REVIEWER COMMENT #1:

In "The impact of CO on secondary organic aerosols formed from the mixture of α-pinene and n-dodecane" Xie et al. present results from smog chamber experiments investigating the formation of secondary organic aerosol (SOA) from 3 different systems of precursors (two single-precursor systems and the mixed system) and each with and without CO added. Each added level complexity represents slightly more realism. NOx, ozone and UV illumination facilitate photochemical oxidation of the precursors. Concentration ratios of precursors to NOx and total precursor OH reactivities are chosen to be more or less constant in the initial mixtures. That approach plus an appropriate set of instrumentation (most importantly mass spectrometers to investigate SOA composition) allow the authors to hypothesize how differences in the mixtures modify radical chemistry as well as SOA yield.

Commendable features/highlights of the paper are the nice figures (including good use of distinctive colors for the 3 different aerosol precursor systems), and the candid discussion of the challenges in attempting to obtain similar conditions across experiments, in particular in terms of oxidant and radical concentrations when changing precursor mixtures, even if certain initial ratios can be controlled.

All in all, I judge the paper of high quality and good interest for the readership of Atmospheric Chemistry & Physics. I recommend its acceptance subject to minor revisions in consideration of my comments below. The comments generally call for a bit more clarity or slightly extended discussion (adding a few details, considering minor restructuring).

Line numbers refer to the preprint PDF.

Main comments:

1)

I wonder if the authors could briefly hypothesize, how changes in RO2 pathways (or other chemistry) between the different systems could relate to the observed changes in SOA yields?

2)

The DMPS is presented as part of the instrument line-up. But I do not recall any of its measurement results being presented or even discussed. How were its data used? Would it be worth discussing its results?

3)

Section 2.2: Precursor mixture ratios were chosen according to OH reactivity. Is it possible to assess, how relevant the resulting mixtures then are to atmospheric conditions?

4)

If Table 1 reports mean values over several experiments for each "experiment number", that should be somehow communicated within Table 1 (or its caption). And standard deviations shown.

Related to that, for Fig. 1:

- It should be clarified how many repeat experiments were done for each system.

- I believe Fig. 1 would work better if the (d) plots were incorporated into panel (c), either as a combined 3rd panel, or as purple lines into the existing (c)-panel plots.

- I would also more explicitly state that time 0 is the start of step iii (lights on, I guess)

5)

Section 4, L534: What instrumental limitations specifically? Figs. 2-4 suggest that accretion product concentrations do indeed decrease in the CO-added cases. Wouldn't the data shown there directly allow for making quantitative assessments?

6)

Sections 5 + 6: The last two sections confused me a bit. Section 6 ("Conclusions") is rather a summary (minus the last short paragraph), whereas Section 5 ("Implications") seems more like the conclusions I would have expected from Section 6.

To improve flow and readability, I suggest swapping those two sections (probably making that last paragraph in the current Section 6 superfluous) and rename them as appropriate.

Minor comments:
Abstract: A quick summary of employed methodology could be added. Presumably measurement methods, though when reading only the abstract, the paper kind-of could be a pure modeling study too.
L22: "better" than what else?
L52: "precursors" of what?
L60: The key findings of those more recent studies should be briefly summarized as well.
L66: Only older studies are cited here, though newer ones have contributed substantially to our understanding of the role of RO2 chemistry in SOA formation (e.g., autoxidation). I suggest somewhat expanding that discussion here accordingly.
L109: (major) wavelengths of those lamps?
L113: NOx cylinder specs?
L118: what kind of aerosol generator?
L122 (and 134): what is "cyclic flushing"?
L128: how was step iii initiated?
L167: DMPS specs?
2.3.1: There must be some mistake with the temperatures, as 310 °C would probably destroy a PTFE filter rather quickly.
L183: What is that weekly "instrument background procedure"? Please explain.
L185: Similarly, why was data only analyzed for a specific section of the mass spectrum?
L198: what is the "4 min chromatography cycle"? Judging from the timings, I guess that is mistake? (L188 even implied that chromatography was not required for the Vocus PTR-MS, but if some chromatography step was included nonetheless, that should of course be described.)
L203: does "set values" refer to calculated concentrations based on what was injected into the glass bulb?
L213-214: are these values to be expected based on previous studies?
Eq. 2: what does the superscript "SUS" refer to?
L216-221: unclear what the correction is trying to achieve (correct for; or "calibrate"?)
L225: "per unit of precursor" could be confusing. I assume DeltaHC is also in units of mass (like DeltaSOA)?
L277: "170-280 Da" ... From Section 2 I had assumed that data below 200 Da was not analyzed (L185)?

... Likewise, Figs. 2 etc...
L288: "the two systems" ... please clarify what the "systems" refer to.

Technical comments:
L224: typo (measured)
L297: missing "the"
L529: check grammar

ANSWER TO REVIEWER #1:

We would like to sincerely thank the referee for carefully reviewing our manuscript and for the constructive feedback provided. The reviewer's comments are presented in **bold blue**, the authors' responses in black, any revised manuscript text is shown in *italicised red font,* and unchanged original text is shown in *italicised black font*.

In addition to the revisions made in response to the reviewers' comments, several further changes were made to improve the overall readability of the manuscript. These changes are listed at the end of the response to Reviewer 2.

Main comments:

1) I wonder if the authors could briefly hypothesize, how changes in RO_2 pathways (or other chemistry) between the different systems could relate to the observed changes in SOA yields?

We thank the reviewer for this suggestion.

The changes in RO_2 pathways and SOA particle mass yields differed between the single- and mixed-precursor systems.

1. Single-precursor systems

AMS measurements showed that CO substantially reduced SOA particle and organic nitrate concentrations. Based on CIMS results, the presence of CO led to a higher relative contribution of CHON and fragment products, and a reduced fraction of C_{16}–C_{24} accretion products. In addition, the relative contributions of representative RO_2 + RO_2 termination products ($C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$) decreased.

These observations indicate that i) CO reduced the contributions of RO_2 + NO reactions, but less markedly than the competing RO_2 termination pathways, and ii) CO decreased the contributions of RO_2 + RO_2 reactions, with a more pronounced effect on longer-chain accretion products than on shorter-chain ones. Products formed via RO_2 + NO reactions tend to exhibit higher volatility than those formed through RO_2 + HO_2 and RO_2 + RO_2 termination. Accretion products, particularly for those with longer carbon chains, are expected to exhibit extremely low volatility and contribute efficiently to SOA formation. These changes are therefore expected to shift the product distribution towards more volatile species, consistent with the observed decrease in SOA particle mass yields.

2. Mixed-precursor system

AMS measurements showed that organic nitrate concentrations were largely unchanged in the presence of CO, whereas SOA particle mass concentrations decreased slightly. Based on CIMS results, the presence of CO did not significantly alter the proportion of CHON and fragment products, and the relative contributions of C_{13}–C_{24} accretion products (excluding C_{15}) slightly decreased. In addition, the fraction of $C_{10}H_{14}O_n$ decreased, whereas that of $C_{12}H_{24}O_n$ increased.

These observations indicate that the influence of CO on RO_2 termination pathways was less pronounced than in the single-precursor systems. Consequently, SOA particle mass yields behaved differently in the mixed-precursor system.

To better clarify the role of RO_2 reaction pathways and their implications for SOA particle mass yields, we have made several structural and content revisions to the manuscript:

(1) We exchanged the positions of the original Sections 4.2 ("Effect of CO on SOA particle mass yields") and 4.3 ("Effect of CO on SOA particle chemical composition"), so that the discussion of SOA particle mass yield changes is now more explicitly linked to the shifts in RO_2 reaction pathways (Line 593-615).

(2) We added a concise overview of RO_2 reaction pathways in the Introduction **(Line 43-51)**.

(3) We added a new Section 2.1, "Generic peroxy radical chemistry", to provide a clearer mechanistic framework **(Line 110-168)**.
(4) In the revised Section 4.2 (formerly 4.3), we place greater emphasis on how CO influences RO_2 reaction pathways **(Line 512-550 and 552-578)**.

Line 593-615:
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.

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.

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).

Line 43-51:
Organic peroxy (RO_2) radicals play a central role in SOA formation (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). They can undergo bimolecular termination reactions with hydroperoxyl (HO_2) radicals, 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). This complexity can substantially modify RO2 reaction pathways, thereby influencing product distributions and yields.

Line 110-168:
2.1 Generic peroxy radical chemistry
The analysis has been informed by the prevailing generic peroxy radical chemistry. RO_2 radicals can undergo bimolecular termination reactions with HO_2 radicals, other RO_2 radicals, or NO_x, leading to the formation of closed-shell products (Atkinson, 2000; Ziemann and Atkinson, 2012).
Hydroperoxides:

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \quad R1$$

Carbonyls and alcohols:

$RO_2 + RO_2 \rightarrow R{=}O + ROH + O_2$ R2

Organic nitrates:

$RO_2 + NO \rightarrow RONO_2$ R3

Peroxynitrates:

$RO_2 + NO_2 \rightarrow RO_2NO_2$ R4

Accretion products:

$RO_2 + RO_2 \rightarrow ROOR + O_2$ R5

RO_2 radicals can also undergo unimolecular reactions that lead to the formation of carbonyls (Goldman et al., 2021; Molteni et al., 2019).

$RO_2 \rightarrow QOOH;\ QOOH + O_2 \rightarrow O_2QOOH;\ O_2QOOH \rightarrow HO_2Q{=}O + OH$ R6

QOOH is a key oxidation intermediate formed via intramolecular hydrogen abstraction by RO_2 radicals.

Besides closed-shell products, RO_2 radicals can also form RO radicals (Orlando et al., 2003).

$RO_2 + NO \rightarrow RO + NO_2$ R7

$RO_2 + RO_2 \rightarrow RO + RO + O_2$ R8

$RO_2 + HO_2 \rightarrow RO + OH + O_2$ R9

HOMs are formed via autoxidation pathways of RO_2 radicals (Bianchi et al., 2019; Goldman et al., 2021).

$RO_2 \rightarrow QOOH;\ QOOH + O_2 \rightarrow O_2QOOH$ R10

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

α-Pinene photooxidation is expected to produce $C_{10}H_{15}O_x$ and $C_{10}H_{17}O_x$ as major RO_2 families. The $C_{10}H_{17}O_x$ 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). $RO_2 + HO_2$ termination (R1) of $C_{10}H_{17}O_x$ forms $C_{10}H_{18}O_n$ hydroperoxides, and $RO_2 + RO_2$ termination (R2) yields $C_{10}H_{16}O_n$ carbonyls and $C_{10}H_{18}O_n$ alcohols. Unimolecular termination (R6) of $C_{10}H_{17}O_x$ generates $C_{10}H_{16}O_n$ carbonyls. The $C_{10}H_{15}O_x$ family is formed via hydrogen abstraction from α-pinene or from first-generation oxidation products (e.g., pinonaldehyde), as well as directly from ozonolysis through the vinyl hydroperoxide pathway (Jenkin et al., 1997; Johnson and Marston, 2008; Kang et al., 2025). $RO_2 + HO_2$ termination (R1) of $C_{10}H_{15}O_x$ forms $C_{10}H_{16}O_n$ hydroperoxides, whereas $RO_2 + RO_2$ termination (R2) produces $C_{10}H_{14}O_n$ carbonyls and $C_{10}H_{16}O_n$ alcohols. Unimolecular termination (R6) of $C_{10}H_{15}O_x$ generates $C_{10}H_{14}O_n$ carbonyls. $RO_2 + RO_2$ reactions (R2) between $C_{10}H_{15}O_x$ and $C_{10}H_{17}O_x$ radicals lead to the formation of $C_{10}H_{14}O_n$ carbonyls and $C_{10}H_{18}O_n$ alcohols, and/or $C_{10}H_{16}O_n$ carbonyls and alcohols.

