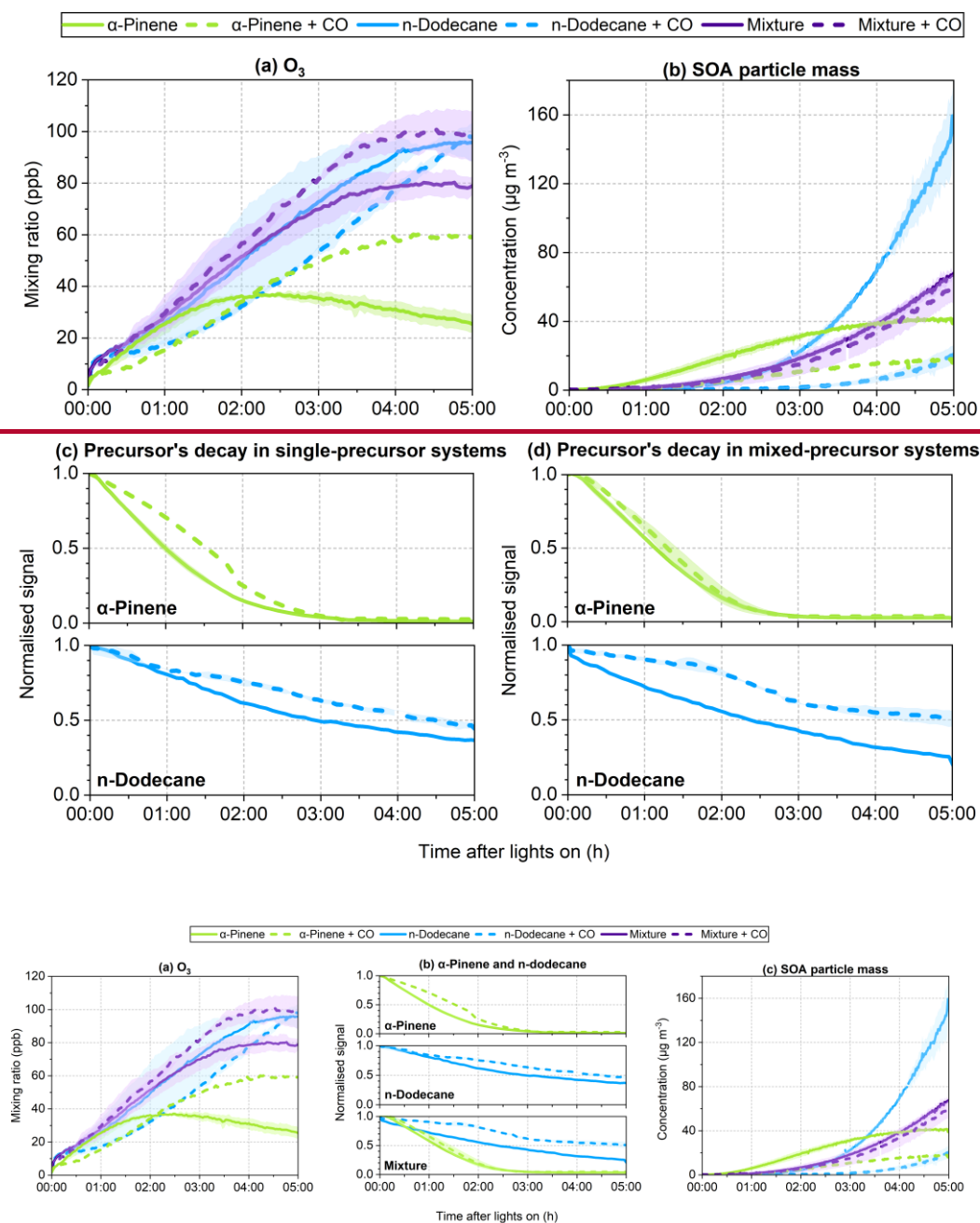
where $\frac{C_{OA}^{SUS}(t)}{C_{seed}^{SUS}(t)} C_{OA}(t) / C_{seed}(t)$ represents the SOA-to-sulfate ratio derived from AMS measurements, and $C_{seed}(0)$ denotes the sulfate concentration at the beginning of the experiment.

340 SOA particle mass yields (Y_{SOA}) for each system were derived from SOA particle mass concentrations ~~measured~~ measured by AMS and precursor concentrations measured by PTR. It is defined as the mass of SOA particles formed per unit of precursor consumed (Gao et al., 2022):

$$Y_{SOA} = \frac{\Delta SOA}{\Delta HC \Delta precursor} \quad (3)$$

345 For the single-precursor systems, ~~ΔHC (hydrocarbon consumption precursor ($\mu g m^{-3}$))~~ denotes the consumption of ~~the individual precursors α -pinene or n-dodecane,~~ whereas ~~for~~ in the mixed-precursor system, it refers to the total consumption of ~~all precursors α -pinene and n-dodecane.~~ In this study, the SOA particle mass yield refers to the overall yield and is calculated as the ratio of the total SOA particle mass formed to the total precursor consumed at the end of the experiment.

3 Results



350

Figure 1: Time series of (a) O_3 , (b) normalised SOA precursor signals, and (c) SOA particle mass concentrations, ~~(e)~~ and ~~(d)~~ normalised signal of the precursors during the photochemical reaction of α -pinene, n-dodecane and their

355 mixture. Time 0 corresponds to the start of step (iii) (Sect. 2.2), when the chamber lights were turned on. Solid and dashed lines denote experiments conducted without and with CO, respectively. ~~The~~Where duplicate experiments were available, the lines represent the mean values, and the shaded area represents the envelope of the measurements from repeat experiments.indicates the range between replicates (Table 1).

360 ~~Fig.~~Figure 1 presents ~~an overview of~~ the temporal evolution of O₃, precursor decay, and SOA particle mass concentrations, ~~and precursor decay~~ during the photochemical reactions. Solid and dashed lines represent experiments conducted in the absence and presence of CO, respectively. The corresponding time series of NO, NO₂, and CO are shown in Fig. ~~S4S5~~. These observations form the basis for evaluating the influence of CO on SOA particle formation and mass yields across different systems. Detailed results from the α -pinene, n-dodecane, and mixed-precursor experiments are presented in the following subsections.

3.1 α -Pinene

3.1.1 SOA particle mass ~~formation and yields~~

365 The initial O₃ concentration in the chamber was negligible. Upon illumination, O₃ gradually accumulated, peaking at 38.5 ppb approximately two hours after lights on in the absence of CO, and then declined over time. ~~(Fig. 1a).~~ In the presence of CO, the peak O₃ concentration (60.7 ppb) was observed near the end of the experiment.

370 The initial α -pinene/NO_x ratio in the α -pinene experiments was approximately 0.8 \pm 0.2 (Table 1). In the absence of CO, NO_x concentrations declined during the first two hours of the reaction and subsequently stabilised, ~~whereas.~~ In contrast, in the presence of CO, ~~they~~NO_x declined continuously throughout the experiment (Fig. ~~S4S5~~). α -Pinene was nearly completely almost entirely consumed within three hours ~~in~~under both ~~experiments~~conditions (Fig. ~~1e1b~~). Notably, ~~its~~the initial consumption rate was ~~slower~~lower in the presence of CO, ~~but increased after.~~ After approximately two hours, ~~however,~~ the decay rate increased and ultimately eventually converged with that observed in the absence of CO.

375 Compared to the experiment without CO, SOA particle mass increased more slowly in the presence of CO ~~resulted in a slower growth rate and a, resulting in~~ substantially lower SOA particle mass ~~concentration~~concentrations (Fig. ~~1b, 1c~~). In both cases, the concentrations stabilised during the final hour of the reaction. By the end of the experiment, SOA particle mass concentrations reached 41.0 $\mu\text{g m}^{-3}$ in the absence of CO and 17.8 $\mu\text{g m}^{-3}$ in its presence. Correspondingly, the α -pinene SOA particle mass yield decreased from 0.14 to 0.08.