The main RO_2 radicals expected from n-dodecane photooxidation are $C_{12}H_{25}O_x$ family (Zhang et al., 2014). $RO_2 + HO_2$ termination (R1) yields $C_{12}H_{26}O_n$ hydroperoxides, while $RO_2 + RO_2$ termination (R2) produces $C_{12}H_{24}O_n$ carbonyls and $C_{12}H_{26}O_n$ alcohols. Unimolecular termination (R6) of $C_{12}H_{25}O_x$ generates $C_{12}H_{24}O_n$ carbonyls.

In the mixture, RO_2 radicals originating from different precursors can undergo cross-reactions. Reactions (R2) between $C_{10}H_{15}O_x$ and $C_{12}H_{25}O_x$ yield $C_{10}H_{14}O_n$ carbonyls and $C_{12}H_{26}O_n$ alcohols or $C_{12}H_{24}O_n$ carbonyls and $C_{10}H_{16}O_n$ alcohols. Similarly, reactions (R2) between $C_{10}H_{17}O_x$ and $C_{12}H_{25}O_x$ lead to the formation of $C_{10}H_{16}O_n$ carbonyls and $C_{12}H_{26}O_n$ alcohols, or $C_{12}H_{24}O_n$ carbonyls and $C_{10}H_{18}O_n$ alcohols.

RO radicals formed via reactions R7–R9 can subsequently undergo unimolecular decomposition, isomerisation, or react with O_2 (Orlando et al., 2003). Reaction of RO radicals with O_2 leads to the formation of carbonyl compounds and HO_2 radicals:

$RO + O_2 \rightarrow R'CHO + HO_2$ R11

RO radicals derived from $C_{10}H_{15}O_x$ can form $C_{10}H_{14}O_n$ carbonyls via this pathway, whereas RO radicals derived from $C_{12}H_{25}O_x$ yield $C_{12}H_{24}O_n$ carbonyls.

Theoretically, $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ carbonyls can be formed via multiple pathways, including $RO_2 + RO_2$ reactions (R2), unimolecular termination of RO_2 radicals (R6), and reaction of RO radicals with O_2 (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 RO_2 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 O_2 (Atkinson, 2007; Ziemann and Atkinson, 2012). On this basis, both unimolecular termination and RO + O_2 reactions are expected to make only minor contributions and are therefore not explicitly considered in this study.

Therefore, $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ carbonyls are expected to be formed predominantly via RO_2 + RO_2 reactions (R2). In contrast, $C_{10}H_{16}O_n$, $C_{10}H_{18}O_n$, and $C_{12}H_{26}O_n$ species can be produced not only through reactions (R2) but also via RO_2 + HO_2 pathways (R1). Accordingly, changes in the relative abundances of $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ compounds are used as indicators to assess the influence of CO on RO_2 chemistry. In general, the presence of CO is expected to reduce the relative contribution of RO_2 + RO_2 termination, which would be reflected in decreased relative abundances of $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ species.

Line 512-550:

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 C_{16}–C_{24} accretion products (Figs. 2 and 4). In addition, the relative contributions of representative RO_2 + RO_2 termination products ($C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$) within the CHO group decreased (Fig. 3). These observations provide evidence for a similar shift in RO_2 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.

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 HO_2 formation, increasing the importance of the RO_2 + HO_2 pathway and thereby altering RO_2 reaction branching. In addition, lower NO concentrations were observed in the presence of CO (Fig. S5), consistent with enhanced conversion of NO to NO_2 via the HO_2 + NO reaction. The increase in HO_2 and decrease in NO reduced the likelihood of RO_2 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 RO_2 + NO → $RONO_2$ pathway, and fragment species originate from the fragmentation of RO radicals (Atkinson, 2000; Ziemann and Atkinson, 2012). Owing to the rapid reaction of RO_2 with NO and the high branching towards RO formation, reactions of RO_2 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 RO_2 + NO reactions decreased, but to a lesser extent than competing RO_2 termination pathways.

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 RO_2 + RO_2 and RO_2 + HO_2 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 C_{16}–C_{24} species decreased (Figs. 2c and 4c), accompanied by an increase in C_{11}–C_{15} species in the α-pinene system and C_{13}–C_{14} 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 elevated fraction of fragment products discussed above. In contrast, longer-chain accretion products are more likely to originate from RO_2 + RO_2 reactions involving non-fragmented C_{10}/C_{12} RO_2 radicals, including reactions between non-fragmented RO_2 radicals and fragmented RO_2 radicals (< C_{10}), or between two non-fragmented RO_2 radicals, yielding C_{20} and C_{24} accretion products in the α-pinene and n-dodecane systems, respectively. Combined with the reduced fractions *of $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ families (Fig. 3), these observations indicate that CO preferentially suppressed RO_2 + RO_2 chemistry, particularly pathways forming longer-chain accretion products.*

Overall, in the single-precursor systems, CO reduced the contributions of both RO_2 + RO_2 and RO_2 + NO reactions. However, reactions of RO_2 with NO decreased to a lesser extent than competing RO_2 termination pathways, and the reduction in RO_2 + RO_2 termination was more pronounced for longer-chain accretion products than for shorter-chain ones.

Line 552-578:
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 C_{13}–C_{24} accretion products (excluding C_{15}) slightly decreased (Fig. 5c); and (iii) within the CHO group, the fraction of the $C_{10}H_{14}O_n$ family decreased, whereas that of the $C_{12}H_{24}O_n$ 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 RO_2 + NO reactions was not substantially reduced under CO conditions.

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 RO_2 + RO_2 termination.

Moreover, CO led to a lower fraction of the $C_{10}H_{14}O_n$ family in the mixture, consistent with the trend observed in the α-pinene 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.

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.

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.

2) The DMPS is presented as part of the instrument line-up. But I do not recall any of its measurement results being presented or even discussed. How were its data used? Would it be worth discussing its results?

DMPS was employed to measure seed aerosol concentrations.

Line 222-224:
*The mass concentration of seed aerosols in the 20–500 nm size range was measured 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).*

3) Section 2.2: Precursor mixture ratios were chosen according to OH reactivity. Is it possible to assess, how relevant the resulting mixtures then are to atmospheric conditions?

Owing to the detection limits of the instruments, the precursor concentrations used in this study were higher than typical atmospheric levels. Nevertheless, the ratio of α-pinene to n-dodecane falls within the range observed in urban and roadside environments.

Line 209-212:

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).*

4) If Table 1 reports mean values over several experiments for each "experiment number", that should be somehow communicated within Table 1 (or its caption). And standard deviations shown.

The experiments listed in Table 1 are individual experiments.

No action

Related to that, for Fig. 1:

- It should be clarified how many repeat experiments were done for each system.

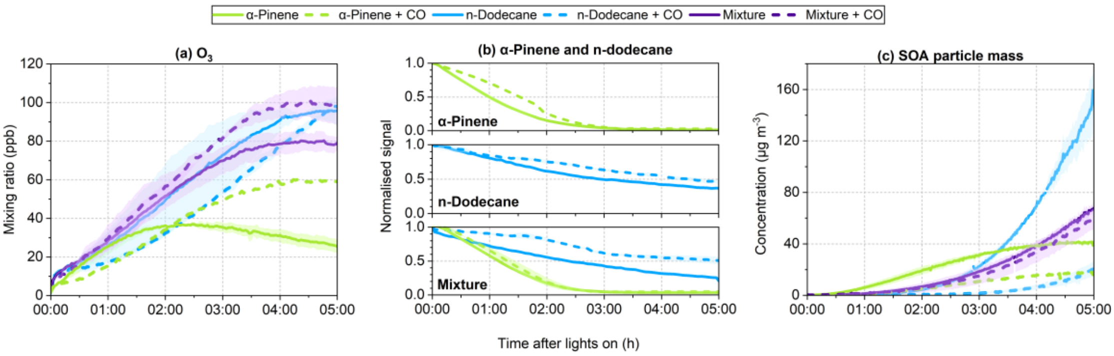
We thank the reviewer for this suggestion. As the number of repeat experiments differed between systems, we have clarified in the revised manuscript that the shaded area indicates the range between replicates listed in Table 1.

Line 303-305:

Solid and dashed lines denote experiments conducted without and with CO, respectively. ***Where duplicate experiments were available, the lines represent the mean values, and the shaded area indicates the range between replicates (Table 1).***

- I believe Fig. 1 would work better if the (d) plots were incorporated into panel (c), either as a combined 3rd panel, or as purple lines into the existing (c)-panel plots.

We thank the reviewer for this suggestion. In the revised figure, the former panels (c) and (d) have been combined into panel (b).



- I would also more explicitly state that time 0 is the start of step iii (lights on, I guess)

We thank the reviewer for this suggestion. We have now clarified that time 0 corresponds to the start of step (iii), when the chamber lights were turned on.

Line 304-305:

*Time 0 corresponds to the start of step (iii) (Sect. 2.2), **when the chamber lights were turned on**.*

5) Section 4, L534: What instrumental limitations specifically? Figs. 2-4 suggest that accretion product concentrations do indeed decrease in the CO-added cases. Wouldn't the data shown there directly allow for making quantitative assessments?

Owing to the lack of available calibration standards and the variability in instrument sensitivity across different oxygenated organic compounds, quantitative analysis using I^--CIMS remains challenging. Consequently, the data presented in Figs. 2-4 (now 2, 4, and 5), as well as the relevant discussion, are based on relative changes rather than absolute concentrations. For example, a decrease in accretion products refers to a reduction in their fraction within the total detected products rather than a decrease in their absolute concentration.

However, when considered alongside AMS measurements, results can be discussed in terms of absolute changes.

Line 251-253:

***Owing to the lack of available calibration standards and the variability in instrument sensitivity across different oxygenated organic compounds**, quantitative analysis using I^--CIMS remains challenging (Lee et al., 2014). As a result, a uniform instrument sensitivity was assumed for all detected products.*

Line 355-356:

*The **overall fraction** of accretion products 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).*

Line 403-404:

*While the overall **fraction** of accretion products was comparable under both conditions, the presence of CO reduced the fraction of C_{16}–C_{24} accretion products (Fig. 4c).*

6) Sections 5 + 6: The last two sections confused me a bit. Section 6 ("Conclusions") is rather a summary (minus the last short paragraph), whereas Section 5 ("Implications") seems more like the conclusions I would have expected from Section 6.

To improve flow and readability, I suggest swapping those two sections (probably making that last paragraph in the current Section 6 superfluous) and rename them as appropriate.

We thank the reviewer for this suggestion. We have reorganised the original Sections 5 and 6, merged them into a single section, and revised the content accordingly to improve readability and logical flow. The final paragraph of the original Section 6 has been removed as suggested.

Line 617-640:

We established a photochemical system in the MAC that incorporated both biogenic and anthropogenic 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.

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.

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 co-emitted pollutants, such as CO and NO_x, which can modify oxidant budgets and shift radical reaction pathways. Consequently, model parameterisations derived under single-precursor or idealised conditions may misrepresent SOA formation in non-pristine environments. Future laboratory studies should better capture the chemical complexity of the real atmosphere to improve the accuracy and applicability of SOA model parameterisations.*

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 OH reactivity and precursor/NO_x ratios were controlled, fully comparable conditions across such systems could not be achieved. This highlights the need for future work to systematically investigate SOA formation under controlled variations in oxidant levels and precursor/NO_x ratios to enhance the reliability and comparability of results.