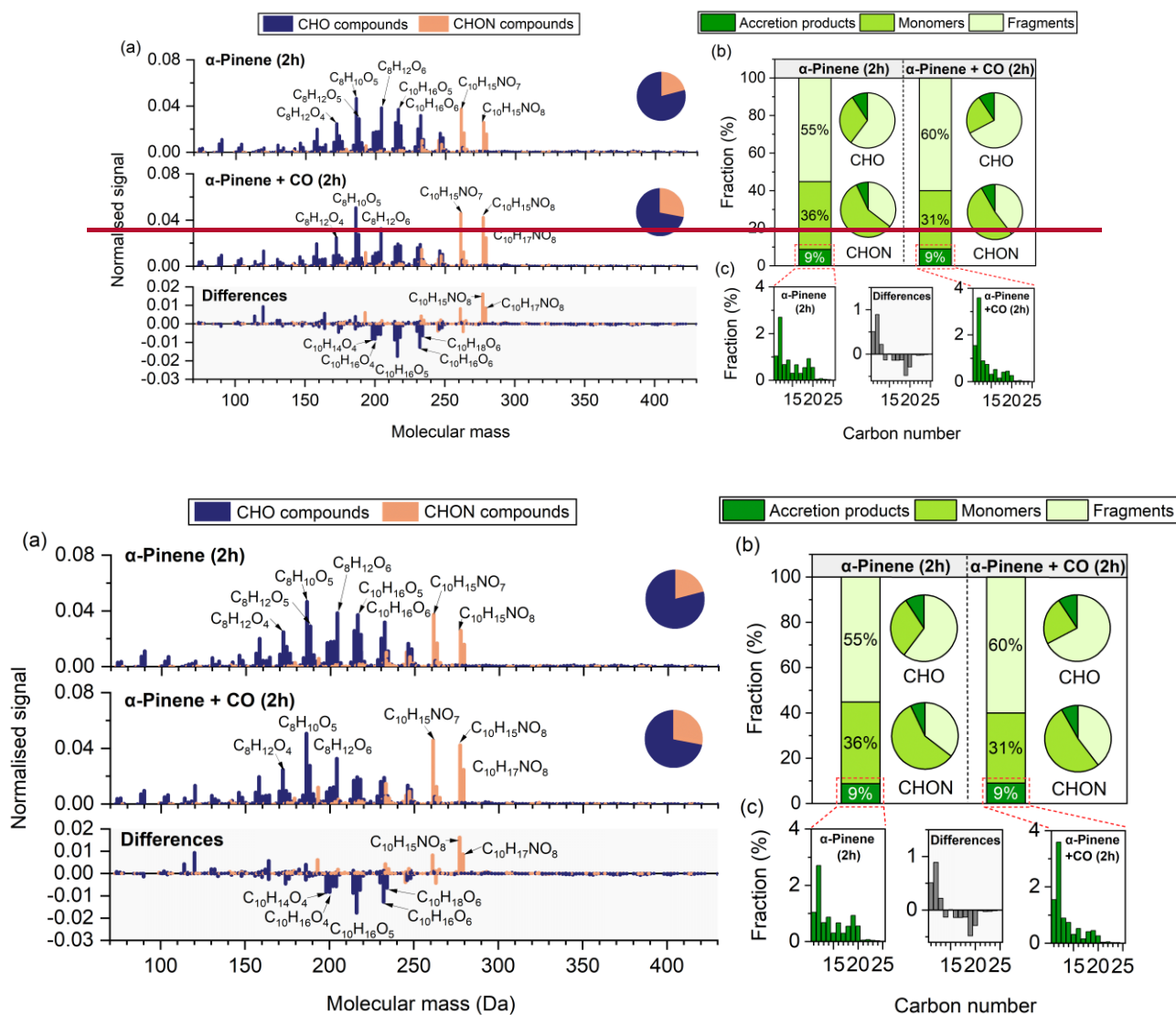


Figure 2: (a) High-resolution mass spectra of particle-phase compounds identified/measured by FIGAERO-CIMS in α -pinene experiments conducted with and without CO, along with their differences and the corresponding difference spectra (with CO minus without CO). Prominent peaks are labeled with their corresponding molecular formulas. All signal intensities are normalised to 1. Pie charts display the proportions of CHO and CHON compounds/groups. (b) Fractions of α -pinene-derived fragments, (C < 10), monomers, (C = 10), and accretion products (C > 10) in the absence and presence of CO. Bar charts represent their relative contributions to the total signal, while pie charts show their relative contributions/distribution within the CHO and CHON compounds/groups. (c) Carbon number distributions of

390 accretion products in the absence (left) and presence (right) of CO. The middle panel shows the differences between ~~them~~the two conditions (with CO minus without CO).

Owing to the absence of data from the final two FIGAERO cycles in the α -pinene experiment with CO, the analysis of ~~α -pinene~~ SOA particle composition was based on the second cycle, corresponding to two hours of reaction, by which time substantial SOA mass had already formed.

395 ~~Fig. Figure~~ 2a presents the high-resolution mass spectra of ~~identified SOA particles~~particle-phase compounds from α -pinene experiments conducted with and without CO, together with their differences. The products were mainly distributed within the molecular mass range of 150 ~~to 280 Da. According to 280 Da.~~ Under both conditions, $C_8H_{10}O_5$ was the most abundant compound. Based on elemental composition, the compounds were classified into CHO and CHON groups. CHON species accounted for 21 % of the total signal in the absence of CO and 28 % in its presence. ~~In both cases, the most abundant compound was $C_8H_{10}O_5$.~~

400 The ~~identified~~ compounds can be categorised into three classes based on carbon number: monomers, fragments, and accretion products (Fig. 2b). Monomers derived from α -pinene consisted of C_{10} products, whereas fragment compounds contained fewer than 10 carbon atoms, while and accretion products contained more than 10. ~~Fragment compounds were the dominant class in both the absence and presence of CO. Fragments dominated under both conditions.~~ accounting for 55 % and 60 % of the total signal, in the absence and presence of CO, respectively. ~~A large fraction of these~~ Within the CHO group, fragments ~~fell within the C_7 to~~ contributed more than 60 %, with a substantial proportion distributed in the C_7 – C_9 range (Fig. S10). ~~Among CHO compounds, fragments made up the largest proportion, whereas monomers dominated the CHON fraction. Notably, differences in carbon number distribution between the two systems were primarily observed~~ S11). Monomers accounted for 36 % and 31 % in the monomer group (Fig. S10), with absence and presence of CO leading, respectively, and were the dominant class within the CHON group, accounting for more than 50 %. The presence of CO led to a lower proportion of C_{10} CHO compounds (e.g., $C_{10}H_{16}O_{4-6}$) and a higher proportion of C_{10} CHON compounds (e.g., $C_{10}H_{15}NO_{7-8}$) compared the experiment without CO (Fig. 2a). The overall ~~contribution of accretion products remained consistent at 9 % in both systems. However, CO reduced the fraction of accretion products containing 16 to 24 carbon atoms compared to the experiment without~~ remained constant at 9 % under both conditions. However, the proportion of C_{16} – C_{24} accretion products was lower in the presence of CO (Fig. 2c).

410 ~~Beyond differences in carbon number distribution, the presence of CO also altered the distribution of hydrogen atom numbers (Fig. S11). Compared with the experiment without CO, CHO compounds containing 14, 16, and 18 hydrogen atoms accounted for a lower fraction in the presence of CO. In contrast, CO led to an increase in the relative abundance of CHON compounds across full range of hydrogen atom numbers detected in this study, consistent with the observed overall increase in CHON contribution.~~

420 The major RO_2 radicals derived from α -pinene react via the R1 and R2 pathways to form the $C_{10}H_{14}O_n$, $C_{10}H_{16}O_n$, and $C_{10}H_{18}O_n$ families. As shown in Fig. 3, in the absence of CO these species accounted for 11.0 %, 13.6 %, and 4.0 % of the CHO group, respectively, and decreased to 9.0 %, 9.5 %, and 2.4 % in its presence.

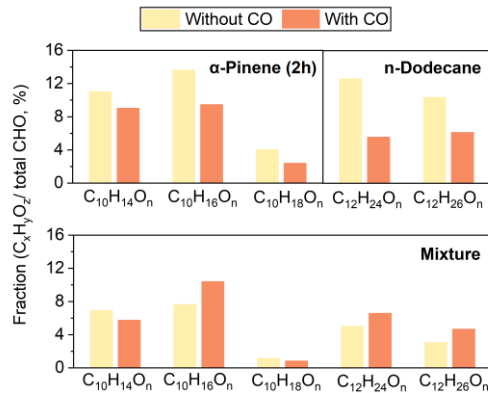


Figure 3: Relative contributions of C₁₀H₁₄O_n, C₁₀H₁₆O_n, C₁₀H₁₈O_n, C₁₂H₂₄O_n, and C₁₂H₂₆O_n to the CHO group in the α -pinene, n-dodecane, and mixture systems in the absence and presence of CO.

3.2 n-Dodecane

3.2.1 SOA particle mass formation and yields

In the n-dodecane experiments, O₃ concentrations were generally higher in the absence of CO than in its presence (Fig. 1a). The temporal evolution of O₃ differed markedly between the two systems conditions. In the absence of CO, O₃ had nearly reached its peak by the end of the experiment, whereas in the presence of CO, O₃ levels it continued to rise throughout the experiment. Despite these differences in formation rates and peak timing, the final O₃ concentrations in both systems converged to similar levels, approaching 100 ppb.

The initial n-dodecane/NO_x ratio was approximately 0.9 ± 0.3 (Table 1). NO_x concentrations declined steadily throughout the reaction experiment under both conditions (Fig. S4S5). In the presence of CO, the consumption decay rate of n-dodecane was slower (Fig. 1e1b). By the end of the experiment, 37 % of the initial n-dodecane remained unreacted in the absence of CO, whereas 47 % remained when CO was present (Fig. 1e1b).

The formation rate of n-dodecane SOA particles increased throughout the experiment (Fig. 1b). In the absence of CO, the final SOA particle mass concentration reached 122.9 μg m⁻³ of SOA particles were produced, corresponding to a mass yield of 0.17 (exp. 5). In the presence of CO, the final SOA particle mass concentration was significantly lower, at it reached 20.5 μg m⁻³, with a yield of 0.04.

3.2.2 SOA particle chemical composition

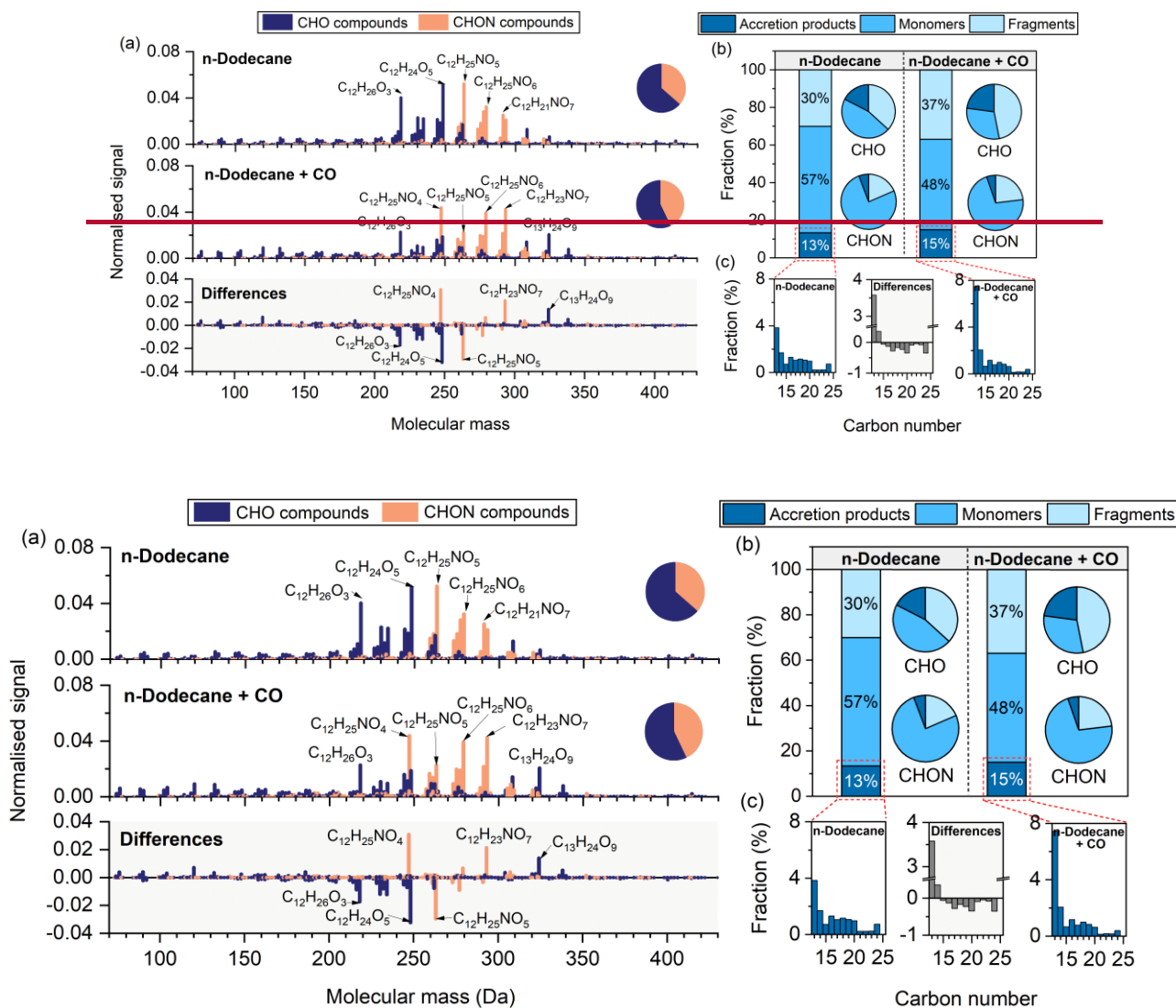


Figure 34: (a) High-resolution mass spectra of particle-phase compounds identified measured by FIGAERO-CIMS in n-dodecane experiments conducted with and without CO, along with their differences and the corresponding difference spectra (with CO minus without CO). Prominent peaks are labelled with their corresponding molecular formulas. All signal intensities are normalised to 1. Pie charts display the proportions of CHO and CHON compounds groups. (b) Fractions of n-dodecane-derived fragments, ($C < 12$), monomers, ($C = 12$), and accretion products ($C > 12$) in the absence and presence of CO. Bar charts represent their relative contributions to the total signal, while pie charts show their relative contributions distribution within the CHO and CHON compounds groups. (c) Carbon number

distributions of accretion products in the absence (left) and presence (right) of CO. The middle panel shows the differences between ~~them~~the two conditions (with CO minus without CO).

460 Compared to α -pinene, ~~the~~ particle-phase products derived from n-dodecane ~~had exhibited~~ generally higher molecular mass distributions, ~~mainly primarily~~ within the range of 210 ~~to~~ 310 Da (Fig. 3a). ~~CHON compounds accounted for 37 % and 43 % of the total signal in the absence and presence of CO, respectively. 4a).~~ In the absence of CO, the most abundant ~~compounds species~~ were $C_{12}H_{25}NO_5$, $C_{12}H_{24}O_5$, and $C_{12}H_{26}O_3$, whereas in the presence of CO, $C_{12}H_{25}NO_4$, $C_{12}H_{23}NO_7$, and $C_{12}H_{25}NO_3$ dominated. CHON compounds accounted for 37 % and 43 % of the total signal in the absence and presence of CO, respectively.

465 In the n-dodecane systems, compounds containing 12 carbon atoms were classified as monomers, those with fewer than 12 as fragments, and those with more than 12 as accretion products (Fig. 3b4b). Monomers dominated under both conditions, accounting for 57 % of the total signal in the absence of CO and 48 % in its presence. ~~Differences in carbon number distribution between~~ Within the two systems were primarily observed in the monomer CHON group (Fig. S10), with monomers accounted for more than 70 %. ~~The presence of CO led~~ to a lower proportion of C_{12} CHO compounds (e.g., $C_{12}H_{24}O_5$ and $C_{12}H_{26}O_3$) and a higher proportion of C_{12} CHON compounds (e.g., $C_{12}H_{25}NO_4$ and $C_{12}H_{23}NO_7$) compared the experiment without CO (Fig. 3a). A (Fig. 4a). However, a few exceptions were observed. For example, ~~an increased contribution from~~ a series of highly oxygenated C_{13} CHO compounds, such as $C_{13}H_{24}O_9$ and $C_{13}H_{22}O_{10}$, ~~was detected~~ accounted for a higher fraction in the presence of CO. ~~In contrast, whereas~~ $C_{12}H_{25}NO_5$ showed accounted for a higher abundance fraction in the absence of CO. Fragments accounted for 30 % and 37 % in the absence and presence of CO, respectively. While the overall ~~contribution fraction~~ of accretion products was comparable ~~between two systems under both conditions~~, the presence of CO ~~led to a reduced~~ the fraction of C_{16} – C_{24} accretion products containing 16–24 carbon atoms compared to experiments without CO (Fig. 3e4c).

480 ~~The hydrogen atom number distribution of n-dodecane-derived CHO compounds displayed two peaks at 12 and 24 hydrogen atoms, likely corresponding to fragments and monomers products, respectively (Fig. S11). In the presence of CO, the relative abundance of CHO compounds containing 22, 24, and 26 hydrogen atoms were lower than those observed in the absence of CO. For the identified CHON species, compounds containing 25 hydrogen atoms were the most abundant. The presence of CO led to a general increase in the relative abundances of CHON compounds across the hydrogen atom numbers observed in this study.~~

485 The major RO_2 radicals derived from n-dodecane react via the R1 and R2 pathways to form the $C_{12}H_{24}O_n$ and $C_{12}H_{26}O_n$ families. As shown in Fig. 3, in the absence of CO these species accounted for 12.6 % and 10.4 % of the CHO group, respectively, and decreased to 5.6 % and 6.1 % in its presence.

3.3 Mixture

3.3.1 SOA particle mass ~~formation and yields~~

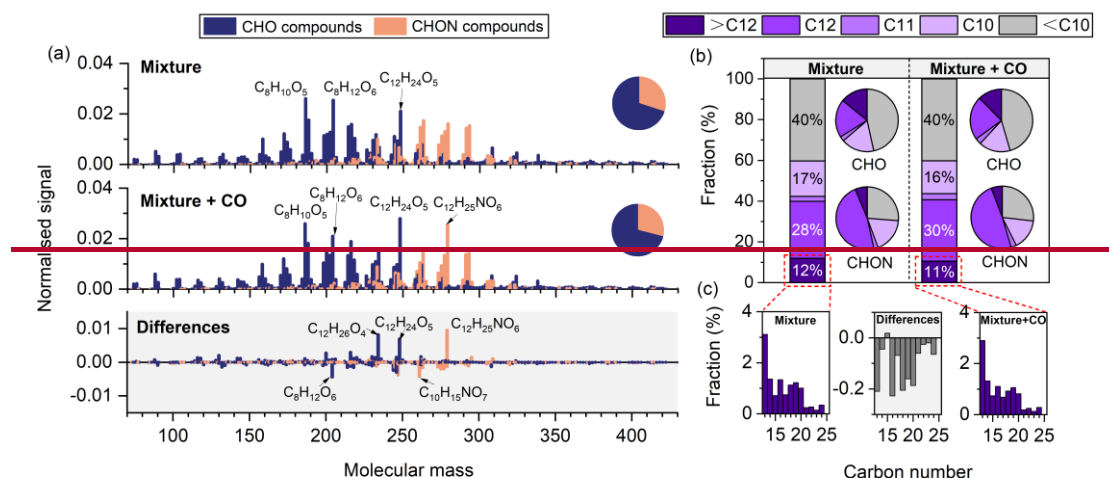
During the first hour of the reaction, O_3 concentrations were comparable ~~between in~~ the two systems absence and presence of

490 CO (Fig. 1a). Thereafter, ~~the CO present system exhibited higher~~ O₃ levels ~~than became higher in~~ the presence of CO-absent
495 system. In both cases, O₃ concentrations peaked during the final hour ~~of the reaction~~, reaching 81.1 ppb without CO and 101.6
ppb with CO.