Minor comments:

Abstract: A quick summary of employed methodology could be added. Presumably measurement methods, though when reading only the abstract, the paper kind-of could be a pure modeling study too.

We thank the reviewer for this suggestion. We have now clarified in the Abstract that the study was conducted in the Manchester Aerosol Chamber and that a series of online measurements was used to characterise gas- and particle-phase species.

Line 15-18:

Here, we investigated the impact of CO on SOA particle mass yields and chemical composition from α-pinene (a biogenic volatile organic compound, VOC), n-dodecane (an anthropogenic intermediate-volatility organic compound, IVOC), and their mixture in the presence of nitrogen oxides (NO_x = NO + NO_2) in the Manchester Aerosol Chamber (MAC) ***using online measurements****.*

L22: "better" than what else?

We thank the reviewer for this comment. We have removed the use of the comparative term "better" and revised the sentence to more explicitly state that the present study extends previous investigations conducted under single-precursor and simplified experimental conditions.

Line 13-18:

Secondary organic aerosol (SOA) formation is strongly influenced by atmospheric conditions. Achieving atmospheric relevance in chamber experiments is essential for understanding and predicting the impacts of SOA on air quality and climate. However, many chamber studies are conducted under simplified conditions or with a single SOA precursor. Here, we investigated the impact of CO on SOA particle mass yields and chemical composition from α-pinene (a biogenic volatile organic compound, VOC), n-dodecane (an anthropogenic intermediate-volatility organic compound, IVOC), and their mixture in the presence of nitrogen oxides (NO_x = NO + NO_2) in the Manchester Aerosol Chamber (MAC) using online measurements.

L52: "precursors" of what?

We thank the reviewer for this comment. The sentence has been rephrased to specify that these compounds are SOA precursors.

Line 39-41:

However, many laboratory experiments are conducted under simplified conditions or with a single ***SOA precursor****, which may introduce uncertainties when extrapolating these results to atmospheric models (Kenagy et al., 2024; Shrivastava et al., 2017; Tsigaridis et al., 2014).*

L60: The key findings of those more recent studies should be briefly summarized as well.

We thank the reviewer for this suggestion. We have added an explanation noting that the overall SOA particle mass yields in the mixture deviate from those predicted by additive calculations.

Line 61-65:

*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 addition of SOA particle mass yields from individual components may lead to inaccurate estimates of total SOA formation in mixed-precursor systems.*

L66: Only older studies are cited here, though newer ones have contributed substantially to our understanding of the role of RO2 chemistry in SOA formation (e.g., autoxidation). I suggest somewhat expanding that discussion here accordingly.

We thank the reviewer for this suggestion. In the revised manuscript, we have added a description of the mechanisms of HOM formation and discussed the effects of precursor mixing and inorganic trace gases on HOM formation.

Line 46-48:

*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).*

Line 126:

HOMs are formed via autoxidation pathways of RO_2 radicals (Bianchi et al., 2019; Goldman et al., 2021).

$$RO_2 \rightarrow QOOH;\ QOOH + O_2 \rightarrow O_2QOOH \qquad R10$$

Line 53-58:

*McFiggans et al. (2019) demonstrated that 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 RO_2 radicals. Second, **isoprene-derived RO_2 radicals can scavenge HOM-RO_2 derived from α-pinene**, leading to the formation of products with higher volatility.*

Line 67-69:

Atmospheric inorganic trace gases, such as CO and NO_x, can alter oxidant levels and RO_2 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).

Line 76-80:

*McFiggans et al. (2019) showed that CO suppressed α-pinene dimer (containing 17 to 20 carbon atoms) formation by a factor of two, while **the amounts of HOMs were suppressed by factors of 4 to 5**. Baker et al. (2024) further demonstrated that, under constant OH conditions, the addition of CO increased the HO_2/RO_2 ratio from approximately 1/100 to about 1/1, **leading to a ~ 60 % reduction in the abundance of HOM-accretion products and a ~ 30 % decrease in the SOA formation potential of HOMs**.*

Line 90-92:

*Pullinen et al. (2020) revealed that higher NO_x concentrations reduced the formation of **gas-phase α-pinene HOM-accretion products**, leading to a lower SOA particle mass yield.*

L109: (major) wavelengths of those lamps?

Illumination was primarily provided by a combination of xenon arc lamps and halogen lamps, producing irradiation over the wavelength range 290–800 nm to mimic the atmospheric radiation spectrum. In addition, to promote OH radical production, a UVC lamp (TUV 130W XPT SE UNP/20, Philips) operating at 254 nm was installed, with more than 90 % of its length masked to prevent excessive irradiation.

Line 172-177:

*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 NO_2 (J_{NO_2}) was 1.38 × 10^{-3} s^{-1}. To promote OH radical production, an additional UVC lamp (TUV 130W XPT SE UNP/20, Philips) was installed, with more than 90 % of its length masked to prevent excessive irradiation.*

L113: NOx cylinder specs?

It is a custom-made cylinder, primarily containing NO_2 with a minor NO impurity.

Line 179-181:

*NO_x was introduced from a **custom-made** cylinder using ECD N_2 as the carrier gas. NO_2 served as the source of O_3, and the subsequent O_3 photolysis generated OH radicals, thereby initiating photochemical oxidation.*

L118: what kind of aerosol generator?

The aerosol generator used in this study was an ATM 230 (Topas). Detailed information is available on the website (https://www.topas-gmbh.de/en/products/generation/product/atm-230).

> "The ATM 230 is designed as a serial instrument with an external compressed air supply. The liquid reservoir is arranged within the housing."

Line 182-184:

*Seed particles with a mass concentration of 40.2 ± 8.0 µg m^{-3} were generated by nebulising aqueous ammonium sulfate solutions ($(NH_4)_2SO4$, ACS reagent, ⩾ 99.0 %, Sigma-Aldrich) using an aerosol generator (**ATM 230, Topas**).*

L122 (and 134): what is "cyclic flushing"?

"Cyclic flushing and filling" refers to automated repeated flush-fill cycles with clean air at a high flow rate for approximately 1.5 h to remove the contamination in the chamber. Each cycle consists of ~7 min of flushing followed by ~7 min of refilling.

Line 189-193:

*(i) Pre-experiment: **Repeated flush-fill cycles were conducted to achieve a low-background condition. During these cycles, the chamber was flushed for approximately 7 min and then refilled with clean air at the same flow rate, with this procedure repeated for about 1.5 h.** Subsequently, SOA precursors, NO_x, CO, and seed aerosols were introduced into the chamber. The temperature and relative humidity were adjusted to approximately 25 °C and 50 ± 5 %, respectively.*

L128: how was step iii initiated?

Upon illumination, photo-oxidation and subsequent SOA formation were initiated.

Line 194-195:

(ii) *Experiment: **When the lights were turned on**, photooxidation and subsequent SOA formation were initiated. Each "experiment" phase lasted for approximately 5 h.*

L167: DMPS specs?

The DMPS consists of a Vienna-design DMA coupled to a CPC (model 3775, TSI Inc.).

Line 222-224:

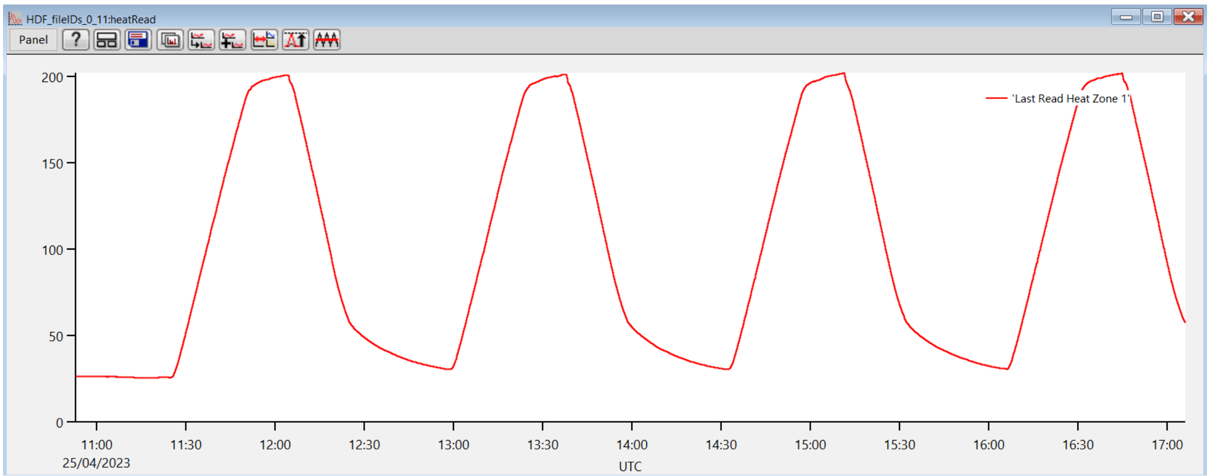
*The mass concentration of seed aerosols in the 20–500 nm size range was measured using a Differential Mobility Particle Sizer (DMPS), **consisting of a Vienna-design differential mobility analyser (DMA)** coupled to a Condensation Particle Counter (CPC, model 3775, TSI Inc.) (Alfarra et al., 2012).*

2.3.1: There must be some mistake with the temperatures, as 310 °C would probably destroy a PTFE filter rather quickly.

We thank the reviewer for pointing this out.

The temperature of 310 °C refers to the set value of the heating unit. As shown in the figure below, the actual temperature experienced by the PTFE filter did not exceed 200 °C throughout the desorption process.

We have corrected the temperature reported in the manuscript and added a clarification that the filters were pre-heated to 200 °C to remove potential contaminants.



Line 231-239:

(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 N_2 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 **200** °C.*

*(iii) 15 min of isothermal soaking at **200** °C.*

*(iv) 20 min of cooling from **200** °C to ambient temperature.*

(v) 2 min of N_2 flushing to clean the instrument.

L183: What is that weekly "instrument background procedure"? Please explain.

We apologise for the error in the original manuscript. The term "instrument background procedure" should be "Chamber background measurement".

Two types of blank measurements were performed in this study.
(1) Chamber background measurement:
All components (SOA precursors, seed particles, CO, and NO_x) were injected into the chamber under the same experimental conditions as the regular experiments, while the chamber was kept in the dark. CIMS data obtained during these background measurements were subtracted from both the gas- and particle-phase data acquired during the "experiment" phase.
(2) Instrument background measurement:
As described in Section 2.4.1, during the 30 min gas-phase sampling, the instrument was flushed with N_2 for 0.5 min every 4.5 min to obtain the gas-phase instrument background signal.

Line 232-233:
During this step, the instrument was flushed with N_2 for 0.5 min every 4.5 min to obtain the gas-phase instrument background signal.

Line 243-246:
To account for background species in the chamber, background measurements were conducted weekly. 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 data acquired during the "experiment" phase.

L185: Similarly, why was data only analyzed for a specific section of the mass spectrum?

We thank the reviewer for pointing this out. The majority of the total signal was observed within the m/z range of 200–550 (iodide adducts).