The initial precursor/NO_x ratio was approximately 0.8 ~~± 0.2~~ (Table 1). NO_x concentrations declined steadily ~~under both~~
495 ~~conditions~~ throughout the reaction under both conditions (Fig. S4S5). In the mixture, the presence of CO led to slower
decay rates for both α-pinene and n-dodecane compared to the experiment without CO (Fig. 1d1b). Nevertheless, α-pinene
was fully consumed within three hours in both cases. By the end of the experiment, 25 % of the initial n-dodecane remained
unreacted in the absence of without CO, whereas 51 % remained when with CO was present.

500 In the absence of CO, the final SOA particle mass concentration reached 63.9 μg m⁻³ ~~of SOA particles were produced~~,
corresponding to a mass yield of 0.11 (exp Exp. 9). In the presence of CO, it reached 58.8 μg m⁻³ ~~of SOA particles were formed~~,
with a yield of 0.16.

3.3.2 SOA particle chemical composition



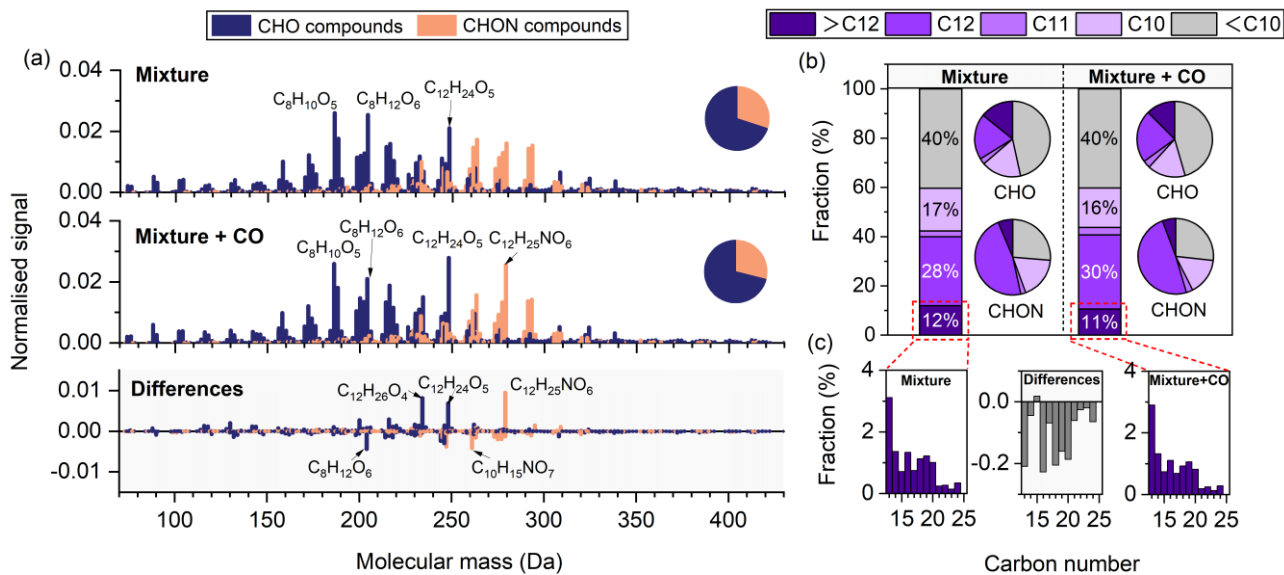


Figure 45: (a) High-resolution mass spectra of particle-phase compounds identified measured by FIGAERO-CIMS in mixture experiments conducted with and without CO, along with their differences and the corresponding difference spectra (with CO minus without CO). Prominent peaks are labelled with their corresponding molecular formulas. All signal intensities are normalised to 1. Pie charts display the proportions of CHO and CHON compounds groups. (b) Fractions of particle-phase products with different carbon numbers in the absence and presence of CO. Bar charts represent their relative contributions to the total signal, while pie charts show their relative contributions distribution within the CHO and CHON compounds groups. (c) Carbon number distributions of products with more than 12 carbon atoms in the absence (left) and presence (right) of CO. The middle panel shows the differences between them the two conditions (with CO minus without CO).

Compared to single-precursor systems, the mixed-precursor system exhibited a broader molecular mass distribution, mainly primarily ranging from 150 to 330 Da (Fig. 4a)–5a). In the absence of CO, $C_8H_{10}O_5$, $C_8H_{12}O_6$, and $C_{12}H_{24}O_5$ showed the highest signal intensities, whereas in the presence of CO, $C_{12}H_{24}O_5$, $C_8H_{10}NO_5$, and $C_{12}H_{25}NO_6$ were most abundant. CHON compounds accounted for 30 % and 29 % of the total signal in the absence and presence of CO, respectively. In the absence of CO, $C_8H_{10}O_5$, $C_8H_{12}O_6$, and $C_{12}H_{24}O_5$ had the highest signal intensities, whereas in the presence of CO, the most abundant compounds were $C_{12}H_{24}O_5$, $C_8H_{10}NO_5$, and $C_{12}H_{25}NO_6$.

In the mixture, the complexity of interactions made it difficult to clearly distinguish monomers, fragments, and accretion products. Nevertheless, compounds with fewer than 10 carbon atoms were reasonably classified as fragments, while those containing more than 12 carbon atoms were considered accretion products. As shown in Fig. S10, the effect of CO on the carbon distribution in the mixture was generally less pronounced than in the single precursor systems. While the relative abundances of C10, C12, and accretion products ($C > 12$) were similar Fragments dominated under both conditions (Fig 4b), small shifts and accounted for 40 % of the total signal in composition were evident each case. Accretion products accounted for

530 ~~12 % and 11 % in the absence and presence of CO, displaying features distinct from those in the single precursor systems. Specifically, CO led to (i) a slightly lower fraction of accretion products containing 13 to 24 carbon atoms (excluding respectively. Except for C₁₅) (Fig. 4e), (ii) an increased species, the fractions of C₁₃–C₂₄ products decreased slightly in the presence of CO. In addition, the presence of CO resulted in an increased proportion of C₁₂ CHO compounds (e.g., C₁₂H₂₆O₄ and C₁₂H₂₄O₅), and (iii) a reduced proportion of C₁₀ CHON compounds (e.g., C₁₀H₁₅NO₇) (Fig. 4a).~~

535 ~~As shown in Fig. S11, the hydrogen atom 5a). Overall, changes in carbon number distribution of mixture derived CHO compounds showed two peaks at 14 and 24 hydrogen atoms, with the peak at 14 being the most abundant. In the presence of CO, the relative abundances of CHO compounds with 12 and 14 hydrogen atoms decreased, while those with 16, 24, and 26 hydrogen atoms increased. Among the identified CHON species, the presence of CO resulted in an increased fraction of 25-hydrogen compounds and a decreased fraction of 15 hydrogen compounds were less pronounced in the mixed-precursor system than in the single-precursor systems (Fig. S11).~~

540 _____

545 The bottom panel of Fig. 3 shows the relative contributions of $C_{10}H_{14}O_n$, $C_{10}H_{16}O_n$, $C_{10}H_{18}O_n$, $C_{12}H_{24}O_n$, and $C_{12}H_{26}O_n$ to the CHO products in the mixture. In the presence of CO, the fractions of $C_{10}H_{14}O_n$ and $C_{10}H_{18}O_n$ decreased from 6.9 % and 1.2 % to 5.5 % and 0.8 %, respectively, whereas those of $C_{10}H_{16}O_n$, $C_{12}H_{24}O_n$, and $C_{12}H_{26}O_n$ increased from 7.6 %, 5.0 %, and 3.1 % to 10.4 %, 6.6 %, and 4.7 %, respectively.

4 Discussion

4.1 Photochemistry

The photochemical reactions in this study involved the simultaneous presence of NO_x and CO, multiple oxidants (OH and O₃), ~~as well as and~~ multiple precursor species. The interactions among these factors substantially ~~increased~~ increase the complexity of the system, making it challenging to establish comparable experimental conditions ~~that allow for a comparison~~ across different precursor systems. ~~To address~~ In this study, two key approaches were adopted: (i) ensuring initial iso-reactivity towards OH radicals, and (ii) ~~maintaining~~ setting comparable initial precursor/NO_x ratios across systems. Additionally, an oxidant closure approach was employed to characterise the photochemical conditions. As OH radicals could not be directly measured ~~directly~~ in this study, their concentrations were estimated from the temporal evolution of O₃ and the consumption of precursors, or alternatively, from the depletion of CO₂ (see details in the Supplementary Information). This approach enabled a quantitative evaluation of the relative contributions of different oxidants to precursor oxidation.

~~This study was designed for OH radicals to serve as the predominant photochemical loss of precursors. Under idealised iso-reactivity conditions, all systems exhibited would exhibit comparable initial OH reactivity, and in the mixture experiments, each precursor molecule would initially had have an equal probability of reacting with OH. However, as the reaction progressed~~ In practice, however, O₃ gradually accumulated and became increasingly important for the also contributed to precursor oxidation of O₃ reacting precursors, resulting in the coexistence of two oxidants in the system. Due to, and the differing reactivities of individual precursors towards O₃, their decay rates varied accordingly (Fig. 1e-d). In the experiments without CO₂, can modify the precursor decay and secondary oxidant formation, thereby influencing the reactivity. n-Dodecane was oxidised exclusively by OH radicals. For α-pinene, although OH remained the dominant photochemical sink in this study, the contribution of O₃ to its decay was not negligible. As shown in Fig. S12, the relative contributions of these oxidants evolved over time, with the role of O₃ generally becoming more important as the reaction proceeded. In the α-pinene single-precursor system, on average approximately 70 80 % of α-pinene decay was ~~attributed~~ attributable to OH oxidation, while the remaining 30 % was driven by ozonolysis (Fig. S12). OH dominated during the early stage of the reaction, contributing over 90 % to α-pinene consumption. However, as the reaction proceeded, the contribution of O₃ became increasingly significant, accounting for over 40 % in the mixture. In contrast, n-dodecane does not react with O₃ and was oxidised exclusively via OH radicals. Thus, although OH remained the dominant oxidant for α-pinene oxidation, the contribution from ozonolysis was still non-negligible. ~20 % was driven by ozonolysis. By comparison, the contribution of ozonolysis was slightly higher in the mixed-precursor system. Thus, fully comparable reactivity across different systems was difficult to maintain throughout the reaction when multiple oxidants were present. This reflects an inherent limitation of defining iso-reactivity with respect to a single oxidant in multi-oxidant systems.

The precursor/NO_x ratio is important for determining the chemical regime of O₃ and SOA formation (Chen et al., 2022) Owing to the chemical coupling among O₃, NO_x, and RO_x (= OH + RO₂ + HO₂), NO_x plays a critical role in determining both the oxidation conditions and the fate of RO₂ radicals, thereby influencing the yields and chemical composition of SOA particles. In this study, NO_x served as the source of OH via O₃ photolysis. The initial precursor/NO_x ratios were maintained at similar

585 levels among different systems, which aimed to minimise systematic discrepancies arising from variations in reaction pathways and thus enabled a more reliable assessment of the effects of CO. Estimated OH levels were largely comparable across systems in the absence of CO (Fig. S5). During the first hour of reaction, O₃ concentrations were also similar, but subsequently both their levels and temporal profiles diverged, leading to differences in overall oxidant levels. However, when multiple precursors are involved, maintaining similar initial precursor/NO_x ratios may not be sufficient to establish comparable chemical regimes across systems. In this study, the temporal profiles of O₃ and NO_x differed substantially between the single- and mixed-precursor systems (Figs. 1a and S5). In the α-pinene system, O₃ concentrations peaked after approximately two hours of reaction and subsequently declined, while NO_x levels stabilised (Fig. 1a and S4). At By this point, over 80 % of α-pinene had been consumed, and the SOA particle formation rate also began to decline (FigFigs. 1b–c). These trends may indicate a diminished rate of reduction in RO₂ + NO reactions. The reduced RO₂ + NO reactivity slowed the depletion of NO, which in turn enhanced the titration of would slow the conversion of NO to NO₂ and thereby limit photochemical O₃ and led to a net O₃ loss production. In contrast, in the n-dodecane and mixture systems, over 50 % of n-dodecane was still unreacted after two hours of reaction, and the SOA particle formation rate continued to increase (FigFigs. 1b–d_c), indicating that the RO₂ + NO pathway reactions remained active. This sustained reactivity enabled continuous conversion of NO consumption, which in turn limited O₃ titration to NO₂ and let to a net accumulation of O₃ enhanced photochemical O₃ production.

600 These results raise an important consideration for studies involving multiple precursors and oxidants. Even when the initial OH reactivity and precursor/NO_x ratios are controlled, differences in precursor reactivities and the close coupling between secondary oxidant formation and precursor oxidation make it challenging to maintain achieving fully comparable chemical regimes experimental conditions across such systems. As remains challenging. Given that the coexistence of multiple precursors and oxidants is a common feature of the ambient atmosphere, future chamber laboratory studies should investigate explore a broader range of precursor/NO_x ratios and systematically assess the effects of varying oxidants to improve our understanding of SOA formation under atmospherically relevant oxidative conditions.

605 The addition of CO further perturbed the photochemical processes, altering both oxidant levels and precursor decay rates. Previous studies have demonstrated that CO can suppress SOA particle formation through two main factors: (i) competition with precursors for OH, which is referred to as oxidant (OH) scavenging, and (ii) an elevated HO₂/RO₂ ratio, which favoured RO₂ + HO₂ termination pathways rather than RO₂ + RO₂ reactions, thereby reducing the formation of accretion products, known as the product scavenging CO can consume OH radicals, preventing their reaction with SOA precursors (McFiggans et al., 2019). At Based on the estimated OH concentrations, evidence for this oxidant scavenging effect was observed. During the initial stage of the reaction, CO reduced the OH concentrations by approximately 50 % to around 1.5 × 10⁶ molecules cm⁻³ (Fig. S5). However, as the reaction progressed, OH levels gradually recovered and eventually reached values comparable to those observed in the absence of CO. S6). However, OH levels gradually recovered as the reaction progressed and eventually reached values comparable to those observed in the absence of CO (except for n-dodecane system). In the presence of CO, the reaction of CO with OH led to enhanced HO₂ formation. Subsequent HO₂ + NO reactions regenerated OH, thereby increasing radical propagation efficiency. In contrast, in the absence of CO, although O₃ photolysis provided a primary source of OH, OH regeneration in the n-dodecane system was likely less efficient, consistent with the decline in OH concentrations. In both the

620 α -pinene and mixture systems, however, OH concentrations continued to increase even without CO, indicating the presence of additional OH regeneration processes, such as OH formation during α -pinene ozonolysis. In addition to its impact on OH concentrations, the presence of CO also modified O₃ levels. In the presence of CO, both the α -pinene and mixture systems exhibited higher peak O₃ concentrations, whereas in the n-dodecane system O₃ showed generally lower O₃ levels. Variations in oxidant concentrations were generally lower. As shown contributed to changes in Fig 1e d, CO influenced the SOA precursor decay rates of (Fig. 1b). In the absence of CO, α -pinene and n-dodecane to different extents. In the α -pinene system, although the α -pinene decay rate was reduced in the almost completely consumed within 3 h. In the presence of CO, the total consumption remained unchanged, and the relative contributions of OH and O₃ showed little variation (Fig. S12). These results suggest that the effect of OH scavenging on its decay was initially suppressed; however, after approximately 2 h the decay of α -pinene was limited. For n-dodecane, OH scavenging had rate increased, likely due to secondary OH production and elevated O₃ concentrations. Such that α -pinene was nevertheless nearly fully consumed within 3 h. As a pronounced effect on its decay, with result, CO did not significantly reducing both the affect the overall extent of α -pinene consumption. In contrast, for n-dodecane, the presence of CO not only slowed the oxidation rate but also reduced the overall extent of consumption rate and overall consumption (Fig. 1e d), leaving a substantial fraction unreacted by the end of the experiment.

4.2 Effect of CO on SOA particle chemical composition

635 4.2.1 Single-precursor systems

640 The presence of CO led to several consistent changes in the chemical composition of SOA particles in both the α -pinene and n-dodecane systems, including an increased relative contribution of the CHON group and fragment species and a reduced fraction of C₁₆-C₂₄ accretion products (Figs. 2 and 4). In addition, the relative contributions of representative RO₂ + RO₂ termination products (C₁₀H₁₄O_n and C₁₂H₂₄O_n) within the CHO group decreased (Fig. 3). These observations provide evidence for a similar shift in RO₂ fate in the presence of CO in both systems. However, owing to the limitations of I-CIMS measurements, the absolute contributions in individual reaction pathways cannot be fully constrained. The following discussion is therefore based partly on relative changes.

645 Organic nitrate concentrations were estimated from AMS measurements using the method described by Kiendler-Scharr et al. (2016). The results show that, in the single-precursor systems, the presence of CO led to a pronounced reduction in organic nitrate concentrations (Fig. S13). This reduction can be attributed to two main factors. First, CO competes with SOA precursors for available OH (Figs. 1b and S6). Second, CO enhances HO₂ formation, increasing the importance of the RO₂ + HO₂ pathway and thereby altering RO₂ reaction branching. In addition, lower NO concentrations were observed in the presence of CO (Fig. S5), consistent with enhanced conversion of NO to NO₂ via the HO₂ + NO reaction. The increase in HO₂ and decrease in NO reduced the likelihood of RO₂ reacting with NO. Despite this absolute reduction, FIGAERO-CIMS results showed that the relative contributions of the CHON group and fragment products increased in the presence of CO (Figs. 2 and 4). CHON products are primarily formed through the RO₂ + NO → RONO₂ pathway, and fragment species originate from the fragmentation of RO radicals (Atkinson, 2000; Ziemann and Atkinson, 2012). Owing to the rapid reaction of RO₂ with NO

655 and the high branching towards RO formation, reactions of RO₂ with NO represent an important source of RO radicals under NO_x conditions (Orlando et al., 2003; Ziemann and Atkinson, 2012). These observations therefore indicate that, in the presence of CO, the contribution of RO₂ + NO reactions decreased, but to a lesser extent than competing RO₂ termination pathways.