Line 248-250:
*The FIGAERO-CIMS data were analysed using the Tofware package (v4.0.0) in Igor Pro 7.0.8 (WaveMetrics©). I^-, H_2OI^-, $CH_2O_2I^-$, and I_3^- were used for mass-to-charge calibration (calibration error ≤ 3 ppm). High-resolution peak identification and fitting were performed in the m/z range of 200–550 (iodide adducts), **which contained the vast majority of the total signal.***

L198: what is the "4 min chromatography cycle"? Judging from the timings, I guess that is mistake? (L188 even implied that chromatography was not required for the Vocus PTR-MS, but if some chromatography step was included nonetheless, that should of course be described.)

We thank the reviewer for noting this point. The VOCUS was not operated with a GC column in this study. The reference to a "chromatography cycle" was a wording error and has been corrected to "sampling" in the revised manuscript.

Line 268-269:
*Measurements were made on a 5 min cycle, consisting of 4 min of **sampling** followed by 1 min of instrumental background.*

L203: does "set values" refer to calculated concentrations based on what was injected into the glass bulb?

We thank the reviewer for this question. The "set values" refer to the target concentrations used in the chamber, rather than concentrations calculated from the injected amounts. For α-pinene, the target concentration was 40 ppb in the single-precursor system and 20 ppb in the mixed-precursor system. For n-dodecane, the corresponding target concentrations were 160 ppb in the single-precursor system and 80 ppb in the mixed-precursor system.

We have replaced the term "set value" with "target value" in the revised manuscript and added a corresponding clarification in Sect. 2.3.

Line 272-275:

*Therefore, alternative approaches were adopted for its quantification: (i) the initial mixing ratios were taken as the **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 temporal evolution of the $C_{10}H_{21}^{+}$ fragment ion (Fig. S4).*

Line 209-211:

*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.*

L213-214: are these values to be expected based on previous studies?

Yes, these values are comparable to those reported in the literature.

> "The RIE values usually used in AMS ambient concentration calculations are 1.4 for organic molecules and 1.1, 1.15, and 3.5-6 for NO_3, SO_4, and NH_4 moieties, respectively." (Canagaratna et al., 2007)
>
> "The ionization efficiency (IE) with respect to nitrate anions was calculated at the beginning and at the end of the campaign using nebulised 350 nm mobility diameter ammonium nitrate particles (BFSP software was used and values varied between 2.2×10^{-7} - 2.5×10^{-7})." (Lannuque et al., 2023)

Line 280-284:

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).

Eq. 2: what does the superscript "SUS" refer to?

We thank the reviewer for this question. SUS refers to the suspended particles. To avoid potential confusion, we have removed this abbreviation.

Line 288-290:

$$C_{OA}(t) = \frac{C_{OA}(t)}{C_{seed}(t)} C_{seed}(0) \qquad (2)$$

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

L216-221: unclear what the correction is trying to achieve (correct for; or "calibrate"?)

We apologise for the ambiguity in the original manuscript. The correction refers to a chamber wall-loss correction applied to the SOA particle mass concentrations derived from AMS measurements. The text has been revised to clarify this point.

Line 285-286:

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

L225: "per unit of precursor" could be confusing. I assume DeltaHC is also in units of mass (like DeltaSOA)?

We apologise for the ambiguity in the original manuscript. We have removed the term "HC (hydrocarbon)" and replaced it with "precursor" to improve clarity. Both SOA and precursor concentrations are expressed in units of μg m^{-3}.

Line 294-296:

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

For the single-precursor systems, $\Delta precursor$ *(μg* m^{-3}*) denotes the consumption of α-pinene or n-dodecane, whereas for the mixed-precursor system, it refers to the total consumption of α-pinene and n-dodecane.*

L277: "170-280 Da" ... From Section 2 I had assumed that data below 200 Da was not analyzed (L185)? ... Likewise, Figs. 2 etc...

We apologise for the ambiguity in the original manuscript. The m/z range 200–550 refers to iodide adducts (including the mass of I^-), whereas the range 170–280 Da corresponds to the molecular masses of the products without I^-. This has now been clarified in the Sect. 2.4.1 by explicitly stating that the masses correspond to iodide adducts.

Line 249-250:

High-resolution peak identification and fitting were performed in the m/z range of 200–550 (iodide adducts), which contained the vast majority of the total signal.

L288: "the two systems" ... please clarify what the "systems" refer to.

We apologise for the ambiguity in the original manuscript. The "systems" referred to the α-pinene system with and without CO. Following revision, the original sentence has been removed, and similar expressions throughout the manuscript have been replaced with "under both conditions".

Line 355-356:

The overall fraction of accretion products remained constant at 9 % ***under*** *both* ***conditions****.*

Line 402-404:

While the overall fraction of accretion products was comparable ***under both conditions****, the presence of CO reduced the fraction of* C_{16}*–*C_{24} *accretion products (Fig. 4c)*

Technical comments:

L224: typo (measured)

We thank the reviewer for pointing out this typo. We have made the corresponding revision.

Line 291-292:

SOA particle mass yields (Y_{SOA}*) for each system were derived from SOA particle mass concentrations measured by AMS and precursor concentrations measured by PTR.*

L297: missing "the"

We thank the reviewer for pointing out this mistake. However, following revisions to the manuscript, the original sentence has been removed in the revised version.

L529: check grammar

We thank the reviewer for pointing out this grammatical error. However, following revisions to the manuscript, the original sentence has been removed in the revised version.

REVIEWER COMMENT #2:

The paper by Xie et al. investigates the SOA formed from aPinene and dodecane, alone, and then in mixtures. The radical budget was altered by addition of CO, which increased the HO2 concentrations. The experiments utilized the FIGAERO-CIMS to determine the chemical composition of the SOA formed under the different conditions. The authors present their results clearly, and there are some questions about determination of OH concentration and their ability to achieve iso-reactivity. Though, there are serious questions about the interpretation of their data with respect to radical chemistry. The discussion then attempts to relate the chemical composition observed in the SOA to understand the radical chemistry taking place within the chamber. The discussion of the radical chemistry suffers greatly by only considering RO2 + RO2 chemistry. The authors state that the formation of specific molecules exclusively forms via RO2 + RO2 reactions, when they do not consider other radical pathways (e.g. alkoxy radicals). The other aspects of the paper are relatively well put together, but the leg on which the paper stands is being able to connect their FIGAERO-MS data to the radical chemistry in the chamber. At the moment, I don't see that clear connection because of my concerns about the radical chemistry discussion.

Major Comments:
Lines 539 – 562: The discussion here focuses purely on the RO2 + RO2 reaction pathway, and does not present a holistic understanding the radical pathways present in the reactions of α-pinene + O_3 or OH. This involves the alkoxy radical pathway, which is important part of both the RO2 + RO2 and RO2 + HO2 reaction schemes. This limitation is serious with this paper specifically because on lines 551-553 the authors state that the C10H14Ox can only be formed via RO2 + RO2. Molteni et al (2019) presents clear pathways to the same proposed products that do not invoke RO2 + RO2 (see R2 and R3a/R3B + R5). Because of the weight on these specific molecules (C10H14Ox) and their corresponding products from dodecane being used as the specific proof of the change of the RO2 + RO2 radical reaction pathways, it is crucial for the authors to change their discussion.
The discussion begins to diverge on lines 525-537: I do not understand what the authors mean by "fragment derived RO2 radicals". My understanding of fragmentation is associated with the alkoxy radical pathway. (Molteni et al. 2019).
More related with the gas-phase reaction pathways:
Section 4.3.1: It appears that the discussion here focuses on RO2 reactions, with the 3 pathways being RO2 + RO2, RO2 + HO2, RO2 + NO, or RO2 (autoxidation). What do the authors expect for the lifetimes of RO2 radicals in the chamber for the different experiments toward the 4 different pathways? (or 3 different pathways if it is not possible to discuss autoxidation) The general increase in N-containing products is surprising in the CO containing experiments. Lines 517-520: What would specifically cause the increase in the RO2 + NO pathway? It seems counter intuitive based on the lower NO levels when CO is present.
Considering the FIGAERO-CIMS can result in the degradation of molecules on the filter, here the authors only present molecular formula measurements (D'Ambro et al, 2017). Do the authors believe there is any serious degradation taking place? No thermograms have been presented, so it is difficult to understand if these are likely intact molecules or fragments.
Minor comments:
Lines 50-62: There is also rich literature about mixtures of VOCs and their impact on new particle formation.
Line 71-73: I understand this is a statement from the Baker paper, but it is simply not true as it stands. The SOA yield of a mixture with a dominant RO2 + RO2 pathway is the SOA yield for those specific conditions. The unspoken aspect of this sentence is that the HO2/RO2 ratio is not environmentally relevant for RO2 + RO2 dominant studies, meaning using a RO2 + RO2 dominant yield when the reality is that the RO2 + HO2 pathway is dominant would create an overestimate of the yields in whatever model you choose to use.
Lines 108 – 110: What is the total spectrum of UV light look like? What is the jNO2? Who is the supplier for the UVC lamp? (since the lights are slightly different with the addition of the 254nm lights compared to the Shao et al. publication)
Line 110-112: were the injections performed with a syringe?
Lines 122 – 125: What was the order of the seed injection and humidification? At the moment it is unclear to me what the phase state of the seed is.

Lines 169-181: Is it wise to heat the PTFE filter over 260 °C? There can be degradation of PTFE and the release of fumes from the filter above that temperature. (Sajid et al. 2017)
Section 2.2: how was OH radical concentration determined in Figure S5? I don't see something in the methods section that describes this, and with the presence of O3 does this complicate the determination of O3 when using aPinene as an OH tracer? I see this is mentioned briefly in section 4.1, but it warrants a clear explanation in the methods section. Since this is a batch mode experiment, how does dilution in the chamber impact the depletion of CO? Why is dodecane not included in mixture of Figure S5?
Section 2.3.2: Is the VOCUS run with a GC column? If so please provide the relevant details. I suspect that there is a GC column because of the mention of a chromatography cycle on line 198.
Section 2, what types of blank measurements were performed with the chamber?
Lines 202-204: how did you verify that the injected concentrations are what you think they were?
Lines 204-205, what fragments were used with this method?
Lines 205 – 206: were calibration performed similar to Figure S2 to verify the robustness of using C10H21+
Section 2.3.3: was a dryer used with the AMS? If not how was it verified that the collection efficiency was the same between the experiment and the calibration? I ask because there was likely different RH conditions between the experiment and the calibration.
Figure 1: because of the presence of O3 what is the difference in the OH vs O3 reactivity in the different experiments? The caption should provide information about what fragments mean. Also, how does the OH produced by aPinene ozonolysis impact the iso-reactivity calculations?
(Continuing with Figure S12) In Figure S12, it is not clear if each bar corresponds to the integrated OH/O3 reactivity or is it for that specific unit time? The y-axis label should be changed, at the moment it appears to indicate a ratio of OH / O3, which isn't what the figure is showing.
Line 465-467: This doesn't appear to be true for the dodecane case because the OH never 'recovered'.
Line 470 – 475: I do not understand this discussion. It would appear to be true at face value if isoreactivity was achieved, but it clearly wasn't perfectly achieved in Figure S5. So aren't the changes in OH concentrations purely able to describe these results?
Figure 5 and section 4.2: I am a bit confused by the purported ~50% difference in the yield with vs. without CO for aPinene. Based on Figure 5 (left panel) the yield should be effectively the same with vs. without CO. Can the authors comment on the apparent discrepancy in the text and Table 1 with the Figure?
Lines 543 -545: the way the percentages are talked about are misleading. Perhaps the authors should talk about the percentage reduction of specific molecular cases e.g. 2% reduction for C10H14Ox is a reduction from ~11% à 9% (Figure 6), which is a reduction of ~20%

References:

Sajid, M., Ilyas, M. PTFE-coated non-stick cookware and toxicity concerns: a perspective. Environ Sci Pollut Res 24, 23436–23440 (2017). https://doi.org/10.1007/s11356-017-0095-y

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D'Ambro, E. L., Lee, B. H., Liu, J., Shilling, J. E., Gaston, C. J., Lopez-Hilfiker, F. D., Schobesberger, S., Zaveri, R. A., Mohr, C., Lutz, A., Zhang, Z., Gold, A., Surratt, J. D., Rivera-Rios, J. C., Keutsch, F. N., and Thornton, J. A.: Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low- and high-NOx conditions, Atmos. Chem. Phys., 17, 159–174, https://doi.org/10.5194/acp-17-159-2017, 2017.