660 AMS measurements showed a decrease in SOA particle mass concentrations in the presence of CO (Fig. 1c). In addition to OH scavenging, another important factor is that CO enhances competition between RO₂ + RO₂ and RO₂ + HO₂ reactions, thereby reducing the formation of accretion products (Baker et al., 2024; McFiggans et al., 2019; Peräkylä et al., 2023). Despite this reduction, CO did not significantly alter the overall fraction of accretion products. However, the relative contribution of C₁₆–C₂₄ species decreased (Figs. 2c and 4c), accompanied by an increase in C₁₁–C₁₅ species in the α-pinene system and C₁₃–C₁₄ species in the n-dodecane system. Accretion products with lower carbon numbers are expected to form via pathways that involve fragmentation of RO radicals (Kang et al., 2025), and their increased relative contribution is consistent with the
665 elevated fraction of fragment products discussed above. In contrast, longer-chain accretion products are more likely to originate from RO₂ + RO₂ reactions involving non-fragmented C₁₀/C₁₂ RO₂ radicals, including reactions between non-fragmented RO₂ radicals and fragmented RO₂ radicals (< C₁₀), or between two non-fragmented RO₂ radicals, yielding C₂₀ and C₂₄ accretion products in the α-pinene and n-dodecane systems, respectively. Combined with the reduced fractions of C₁₀H₁₄O_n and C₁₂H₂₄O_n families (Fig. 3), these observations indicate that CO preferentially suppressed RO₂ + RO₂ chemistry, particularly pathways
670 forming longer-chain accretion products.

Overall, in the single-precursor systems, CO reduced the contributions of both RO₂ + RO₂ and RO₂ + NO reactions. However, reactions of RO₂ with NO decreased to a lesser extent than competing RO₂ termination pathways, and the reduction in RO₂ + RO₂ termination was more pronounced for longer-chain accretion products than for shorter-chain ones.

675 **4.2.2 Mixed-precursor system**

Compared with the single-precursor systems, the influence of CO on SOA chemical composition differed in the mixed-precursor system. Specifically, (i) the presence of CO did not significantly alter the relative contributions of the CHON group and fragment species (Figs. 5a–b); (ii) the fractions of C₁₃–C₂₄ accretion products (excluding C₁₅) slightly decreased (Fig. 5c); and (iii) within the CHO group, the fraction of the C₁₀H₁₄O_n family decreased, whereas that of the C₁₂H₂₄O_n family increased (Fig. 3).

In the mixed-precursor system, organic nitrate concentrations exhibited little variation in the presence of CO (Fig. S13), consistent with the largely unchanged relative contribution of the CHON group and fragment species. This suggests that the contribution of RO₂ + NO reactions was not substantially reduced under CO conditions.

685 SOA particle mass concentrations and the fraction of accretion products both decreased slightly in the presence of CO (Figs. 1c and 5), suggesting a slight reduction in the contribution of RO₂ + RO₂ termination.

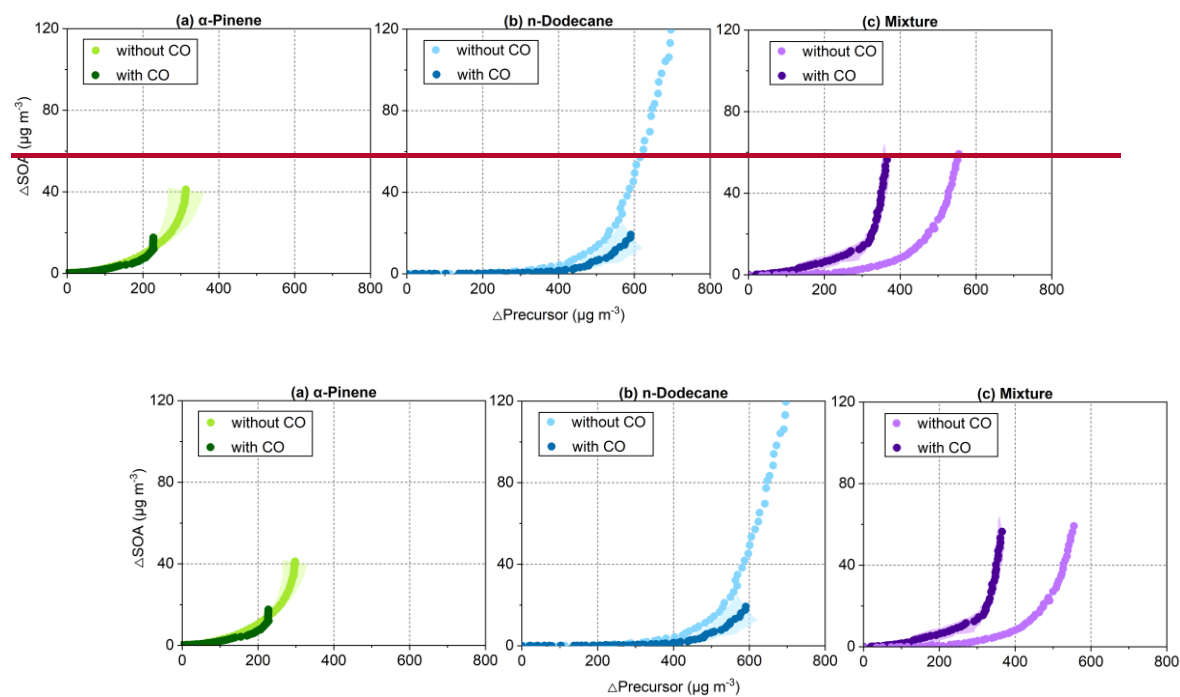
Moreover, CO led to a lower fraction of the C₁₀H₁₄O_n family in the mixture, consistent with the trend observed in the α-pinene

690 single-precursor system. In contrast to the n-dodecane single-precursor system, however, the relative contribution of the
 $C_{12}H_{24}O_n$ family increased in the presence of CO in the mixture. Together with the increase in the fraction of C_{12} species and
decrease in that of C_{10} species (Fig. S11), these observations may indicate that CO affected $RO_2 + RO_2$ termination involving
 α -pinene-derived RO_2 more strongly than that involving n-dodecane-derived RO_2 .

695 Overall, in the mixed-precursor system, the influence of CO on RO_2 termination pathways was less pronounced than in the
single-precursor systems and may have affected n-dodecane- and α -pinene-derived RO_2 to different extents.

700 Although the underlying mechanism cannot be fully resolved in this study, the observed changes in product distributions
provide important evidence for shifts in RO_2 reaction pathways in the mixed-precursor system under different conditions. As
 α -pinene and n-dodecane were used as representative precursors, these findings may be specific to the present system. Future
chamber studies covering a broader range of precursor combinations are therefore needed to assess the generality of the
observed behaviour.

4.3 Effect of CO on SOA particle mass yields



705 **Figure 56:** Growth curves of SOA particles ~~formed from for~~ (a) α -pinene, (b) n-dodecane, and (c) mixture experiments, defined as the ratio of ~~the SOA particle mass concentrations of formed SOA particles~~ the SOA particle mass concentrations of formed SOA particles ~~concentration to the reacted consumed precursor mass of precursors~~ concentration to the reacted consumed precursor mass of precursors. Shaded areas represent the ~~envelope from repeated~~ envelope from repeated ~~range between replicate~~ range between replicate experiments.

710 ~~The influence of CO on SOA particle mass yields differed significantly between the single precursor and mixture systems. In the single precursor systems, CO consistently suppressed the yields, with the effect being more pronounced for n-dodecane than for α pinene. In the presence of CO, SOA particle mass concentration and yield decreased by 83 % and 79 % for n-dodecane, and by 57 % and 43 % for α pinene, respectively. One possible factor contributing to this difference is that OH scavenging effect was stronger in the n dodecane than in the α pinene system. By contrast, in the mixture, even though OH scavenging was evident, the presence of CO led to only an 8 % decrease in SOA particle mass concentration, whereas the final mass yield showed an increase. To better understand this observation, it may be necessary to distinguish the respective contributions of OH scavenging and product scavenging to the overall effects of CO on yields. Future relevant studies should therefore consider compensating for OH loss to clarify the individual roles of these two scavenging processes.~~

720 ~~Fig. 5Figure 6 presents the SOA particle growth curves for each system. The slope of the curve represents the incremental SOA particle mass yield at a given stage of precursor consumption, while the final position of the curve reflects the overall yield achieved by the end of the experiment. The induction period is defined as the amount of SOA precursor consumed before SOA particle formation begins (Zhou et al., 2019). Compared with the α -pinene system, the n-dodecane systems had system exhibited a longer induction period, with the mixture falling while that of the mixed-precursor system lay in between. In the presence of CO, the induction period was extended in the n-dodecane system but remained largely unchanged in the α -pinene system. Notably, the induction period in the mixture system was shortened in the presence of CO. This phenomenon suggests These behaviours suggest a distinct influence of CO on the SOA formation pathways in the mixed-precursor system compared with the single precursor particle mass yields across different systems, as will be discussed in the following section.~~