ANSWER TO REVIEWER #2:

We would like to sincerely thank the referee for carefully reviewing our manuscript and for the constructive feedback provided. The reviewer's comments are presented in **bold blue**, the authors' responses in black, any revised manuscript text is shown in *italicised red font,* and unchanged original text is shown in *italicised black font*.

In addition to the revisions made in response to the reviewers' comments, several further changes were made to improve the overall readability of the manuscript and are summarised at the end of this response.

Major Comments:

Lines 539 – 562: The discussion here focuses purely on the RO2 + RO2 reaction pathway, and does not present a holistic understanding the radical pathways present in the reactions of α-pinene + O_3 or OH. This involves the alkoxy radical pathway, which is important part of both the RO2 + RO2 and RO2 + HO2 reaction schemes. This limitation is serious with this paper specifically because on lines 551-553 the authors state that the C10H14Ox can only be formed via RO2 + RO2. Molteni et al (2019) presents clear pathways to the same proposed products that do not invoke RO2 + RO2 (see R2 and R3a/R3B + R5). Because of the weight on these specific molecules (C10H14Ox) and their corresponding products from dodecane being used as the specific proof of the change of the RO2 + RO2 radical reaction pathways, it is crucial for the authors to change their discussion.

We thank the reviewer for raising these crucial points.

We acknowledge that the original manuscript did not adequately discuss alkoxy radical pathways, unimolecular termination, or ozonolysis products, all of which potentially contribute to the formation of $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ carbonyls. Here, we provide a detailed discussion of these reaction pathways.

(1) Carbonyls by unimolecular termination channel
$RO_2 \rightarrow QOOH$; $QOOH + O_2 \rightarrow O_2QOOH$; $O_2QOOH \rightarrow HO_2Q{=}O + OH$

Theoretically, RO_2 radicals ($C_{10}H_{15}O_x$) formed from α-pinene oxidation can produce $C_{10}H_{14}O_n$ carbonyls through such a series of isomerisation, oxidation, and unimolecular decomposition reactions. Similarly, RO_2 radicals derived from n-dodecane ($C_{12}H_{25}O_x$) can lead to the formation of $C_{12}H_{24}O_n$ carbonyls.

However, under ambient-temperature conditions and in the presence of NO_x, unimolecular termination pathways are not expected to be dominant. Goldman et al. (2021) showed that, at a pressure of 0.5 bar, temperatures below 300 K, and NO concentrations ranging from 1 ppb to 1 ppm, reactions of n-propyl and γ-isobutanol RO_2 radicals are dominated by RO radical formation, and that increasing NO concentrations shift the onset of unimolecular termination to higher temperatures. On this basis, we assume that the contribution of carbonyl compounds formed via unimolecular termination pathways is negligible in this study.

(2) Alkoxy-O_2 channel
$RO + O_2 \rightarrow R'CHO + HO_2$

RO radicals derived from $C_{10}H_{15}O_x$ can form $C_{10}H_{14}O_n$ carbonyls via this pathway, and RO radicals derived from $C_{12}H_{25}O_x$ yield $C_{12}H_{24}O_n$ carbonyls.

Previous studies have shown that C-C bond scission of RO radicals derived from α-pinene has a very low energy barrier, with reaction rates far exceeding those of reactions with O_2 (Dibble, 2001). For linear RO radicals formed from alkanes, isomerisation generally dominates over reactions with O_2 and unimolecular decomposition. For example, for 2-pentoxy and 2-hexoxy radicals, isomerisation ≫ reaction with O_2 ≈ decomposition (Ziemann and

Atkinson, 2012). On this basis, the contribution of the RO + O_2 pathway is expected to be minor and is therefore not explicitly considered in this study.

(3) Ozonolysis

α-Pinene ozonolysis can produce the $C_{10}H_{15}O_x$ RO_2 family. $C_{10}H_{14}O_n$ carbonyls are expected to be formed predominantly via RO_2 + RO_2 reactions, whereas $C_{10}H_{16}O_n$ products can originate from both RO_2 + HO_2 and RO_2 + RO_2 reactions. Consequently, variations in the relative abundance of $C_{10}H_{14}O_n$ species can be used as an indicator of changes in the RO_2 + RO_2 pathway.

Overall, under certain conditions, alkoxy-O_2 reactions or unimolecular termination channels may contribute with substantial branching ratios. However, in this study, their contributions are expected to be minor. These channels are discussed in the newly added Section 2.1, as outlined in response to reviewer 1.

Line 155-162:

Theoretically, $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ carbonyls can be formed via multiple pathways, including RO_2 + RO_2 reactions (R2), unimolecular termination of RO_2 radicals (R6), and reaction of RO radicals with O_2 (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 RO_2 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 O_2 (Atkinson, 2007; Ziemann and Atkinson, 2012). On this basis, both unimolecular termination and RO + O_2 reactions are expected to make only minor contributions and are therefore not explicitly considered in this study.

The discussion begins to diverge on lines 525-537: I do not understand what the authors mean by "fragment derived RO2 radicals". My understanding of fragmentation is associated with the alkoxy radical pathway. (Molteni et al. 2019).

We thank the reviewer for pointing this out and apologise for the ambiguity in the original manuscript.

We have removed the original statement and clarified the origin of these species in the revised manuscript. The formation of RO_2 radicals containing fewer than 10 carbon atoms necessarily involves fragmentation of RO radicals; therefore, these species are more appropriately described as fragmented RO_2 radicals (Kang et al., 2025).

Line 534-546:

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 RO_2 + RO_2 and RO_2 + HO_2 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 C_{16}–C_{24} species decreased (Figs. 2c and 4c), accompanied by an increase in C_{11}–C_{15} species in the α-pinene system and C_{13}–C_{14} 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 elevated fraction of fragment products discussed above. In contrast,* ***longer-chain accretion products are more likely to originate from RO_2 + RO_2 reactions involving non-fragmented C_{10}/C_{12} RO_2 radicals, including reactions between non-fragmented RO_2 radicals and fragmented RO_2 radicals (< C_{10}), or between two non-fragmented RO_2 radicals****, yielding C_{20} and C_{24} accretion products in the α-pinene and n-dodecane systems, respectively. Combined with the reduced fractions of $C_{10}H_{14}O_n$ and $C_{12}H_{24}O_n$ families (Fig. 3), these observations indicate that CO preferentially suppressed RO_2 + RO_2 chemistry, particularly pathways forming longer-chain accretion products.*

More related with the gas-phase reaction pathways:

Section 4.3.1: It appears that the discussion here focuses on RO2 reactions, with the 3 pathways being RO2 + RO2, RO2 + HO2, RO2 + NO, or RO2 (autoxidation). What do the authors expect for the lifetimes of RO2 radicals in the chamber for the different experiments toward the 4 different pathways? (or 3 different pathways if it is not possible to discuss autoxidation) The general increase in N-containing products is surprising in the CO containing experiments. Lines 517-520: What would specifically cause the increase in the RO2 + NO pathway? It seems counter intuitive based on the lower NO levels when CO is present.

We respond to the reviewer's comments point by point below.

(1) What do the authors expect for the lifetimes of RO2 radicals in the chamber for the different experiments toward the 4 different pathways? (or 3 different pathways if it is not possible to discuss autoxidation)

Compared with experiments conducted without CO, the presence of CO is expected to modify the RO_2 fate as follows.
1. CO reacts with OH to form HO_2, increasing HO_2 concentrations.
2. Elevated HO_2 enhances the HO_2 + NO reaction, resulting in lower NO concentrations.
3. HO_2 competes with RO_2 and NO for reaction with RO_2, and together with the reduced NO concentrations decreases the relative importance of RO_2 + RO_2 and RO_2 + NO pathways.

Consequently, in the presence of CO, the lifetime of RO_2 radicals with respect to reactions with NO and other RO_2 radicals is expected to increase, whereas their lifetime towards reaction with HO_2 is expected to decrease.

(2) The general increase in N-containing products is surprising in the CO containing experiments. Lines 517-520: What would specifically cause the increase in the RO2 + NO pathway? It seems counter intuitive based on the lower NO levels when CO is present.

We thank the reviewer for pointing this out.

In the single-precursor systems, the presence of CO did not enhance the RO_2 + NO pathway. Instead, only its **relative contribution** increased, while the absolute abundance was significantly suppressed. Evidence for this behaviour is provided by both AMS and CIMS measurements. (Figure S13 has been added to the Supplementary Information)

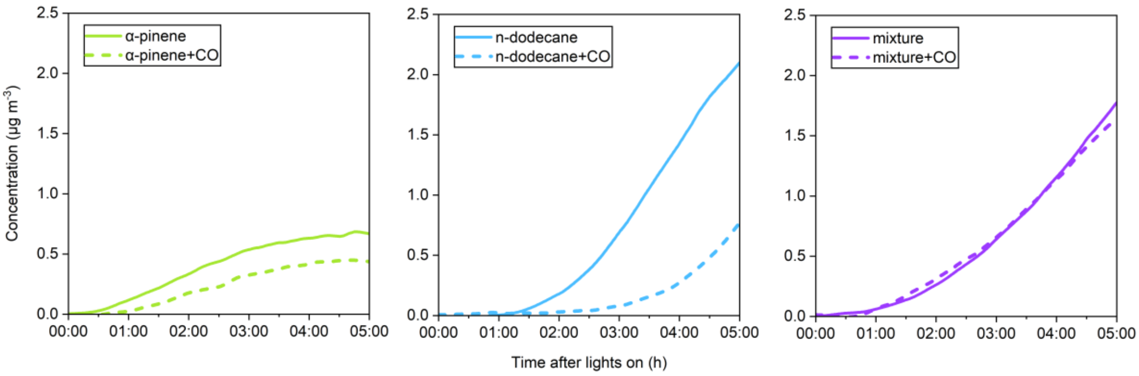
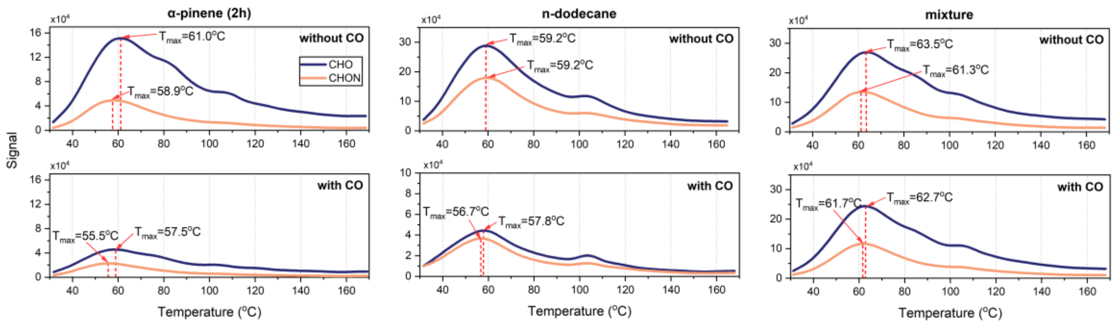


Figure S13: The concentrations of organic nitrates estimated from AMS measurements.

In the single-precursor systems, the presence of CO led to a pronounced decrease in organic nitrate concentrations, suggesting a reduced likelihood of RO_2 reacting with NO.

The relative contribution of CHON and fragment products increased in the presence of CO (Fig. 2 and 4). CHON products are mainly formed through the RO_2 + NO → $RONO_2$ channel, while fragment species originate from the fragmentation of RO radicals. Owing to the rapid reaction of RO_2 with NO and the high branching toward RO formation, reactions of RO_2 with NO represent an important source of RO radicals under NO_x conditions. These observations therefore indicate that, in the presence of CO, the contribution of the RO_2 + NO reactions decreased, but to a lesser extent than competing RO_2 termination pathways.

Consequently, the overall decrease in CHO mass exceeded the reduction in CHON mass, resulting in an apparent increase in the **normalised** contribution of CHON compounds.



Thermograms of CHO and CHON compounds.

Moreover, the thermograms derived from FIGAERO-CIMS showed that, in the single-precursor experiments, CHON compounds exhibited slightly lower T_{max} values in the presence of CO than in its absence, indicating higher volatility during thermal desorption.

In the revised manuscript, this behaviour is interpreted by considering both the concentrations of organic nitrates estimated from AMS measurements and the changes in the fractions of CHON and fragment products from CIMS measurements.

Line 520-532:

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 HO_2 formation, increasing the importance of the RO_2 + HO_2 pathway and thereby altering RO_2 reaction branching. In addition, lower NO concentrations were observed in the presence of CO (Fig. S5), consistent with enhanced conversion of NO to NO_2 via the HO_2 + NO reaction. The increase in HO_2 and decrease in NO reduced the likelihood of RO_2 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 RO_2 + NO → $RONO_2$ pathway, and fragment species originate from the fragmentation of RO radicals (Atkinson, 2000; Ziemann and Atkinson, 2012). Owing to the rapid reaction of RO_2 with NO and the high branching towards RO formation, reactions of RO_2 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 RO_2 + NO reactions decreased, but to a lesser extent than competing RO_2 termination pathways.***

Line 548-550:

Overall, in the single-precursor systems, CO reduced the contributions of both RO_2 + RO_2 and RO_2 + NO reactions. ***However, reactions of RO_2 with NO decreased to a lesser extent than competing RO_2 termination pathways****, and the reduction in RO_2 + RO_2 termination was more pronounced for longer-chain accretion products than for shorter-chain ones.*

Considering the FIGAERO-CIMS can result in the degradation of molecules on the filter, here the authors only present molecular formula measurements (D'Ambro et al, 2017). Do the authors believe there is any serious degradation taking place? No thermograms have been presented, so it is difficult to understand if these are likely intact molecules or fragments.

We thank the reviewer for pointing this out.

We acknowledge that minor thermal decomposition is present in the FIGAERO-CIMS measurements in this study. Several compounds with relatively low carbon numbers were found to exhibit comparatively high $\overline{OSc}$ values and elevated T_{max}. Nevertheless, 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. (Figure S2 has been added to the Supplementary Information)

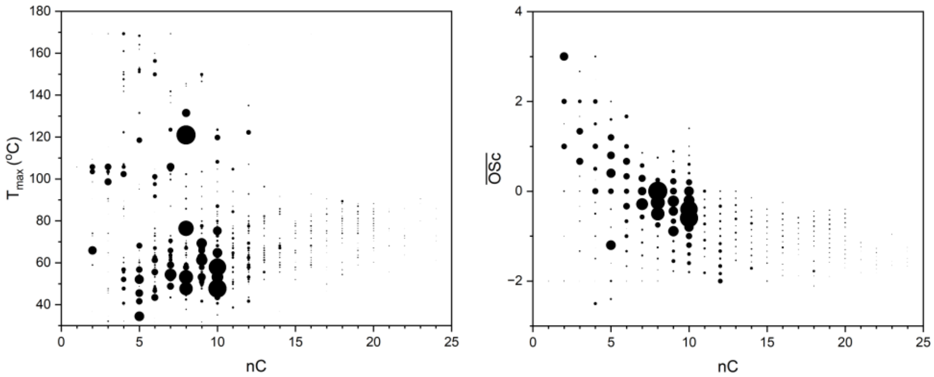


Figure S2. (Left panel) Maximum desorption temperature (T_{max}) against carbon number (nC) and (right panel) average carbon oxidation states ($\overline{OSc}$) against nC for all the particle-phase products for α-pinene system. The marker size is proportional to the signal intensity.

Line 253-257:

*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.*

Minor comments:

Lines 50-62: There is also rich literature about mixtures of VOCs and their impact on new particle formation.

We thank the reviewer for this suggestion.

We agree that many studies have investigated the SOA formation from the multi-precursor systems. The original sentence has been revised to clarify that many chamber studies are conducted under simplified conditions or with a single SOA precursor, and corresponding modifications have also been made in the Abstract. We have also added a statement noting that an increasing number of studies have focused on multi-precursor systems.

Line 13-15:

Secondary organic aerosol (SOA) formation is strongly influenced by atmospheric conditions. Achieving atmospheric relevance in chamber experiments is essential for understanding and predicting the impacts of SOA on air quality and climate. However, many chamber studies are conducted under simplified conditions or with a single SOA precursor.

Line 36-41:

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 conditions or with a single SOA precursor, which may introduce uncertainties when extrapolating these results to atmospheric models (Kenagy et al., 2024; Shrivastava et al., 2017; Tsigaridis et al., 2014).

Line 53:

An increasing number of studies have focused on mixtures of multiple precursors.

Line 71-73: I understand this is a statement from the Baker paper, but it is simply not true as it stands. The SOA yield of a mixture with a dominant RO2 + RO2 pathway is the SOA yield for those specific conditions. The unspoken aspect of this sentence is that the HO2/RO2 ratio is not environmentally relevant for RO2 + RO2 dominant studies, meaning using a RO2 + RO2 dominant yield when the reality is that the RO2 + HO2 pathway is dominant would create an overestimate of the yields in whatever model you choose to use.

We thank the reviewer for this suggestion.

We have added a discussion comparing RO_2 reaction pathways under atmospherically relevant and laboratory conditions, emphasising that the relatively low HO_2/RO_2 ratios typically present in laboratory experiments can lead to an overestimation of SOA particle mass yields.

Line 69-80:

In laboratory 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 HO_2/RO_2 ratios compared with atmospheric conditions, favouring RO_2 + RO_2 reactions over RO_2 + HO_2 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 produce HO_2 radicals, thereby shifting the HO_2/RO_2 ratio and increasing the importance of the RO_2 termination via HO_2 (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, while the amounts of HOMs were suppressed by factors of 4 to 5.* ***Baker et al. (2024) further demonstrated that, under constant OH conditions, the addition of CO increased the HO_2/RO_2 ratio from approximately 1/100 to about 1/1, leading to a ~ 60 % reduction in the abundance of HOM-accretion products and a ~ 30 % decrease in the SOA formation potential of HOMs***.

Lines 108 – 110: What is the total spectrum of UV light look like? What is the jNO2? Who is the supplier for the UVC lamp? (since the lights are slightly different with the addition of the 254nm lights compared to the Shao et al. publication)

We apologise that the spectrum of the UVC lamp was not measured in this study.

The actinic flux spectrum of the built-in light sources (two xenon arc lamps and a series of halogen lamps) in the MAC is shown in Shao et al. (2022). An additional UVC lamp was installed to promote OH radical production, with more than 90 % of its length masked to prevent excessive irradiation.

The J_{NO_2} was 1.38×10^{-3} s^{-1}.

The supplier for the UVC lamp is Philips (TUV 130W XPT SE UNP/20).

Line 172-177:

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 NO_2 (J_{NO_2}) was 1.38×10^{-3} s^{-1}. To promote OH radical production, an additional UVC lamp (TUV 130W XPT SE UNP/20, Philips) was installed, with more than 90 % of its length masked to prevent excessive irradiation.

Line 110-112: were the injections performed with a syringe?

Yes, the injections were performed using a syringe. The required volume of liquid precursor was calculated based on its density, the target concentration, and the chamber volume. The liquid sample was then injected into a pre-heated VOC bulb using a syringe and subsequently introduced into the chamber by flushing with N_2.

Line 177-179:

*The liquid precursors (α-pinene, analytical standard, Sigma-Aldrich; n-dodecane, anhydrous, ≥ 99.0 %, Sigma-Aldrich) were initially injected **via syringe** into a heated glass bulb to facilitate vaporisation, after which the vapours were carried into the chamber by electronic capture device-grade nitrogen (ECD N_2).*

Lines 122 – 125: What was the order of the seed injection and humidification? At the moment it is unclear to me what the phase state of the seed is.

Compressed air was passed through the humidifier when flushing the seed into the chamber, hence ensuring the deliquescence of the seed as they were generated.

Line 182-186:

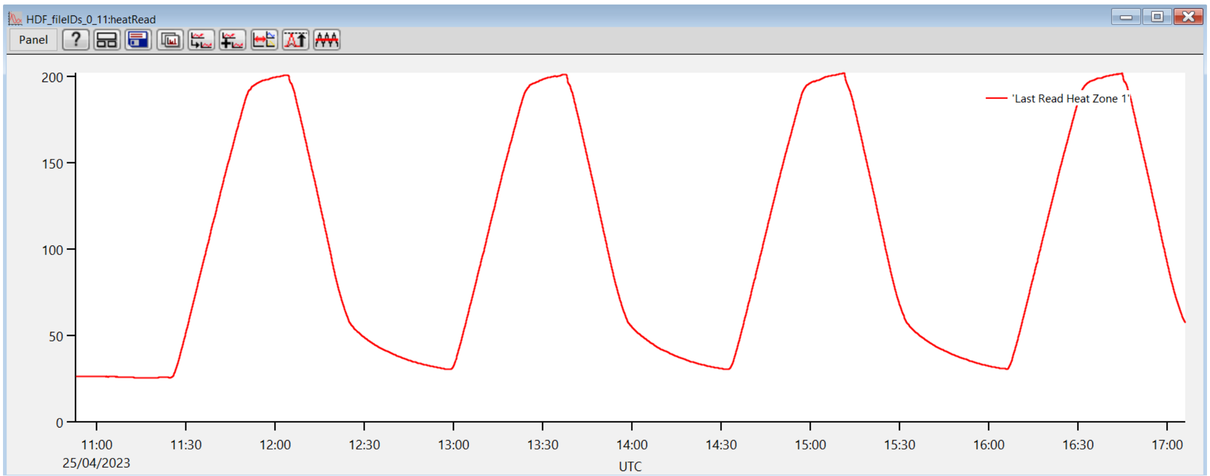
*Seed particles with a mass concentration of 40.2 ± 8.0 µg m^{-3} were generated by nebulising aqueous ammonium sulfate solutions ($(NH_4)_2SO_4$, ACS reagent, ≥ 99.0 %, Sigma-Aldrich) using an aerosol generator (ATM 230, Topas). **During seed injection, the carrier air was passed through the humidifier, 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).*

Lines 169-181: Is it wise to heat the PTFE filter over 260 °C? There can be degradation of PTFE and the release of fumes from the filter above that temperature. (Sajid et al. 2017)

We thank the reviewer for pointing this out.