730 ~~In the single-precursor systems, CO substantially reduced SOA formation, with a stronger effect for n-dodecane than for α -pinene. In the presence of CO, SOA particle mass concentrations and overall yields decreased by 83 % and 79 %, respectively, for n-dodecane, and by 57 % and 43 % for α -pinene. In contrast, the mixed-precursor system exhibited only an 8 % decrease in SOA mass concentration, and the overall yield increased slightly.~~

735 ~~Chemical composition analysis indicates that, in the single-precursor systems, the contributions of accretion products derived from $RO_2 + RO_2$ termination, particularly those with longer carbon chains, decreased in the presence of CO. These accretion products are expected to exhibit extremely low volatility and contribute efficiently to SOA formation (Peräkylä et al., 2023). At the same time, although the absolute concentration of organic nitrates decreased, the fractions of CHON and fragment products increased in the presence of CO. This suggests that $RO_2 + NO$ reactions were also reduced, but less markedly than the competing RO_2 termination pathways. Products formed via $RO_2 + NO$ reactions are generally expected to exhibit higher volatility than those formed through $RO_2 + HO_2$ and $RO_2 + RO_2$ termination (Presto et al., 2005; Zhao et al., 2018). All these changes are therefore expected to shift the product distribution towards more volatile species, consistent with the observed decrease in SOA particle mass yields.~~

745 ~~Compared with the single-precursor systems, changes in RO_2 reaction pathways in the mixture appeared to exert a weaker influence on the formation of lower-volatility products. Consequently, SOA particle mass concentrations and yields behaved~~

differently in the mixed-precursor system.

Competition between CO and SOA precursors for available OH was also a factor influencing the yields (McFiggans et al., 2019). However, the impact of differences in OH concentrations on SOA particle mass yields and chemical composition cannot be fully assessed in this study. Future work may need to re-adjust OH concentrations so that the systems can be maintained at comparable oxidation stages, thereby enabling more direct comparisons (Baker et al., 2024; McFiggans et al., 2019)

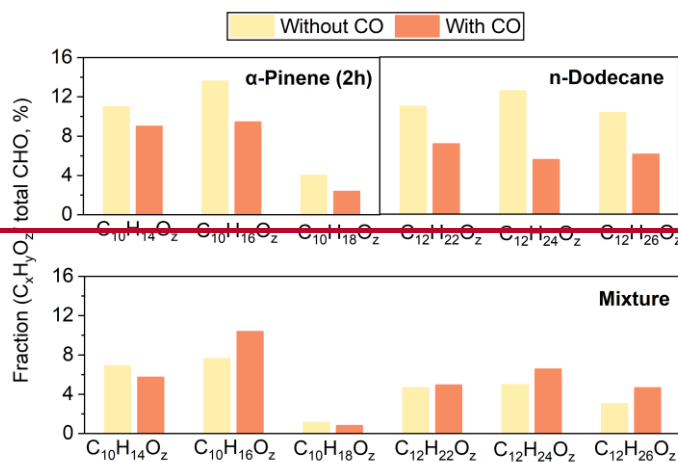


Figure 6: Relative contributions of C₁₀H₁₄O_z, C₁₀H₁₆O_z, C₁₀H₁₈O_z, C₁₂H₂₂O_z, C₁₂H₂₄O_z, and C₁₂H₂₆O_z to the total CHO compounds in the α-pinene, n-dodecane, and mixture systems in the absence and presence of CO.

4.3.1 Single precursor systems

The presence of CO led to several consistent changes in the chemical composition of SOA particles in both the α-pinene and n-dodecane systems, including an increased contribution of CHON compounds, a reduced fraction of C₁₆-to-C₂₄-accretion products, and shifts in the distribution of hydrogen atom numbers. These observations provide evidence for a similar alteration in RO₂-fate in the presence of CO for both systems.

CHON compounds constituted a significant fraction of the SOA particles, indicating that reactions with NO were also an important RO₂-termination pathway in our experiments. In the presence of CO, the increase in total CHON fractions in both α-pinene and n-dodecane systems was mainly attributed to enhanced contributions from specific C₁₀- and C₁₂-CHON

compounds, respectively (Fig. S10). These findings suggest that the suppression of $\text{RO}_2 + \text{RO}_2$ termination pathways induced by CO may have increased the relative importance of monomer-derived $\text{RO}_2 + \text{NO}$ reactions.

770 The presence of CO did not significantly alter the overall contribution of accretion products to the SOA particles in the single-precursor systems. However, the contribution of those containing 16 to 24 carbon atoms decreased in both systems (Fig. 2e and 3e). Correspondingly, in the α pinene system, the relative abundance of accretion products with 11 to 15 carbon atoms increased, while in the n-dodecane system, those with 13 to 14 carbon atoms became more abundant. Accretion products are typically formed via the chemical bonding of two RO_2 -radicals. Compounds with fewer carbon atoms are likely derived from reactions involving fragment-derived RO_2 -radicals, whereas those with higher carbon numbers are more likely formed through reactions between monomer-derived RO_2 -radicals and fragment-derived RO_2 -radicals, or between two monomer-derived RO_2 -radicals. An elevated HO_2/RO_2 ratio can suppress $\text{RO}_2 + \text{RO}_2$ pathway, thereby altering the product distribution. Previous studies have quantitatively assessed the effect of CO on the chemical composition of SOA from α pinene, reporting a twofold reduction in C_{17} -to- C_{20} HOM dimers. After compensating for the OH consumption by CO, α pinene-derived HOM accretion products were reduced by approximately 60% under CO-present conditions. In this study, quantitative assessment of accretion product concentrations was not possible due to instrumental limitations. Nevertheless, based on the changes in the relative contributions of accretion products and the SOA particle mass concentration, it can be inferred that the suppression effect of CO on $\text{RO}_2 + \text{RO}_2$ reactions was more pronounced for monomer-derived RO_2 -radicals than for fragment-derived ones.

785 The shifts in hydrogen atom distributions further supported the above interpretation of altered RO_2 termination pathways under CO-present conditions. Fig. S11 presents the distribution of hydrogen atom numbers across different systems. Similar patterns were observed in both the α pinene and n-dodecane systems. In the α pinene system, the presence of CO led to a decrease in the relative abundance of CHO compounds containing 14, 16, and 18 hydrogen atoms. Specifically, the relative contributions of $\text{C}_{10}\text{H}_{14}\text{O}_x$, $\text{C}_{10}\text{H}_{16}\text{O}_x$, and $\text{C}_{10}\text{H}_{18}\text{O}_x$ species to CHO compounds were reduced by 2.0 %, 4.2 %, and 1.6 %, respectively, in the presence of CO (Fig. 6). The main RO_2 -radicals generated from α pinene photooxidation are $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$. HO_2 termination of $\text{C}_{10}\text{H}_{15}\text{O}_x$ radicals forms multifunctional hydroperoxides ($\text{C}_{10}\text{H}_{16}\text{O}_x$), whereas RO_2 termination produces $\text{C}_{10}\text{H}_{14}\text{O}_x$ carbonyls and $\text{C}_{10}\text{H}_{16}\text{O}_x$ alcohols. Similarly, HO_2 termination of $\text{C}_{10}\text{H}_{17}\text{O}_x$ radicals forms $\text{C}_{10}\text{H}_{18}\text{O}_x$ hydroperoxides, and RO_2 termination yields $\text{C}_{10}\text{H}_{16}\text{O}_x$ carbonyls and $\text{C}_{10}\text{H}_{18}\text{O}_x$ alcohols. Cross reactions between $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$ radicals lead to the formation of $\text{C}_{10}\text{H}_{14}\text{O}_x$ carbonyls and $\text{C}_{10}\text{H}_{18}\text{O}_x$ alcohols, and/or $\text{C}_{10}\text{H}_{16}\text{O}_x$ carbonyls and alcohols. Therefore, while $\text{C}_{10}\text{H}_{16}\text{O}_x$ and $\text{C}_{10}\text{H}_{18}\text{O}_x$ species can be produced through multiple termination pathways, the formation of $\text{C}_{10}\text{H}_{14}\text{O}_x$ occurs exclusively via $\text{RO}_2 + \text{RO}_2$ reactions. For n-dodecane, the presence of CO led to a decrease in the relative abundance of CHO compounds containing 22, 24, and 26 hydrogen atoms. Specifically, the relative contributions of $\text{C}_{12}\text{H}_{22}\text{O}_x$, $\text{C}_{12}\text{H}_{24}\text{O}_x$, and $\text{C}_{12}\text{H}_{26}\text{O}_x$ species decreased by 3.8 %, 7.0 %, and 4.2 %, respectively, in the presence of CO (Fig. 6). The discussion here focuses primarily on the $\text{C}_{12}\text{H}_{24}\text{O}_x$ and $\text{C}_{12}\text{H}_{26}\text{O}_x$ families. The main RO_2 -radicals generated from n-dodecane photooxidation is $\text{C}_{12}\text{H}_{25}\text{O}_x$. HO_2 termination yields $\text{C}_{12}\text{H}_{26}\text{O}_x$ hydroperoxides, while RO_2 termination produces $\text{C}_{12}\text{H}_{24}\text{O}_x$ carbonyls and $\text{C}_{12}\text{H}_{26}\text{O}_x$ alcohols. The $\text{C}_{12}\text{H}_{24}\text{O}_x$ family is formed exclusively through $\text{RO}_2 + \text{RO}_2$ reactions. The reductions in the relative abundances of $\text{C}_{10}\text{H}_{14}\text{O}_x$ and $\text{C}_{12}\text{H}_{24}\text{O}_x$ in the α pinene and n-dodecane systems, respectively, thus provide further evidence that the presence of CO suppressed the $\text{RO}_2 + \text{RO}_2$ reaction pathway.