The temperature of 310 °C refers to the set value of the heating unit. As shown in the figure below, the actual temperature experienced by the PTFE filter did not exceed 200 °C throughout the desorption process.

We have corrected the temperature reported in the manuscript and added a clarification that the filters were pre-heated to 200 °C to remove potential contaminants.



Line 231-239:

(vi) 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 N_2 for 0.5 min every 4.5 min to obtain the gas-phase instrument background signal.

*(vii) 25 min of temperature-programmed thermal desorption of the collected particles, with the temperature ramped from ambient to **200** °C.*

*(viii) 15 min of isothermal soaking at **200** °C.*

*(ix) 20 min of cooling from **200** °C to ambient temperature.*

(x) 2 min of N_2 flushing to clean the instrument.

Section 2.2: how was OH radical concentration determined in Figure S5? I don't see something in the methods section that describes this, and with the presence of O3 does this complicate the determination of O3 when using aPinene as an OH tracer? I see this is mentioned briefly in section 4.1, but it warrants a clear explanation in the methods section. Since this is a batch mode experiment, how does dilution in the chamber impact the depletion of CO? Why is dodecane not included in mixture of Figure S5?

We respond to the reviewer's comments point by point below.

(1) How was OH radical concentration determined in Figure S5?

OH concentrations were estimated from the evolution of O_3 and the consumption of precursors, or alternatively, from the depletion of CO.

Based on the consumption of α-pinene or n-dodecane:

$$[OH] = \frac{\frac{[VOC]_i - [VOC]_{i+1}}{\Delta t} - k_{VOC+O_3}[VOC]_i[O_3]}{k_{VOC+OH}[VOC]_i}$$

Based on the decay of CO:

$$[OH] = \frac{[CO]_i - [CO]_{i+1}}{k_{CO+OH}[CO]_i \Delta t}$$

These equations have been added to the Supplementary Information.

(2) With the presence of O3 does this complicate the determination of O3 when using aPinene as an OH tracer?

No. When deriving OH radical concentrations using α-pinene as a tracer, the loss of α-pinene via ozonolysis was explicitly included in the calculation. As a result, the contribution of O_3 chemistry was accounted for in the calculated OH concentrations.

No action

(3) Since this is a batch mode experiment, how does dilution in the chamber impact the depletion of CO?

The upper and lower frames of the chamber can move freely, allowing the chamber volume to expand or collapse when sample air is extracted. Therefore, the contents of the chamber are not diluted over time and such processes do not influence the depletion of CO.

No action

(4) Why is dodecane not included in mixture of Figure S5?

We apologise for the ambiguity in the original figure. As the n-dodecane concentration was not quantified, we preferred to present OH concentrations estimated based on α-pinene and CO for the mixed-precursor system. In the revised figure, we have now additionally included the OH concentrations estimated from the decay of n-dodecane for completeness. The OH concentrations derived from n-dodecane show good agreement with those calculated from α-pinene and CO.

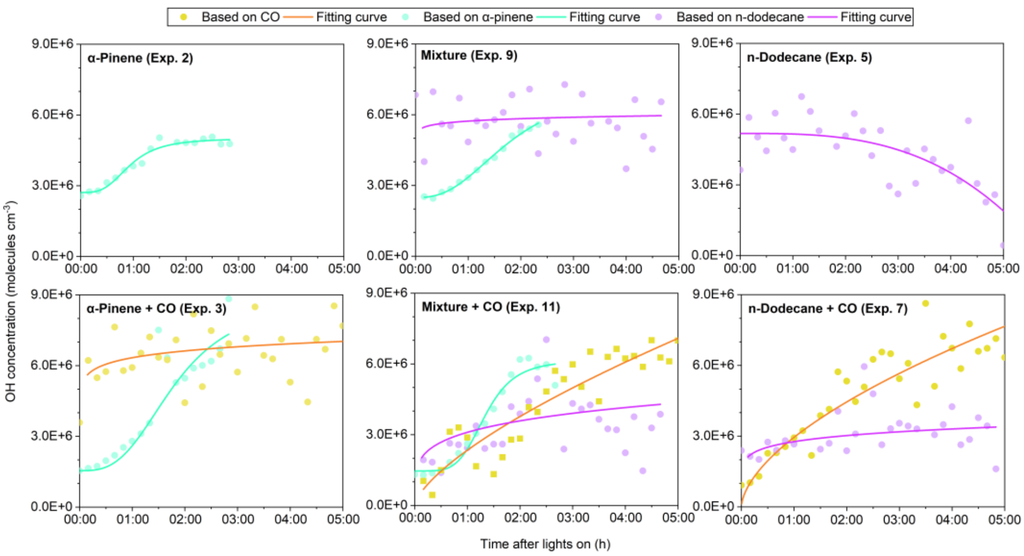


Figure S6: Estimated OH concentrations derived from the decay of precursors or CO. Fitting curves are shown as a visual guide. Data are from representative experiments.

Section 2.3.2: Is the VOCUS run with a GC column? If so please provide the relevant details. I suspect that there is a GC column because of the mention of a chromatography cycle on line 198.

We thank the reviewer for noting this point. The VOCUS was not operated with a GC column in this study. The reference to a "chromatography cycle" was a wording error and has been corrected to "sampling" in the revised manuscript.

Line 268-269:

Measurements were made on a 5 min cycle, consisting of 4 min of ***<u>sampling</u>*** *followed by 1 min of instrumental background.*

Section 2, what types of blank measurements were performed with the chamber?

Chamber background measurements were conducted weekly. All components (SOA precursors, seed particles, CO, and NO_x) were injected into the chamber under the same experimental conditions as the regular experiments, while the chamber was kept in the dark. CIMS data obtained during these background measurements were subtracted from both the gas- and particle-phase data acquired during the "experiment" phase.

Line 243-246:

To account for background species in the chamber, background measurements were conducted weekly. 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 data acquired during the "experiment" phase.

Lines 202-204: how did you verify that the injected concentrations are what you think they were?

The injection approach used in this study is reliable. The required volume of each precursor was calculated based on its density, the target concentration, and the chamber volume. Quantitative measurements of α-pinene confirm the reliability of this approach, as the injected concentrations deviated from the target values by less than 25% in the majority of experiments.

Moreover, this study focuses on the relative differences in SOA yields between the CO-present and CO-absent conditions. Therefore, any minor deviations in the absolute injected concentrations are unlikely to substantially affect the conclusions.

No action

Lines 204-205, what fragments were used with this method?

Fragment ions originating from *n*-dodecane generally exhibit the formula $C_nH_{2n+1}^+$. $C_{10}H_{21}^+$ fragment ion was used to infer the relative consumption of n-dodecane.

Line 272-275:

Therefore, alternative approaches were adopted for its quantification: (i) the initial concentrations were taken as the 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 temporal evolution of the ***$C_{10}H_{21}^+$*** *fragment ion (Fig. S4).*

Lines 205 – 206: were calibration performed similar to Figure S2 to verify the robustness of using C10H21+

No, calibration was not performed similar to α-pinene because the absence of an n-dodecane calibration standard.

We estimated the expected n-dodecane concentration using the OH concentration derived from CO decay, and this estimate was compared with the measured $C_{10}H_{21}^+$ signal (Fig. S4). As shown in this figure, the predicted and measured values agree well during the first three hours of reaction, whereas deviations occur at later times, likely due to interference from other oxidation products or fragments. The SOA particle mass yields of n-dodecane and the mixture may be overestimated by up to ~30 % in this study. Nevertheless, this uncertainty does not affect the overall trends and relative differences in yields.

We have clarified this limitation in the manuscript.

Line 275-277:

However, interference from other oxidation products or fragments cannot be fully excluded and may have led to an overestimation of SOA particle mass yields. Nevertheless, this uncertainty is unlikely to affect the overall trends or relative differences in yields.

Section 2.3.3: was a dryer used with the AMS? If not how was it verified that the collection efficiency was the same between the experiment and the calibration? I ask because there was likely different RH conditions between the experiment and the calibration.

Yes, a dryer was installed upstream of the AMS inlet.

No action

Figure 1: because of the presence of O3 what is the difference in the OH vs O3 reactivity in the different experiments? The caption should provide information about what fragments mean. Also, how does the OH produced by aPinene ozonolysis impact the iso-reactivity calculations?

We respond to the reviewer's comments point by point below.

(1) because of the presence of O3 what is the difference in the OH vs O3 reactivity in the different experiments?

The OH and O_3 reactivities are defined by the following equations:

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

$$O_3 \text{ reactivity } (s^{-1}) = \sum C_{precursor,i} \times k_{O_3,i}$$

n-Dodecane does not react with O_3; therefore, its O_3 reactivity is zero. For α-pinene, k_{O_3} (9.6×10^{-17} cm^3 molecule^{-1} s^{-1}) is much smaller than k_{OH} (5.33×10^{-11} cm^3 molecule^{-1} s^{-1}), so its O_3 reactivity is also very low relative to its OH reactivity and can be approximated as zero. Consequently, the discussion here mainly focuses on differences in OH reactivity.

O_3 can influence precursor decay as well as the formation of secondary oxidants, thereby affecting the OH reactivity.

At the beginning of the reaction, owing to the iso-reactivity condition, all systems exhibited comparable reactivity. As the reaction proceeded, differences emerged due to changes in precursor concentrations. Because α-pinene decayed faster in normalised terms than *n*-dodecane, the reactivity over the course of the experiment followed the order: n-dodecane > mixture > α-pinene.

Line 461-472:

Under idealised iso-reactivity conditions, all systems would exhibit comparable initial OH reactivity, and in the mixture each precursor molecule would initially have an equal probability of reacting with OH. ***In practice, however, O₃ also contributed to precursor oxidation, and the differing reactivities of individual precursors towards O₃ 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 O_3 to its decay was not negligible. As shown in Fig. S12, the relative contributions of these oxidants evolved over time, with the role of O_3 generally becoming more important as the reaction proceeded. In the α-pinene single-precursor system, on average approximately 80 % of α-pinene decay was attributable to OH oxidation, while the remaining ~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.

(2) Also, how does the OH produced by aPinene ozonolysis impact the iso-reactivity calculations?

OH reactivity is defined as the sum of the products of the concentrations of each SOA precursor and their reaction rate coefficients with OH.

The calculation of iso-reactivity does not involve the OH concentration and is therefore not affected by OH produced from α-pinene ozonolysis.

No action

(Continuing with Figure S12) In Figure S12, it is not clear if each bar corresponds to the integrated OH/O3 reactivity or is it for that specific unit time? The y-axis label should be changed, at the moment it appears to indicate a ratio of OH / O3, which isn't what the figure is showing.

We thank the reviewer for this suggestion and apologise for a minor error in the calculation of the fractional contributions shown in the original version of Fig. S11. This has now been corrected in the revised figure (now Fig. S12), and the correction does not affect the overall interpretation of the results.

The pink and purple portions of each bar represent the fractional contributions of ozonolysis and OH oxidation, respectively, to α-pinene decay. These contributions are calculated based on the relative magnitudes of $k_{VOC+O_3}[VOC]_i[O_3]$ and $k_{VOC+OH}[VOC]_i[OH]$.

Owing to differences in the time resolution of the instruments, all values were averaged over 10-min intervals.

The y-axis label has been revised to "Fractional contribution to α-pinene oxidation" to clarify the meaning of the plotted values.