4.3.2 Mixed-precursor system

Compared with the single-precursor systems, the influence of CO on the chemical composition of SOA in the mixed-precursor system was different: (i) the addition of CO did not significantly alter the proportion of CHON compounds, indicating that the relative importance of the $\text{RO}_2 + \text{NO}$ pathway remained largely unchanged; (ii) the relative contributions of C_{12} -to- C_{24} accretion products (excluding C_{15}) slightly decreased, indicating a moderate suppression of the $\text{RO}_2 + \text{RO}_2$ pathway; (iii) the changes in hydrogen atom distributions differed from those observed in the single-precursor systems, possibly implying a distinct influence on the RO_2 reaction pathways.

In the mixed-precursor system, RO_2 -termination reactions were expected to be more complex than those in single-precursor systems. In addition to the pathways discussed above, cross-reactions between RO_2 radicals originating from different precursors may also occur. $\text{RO}_2 + \text{RO}_2$ reactions between $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{12}\text{H}_{25}\text{O}_x$ yield $\text{C}_{10}\text{H}_{14}\text{O}_z$ carbonyls and $\text{C}_{12}\text{H}_{26}\text{O}_z$ alcohols or $\text{C}_{12}\text{H}_{24}\text{O}_z$ carbonyls and $\text{C}_{10}\text{H}_{16}\text{O}_z$ alcohols. Similarly, reactions between $\text{C}_{10}\text{H}_{17}\text{O}_x$ and $\text{C}_{12}\text{H}_{25}\text{O}_x$ lead to the formation of $\text{C}_{10}\text{H}_{16}\text{O}_z$ carbonyls and $\text{C}_{12}\text{H}_{26}\text{O}_z$ alcohols, or $\text{C}_{12}\text{H}_{24}\text{O}_z$ carbonyls and $\text{C}_{10}\text{H}_{18}\text{O}_z$ alcohols. In the mixture, the presence of CO led to a decrease in the relative contributions of $\text{C}_{10}\text{H}_{14}\text{O}_z$ and $\text{C}_{10}\text{H}_{18}\text{O}_z$ families by 1.2 % and 0.3 %, respectively, while the relative contributions of $\text{C}_{10}\text{H}_{16}\text{O}_z$, $\text{C}_{12}\text{H}_{24}\text{O}_z$, and $\text{C}_{12}\text{H}_{26}\text{O}_z$ families increased by 2.8 %, 1.6 %, and 1.6 %, respectively (Fig. 6). Based on the carbon number distributions observed in the single-precursor systems, it was reasonably assumed that C_{10} -compounds in the mixture primarily originated from α -pinene, while C_{12} -compounds were mainly derived from n-dodecane. The decrease in the fraction of the $\text{C}_{10}\text{H}_{14}\text{O}_z$ family suggests that, in the presence of CO, the relative abundance of the RO_2 -termination involving a pinene-derived RO_2 - and/or cross-reactions between $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{12}\text{H}_{25}\text{O}_x$ became less pronounced in the mixture. In contrast, the relative abundance of $\text{C}_{12}\text{H}_{24}\text{O}_z$ family increased in the mixture in the presence of CO. Taken together with the observed increase in the contribution of C_{12} -species and decrease in C_{10} -species in the mixture (Fig. S10), this suggests that CO exerted a weaker suppression effect on cross-reactions involving n-dodecane-derived RO_2 - than on those involving α -pinene-derived RO_2 -. However, due to the lack of quantitative measurements on individual accretion products, the extent of this effect remains unclear. Moreover, as α -pinene and n-dodecane were used as representative precursors, the findings may be specific to the present system. These uncertainties highlight the need for future chamber studies to investigate a broader range of precursor combinations to assess the generality of the observed behaviour.

5.

5 Conclusions and implications

We established a photochemical system in the MAC that incorporated both biogenic and anthropogenic precursors, together with coexisting CO and NO_x . Compared to the chamber studies conducted under simplified conditions, this setup is more representative of polluted atmospheric environments, enabling a better characterisation of real-world SOA formation processes. Our findings show that, under altered reaction conditions, the changes in SOA precursors in the presence of CO and NO_x . The results show that the influence of CO on SOA particle mass yields and chemical composition differed markedly between single- and mixed-precursor systems.

840 In the single-precursor systems, the presence of CO led to a notable reduction in SOA particle mass yields, with a stronger effect for n-dodecane than for α -pinene. By contrast, no such suppression was observed in the mixture. Chemical composition analysis indicated that, in the single-precursor systems, CO reduced the contributions of both $RO_2 + RO_2$ and $RO_2 + NO$ reactions. In the mixed-precursor system, however, $RO_2 + NO$ reactions showed no evident reduction, while the decrease in $RO_2 + RO_2$ termination was comparatively small. In addition, CO affected the two precursors to different extents in the mixture.

845 Although biogenic precursors contribute more substantially to SOA formation on a global scale, anthropogenic precursors can play a significant role in urban and suburban environments (Srivastava et al., 2022; Stone et al., 2010; Volkamer et al., 2006). Such regions are often characterised by elevated levels of ~~other~~co-emitted pollutants ~~with strong anthropogenic sources~~, such as CO and NO_x , which can ~~alter~~modify oxidant budgets and shift radical reaction pathways. Consequently, model parameterisations derived under single-precursor or idealised conditions may misrepresent SOA formation in non-~~clean~~pristine environments. Future laboratory studies should ~~simulate~~better capture the chemical complexity of the real atmosphere ~~by incorporating representative precursor mixture to improve the accuracy and common trace gases, thereby providing a more reliable basis for the development~~applicability of ~~accurate~~ SOA model parameterisations.

855 However, establishing experimental conditions that account for atmospheric chemical complexity while remaining comparable across different systems remains challenging. The nonlinear interactions among multiple precursors, inorganic trace gases, and oxidants substantially increase the complexity of the system. In this study, even when the initial experimental conditions were designed to maintain comparable OH reactivity and precursor/ NO_x ratios and iso reactivity towards OH across systems. However, results showed that variations in oxidant levels still led to differences in precursor decay rates and potentially the SOA formation were controlled, fully comparable conditions across such systems could not be achieved. This highlights the need for ~~carefully defining comparable reaction conditions across parallel experiments involving complex photochemical systems where multiple precursors and oxidants coexist. Future~~future work ~~should~~to systematically investigate SOA formation under controlled variations in oxidant levels and precursor/ NO_x ratios to ~~improve~~enhance the reliability and comparability of ~~experimental~~ results.

6 Conclusions

865 This study investigated the impact of CO on SOA particle mass yields and chemical composition from a biogenic VOC (α -pinene), an anthropogenic IVOC (n-dodecane), and their mixture in the presence of NO_x . ~~The results indicate that the effects differed between the single and mixed precursor systems.~~

870 ~~In the single precursor systems, the presence of CO led to a notable reduction in SOA particle mass yields, with the suppression being more pronounced for n-dodecane than for α -pinene. By contrast, no such suppression was observed in the mixture.~~

~~Chemical composition analysis revealed consistent trends in the single precursor systems, indicating similar shifts in RO_2~~

875 ~~termination pathways. In both α -pinene and n-dodecane single-precursor systems, the presence of CO increased the relative abundance of CHON species and decreased the fraction of C₁₆-to-C₂₄ accretion products. The α -pinene system showed a reduction in the fraction of the C₁₀H₁₄O_x family, while the n-dodecane system exhibited a decrease in the fraction of C₁₂H₂₄O_x family. These findings suggest that the RO₂+RO₂ pathway was suppressed under CO-present conditions. In the mixed-precursor systems, the reduction in the fraction of C₁₆-to-C₂₄ accretion products was more moderate, and the contribution of CHON species remained largely unchanged. The fraction of C₁₀H₁₄O_x family decreased, whereas the C₁₂H₂₄O_x family increased. These contrasting changes may suggest that CO suppressed the two precursors to different extents in the mixture, with its influence on n-dodecane being less pronounced than in the single-precursor system, thereby resulting in a relatively small overall impact of CO in the mixture.~~

880 ~~These results demonstrate that variations in reaction conditions led to different responses in SOA particle mass yields and composition between the single and mixed-precursor systems, highlighting the need for laboratory experiments conducted under atmospherically relevant conditions.~~

885 **Data availability**

All the data in the figures of this study are available upon request to the corresponding authors (g.mcfiggans@manchester.ac.uk and aristeidis.voliotis@manchester.ac.uk)

Author contribution

890 GX, AV, and GM conceived the study. GX and AV conducted the experiments. AV, TJB, YS, HW, DH provided assistance in instrument operation and data analysis. GX conducted the data analysis and wrote the manuscript with inputs from all the co-authors.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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