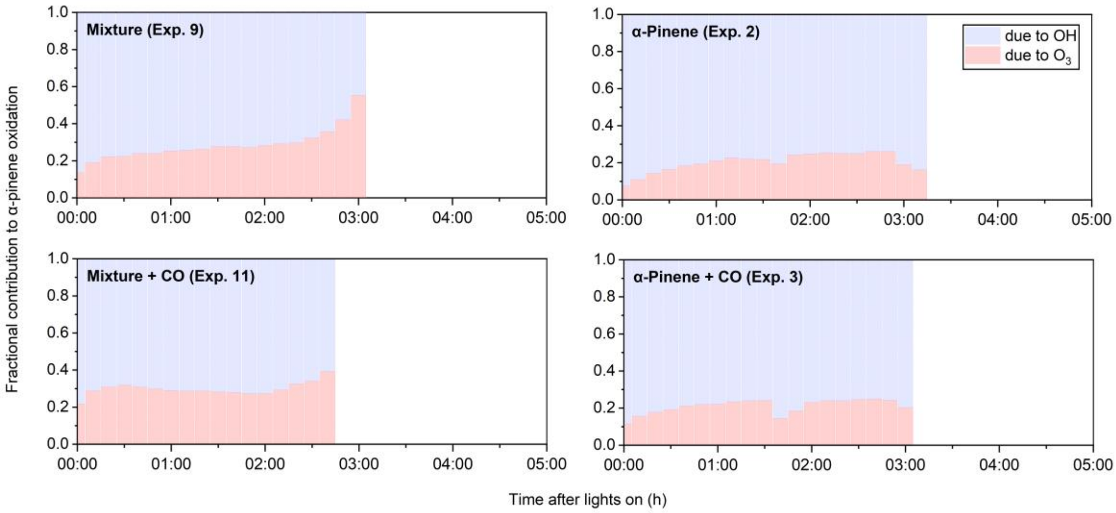


Figure S12: Relative contributions of O₃ and OH to α-pinene oxidation. These contributions are calculated based on the relative magnitudes of $k_{VOC+O_3}[VOC]_i[O_3]$ and $k_{VOC+OH}[VOC]_i[OH]$. Data are from representative experiments.

Line 465-467: This doesn't appear to be true for the dodecane case because the OH never 'recovered'.

We thank the reviewer for pointing this out and apologise for the ambiguity in the original manuscript.

In the n-dodecane system without CO, the OH concentrations gradually decreased as the reaction proceeded. This decline likely reflects less efficient OH regeneration.

Line 491-501:

*The addition of CO further perturbed the photochemical processes, altering both oxidant levels and precursor decay rates. CO can consume OH radicals, preventing their reaction with SOA precursors (McFiggans et al., 2019). 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 × 10^6 molecules cm^{-3} (Fig. 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 HO_2 formation. Subsequent HO_2 + NO reactions regenerated OH, thereby increasing radical propagation efficiency. **In contrast, in the absence of CO, although O_3 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 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.*

Line 470 - 475: I do not understand this discussion. It would appear to be true at face value if isoreactivity was achieved, but it clearly wasn't perfectly achieved in Figure S5. So aren't the changes in OH concentrations purely able to describe these results?

We respond to the reviewer's comments point by point below.

(1) It would appear to be true at face value if isoreactivity was achieved, but it clearly wasn't perfectly achieved in Figure S5

We thank the reviewer for raising this important point.

Iso-reactivity is defined by precursor concentrations and their respective reaction rate coefficients with OH, and is independent of the OH concentration itself. Therefore, the OH concentrations shown in Fig. S5 cannot be used to determine whether iso-reactivity was achieved. In addition, iso-reactivity ensures that different precursors have the same initial potential to react with OH; however, it does not guarantee identical oxidative conditions are maintained throughout the entire experiment.

We have clarified this point in the revised manuscript.

Line 461-465:

Under idealised iso-reactivity conditions, all systems would exhibit comparable initial OH reactivity, and in the mixture each precursor molecule would initially have an equal probability of reacting with OH. In practice, however, O_3 also contributed to precursor oxidation, and the differing reactivities of individual precursors towards O_3 can modify the precursor decay and secondary oxidant formation, thereby influencing the reactivity.

(2) So aren't the changes in OH concentrations purely able to describe these results?

We thank the reviewer for raising this important point.

These results can be described by the changes in OH and O_3 concentration.

In addition, we have revised our previous statement regarding the OH scavenging effect of CO in the α-pinene system. In the original manuscript, we stated that "the effect of OH scavenging on the decay of α-pinene was limited." We now clarify that an OH scavenging effect does occur, as evidenced by the reduced α-pinene decay rate during the early stage of the reaction. However, this initial suppression is later compensated by the regeneration of OH and the concurrent increase in O_3 concentration, such that the overall extent of α-pinene consumption is not substantially reduced. Accordingly, we now state that "CO did not significantly affect the overall extent of α-pinene consumption."

Line 503-509:

Variations in oxidant concentrations contributed to changes in SOA precursor decay rates (Fig. 1b). In the absence of CO, α-pinene was almost completely consumed within 3 h. In the presence of CO, its decay was initially suppressed; however, after approximately 2 h the decay rate increased, likely due to secondary OH production and elevated O_3 concentrations. Such that α-pinene was nevertheless nearly fully consumed within 3 h. As a result, CO did not significantly 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, leaving a substantial fraction unreacted by the end of the experiment.

Figure 5 and section 4.2: I am a bit confused by the purported ~50% difference in the yield with vs. without CO for aPinene. Based on Figure 5 (left panel) the yield should be effectively the same with vs. without CO. Can the authors comment on the apparent discrepancy in the text and Table 1 with the Figure?

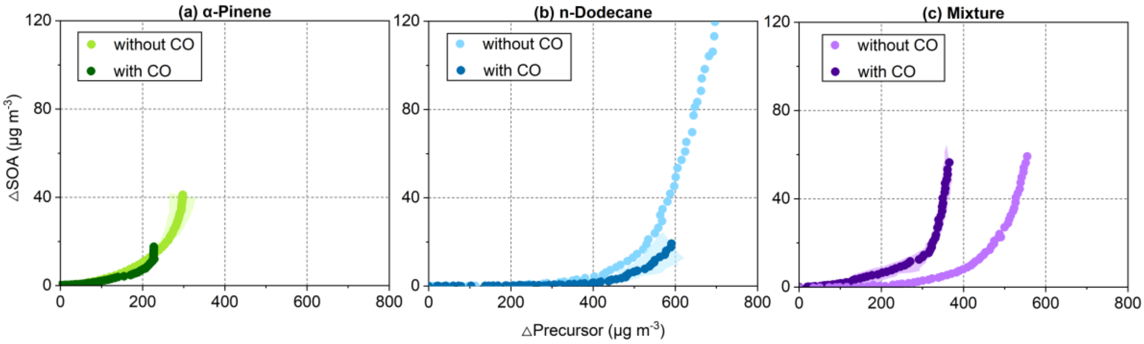


Figure 6: Growth curves of SOA particles for (a) α-pinene, (b) n-dodecane, and (c) mixture experiments, defined as the ratio of SOA particle mass concentration to consumed precursor mass. Shaded areas represent the range between replicate experiments.

We thank the reviewer for raising this important point and apologise that in the original figure the Δprecursor for α-pinene under CO-absent conditions was slightly shifted towards higher values. This has now been corrected, and the correction does not affect any of the results or conclusions.

The yields reported in the text refer to the <u>overall yield</u>, defined as $\triangle SOA_{max}/\triangle precursor_{max}$.

In the presence of CO, $\triangle SOA_{max}$ was approximately 18 μg m^{-3}, $\triangle precursor_{max}$ was approximately 230 μg m^{-3}, corresponding to an SOA yield of ~ 0.08.
In the absence of CO, $\triangle SOA_{max}$ was approximately 41 μg m^{-3}, $\triangle precursor_{max}$ was approximately 297 μg m^{-3}, corresponding to an SOA yield of ~0.14.

Compared with the CO-absence case, the SOA particle mass yield in the presence of CO was therefore reduced by approximately 43%.

To address this potential confusion, we have revised the corresponding descriptions in both the Methodology and the yield discussion.

Line 296-298:

*In this study, the SOA particle mass yield refers to the **<u>overall yield</u>**, calculated from the total SOA formed and the precursor consumed at the end of the experiment.*

Line 584-597:

Figure 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 system exhibited a longer induction period, 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. These behaviours suggest a distinct influence of CO on the SOA particle mass yields across different systems.*

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.*

Lines 543 -545: the way the percentages are talked about are misleading. Perhaps the authors should talk about the percentage reduction of specific molecular cases e.g. 2% reduction for C10H14Ox is a reduction from ~11% à 9% (Figure 6), which is a reduction of ~20%

We thank the reviewer for this suggestion. We agree that the original description of the percentages could be misleading.

We have revised the text to describe the fractions under CO-absent and CO-present conditions separately, without explicitly discussing the percentage reduction.

In addition, to improve the flow of the manuscript, these descriptions and Fig. 6 (now Fig. 3) have been moved to the Results section. As the variation in the fraction of $C_{12}H_{22}O_n$ was not relevant to the discussion of the results, the corresponding data has been removed.

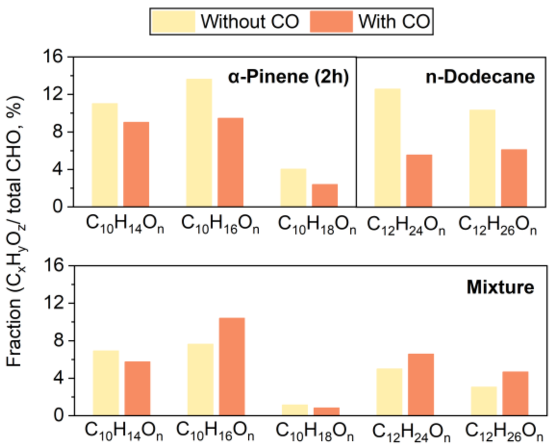


Figure 3: Relative contributions of $C_{10}H_{14}O_n$, $C_{10}H_{16}O_n$, $C_{10}H_{18}O_n$, $C_{12}H_{24}O_n$, and $C_{12}H_{26}O_n$ to the CHO group in the α-pinene, n-dodecane, and mixture systems in the absence and presence of CO.

Line 359-361:

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.

Line 406-408:

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.

Line 446-449:

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.

Additional revisions:

1. **The first paragraph of the Introduction has been shortened**

Line 26-32:

Secondary organic aerosol (SOA) constitutes a substantial fraction of ambient aerosol and has significant impacts on air quality, climate and human health. It is formed through the oxidation of gas-phase organic compounds 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). These processes are complex and strongly influenced by atmospheric conditions (Hallquist et al., 2009; Kroll and Seinfeld, 2008; Xu et al., 2015). Despite extensive research, achieving a comprehensive understanding and accurate prediction of SOA formation remain challenging (Kenagy et al., 2024; Shrivastava et al., 2017).

2. **The discussion of the influence of NO_x on SOA formation has been revised (Introduction)**

Line 81-94:

In the ambient atmosphere, high concentrations of CO are often co-emitted with other anthropogenic pollutants, such as NO_x. NO_x can react with RO_x radicals (RO_x = OH + HO_2 + RO_2), thereby influencing RO_x cycling and, consequently, the formation of SOA and O_3 (Chen et al., 2022; Clapp and Jenkin, 2001; Pusede et al., 2015). RO_2 radicals react rapidly with NO to form alkoxy radicals (RO) or organic nitrates (Atkinson, 2000; Chen et al., 2022; Kang et al., 2025; Ziemann and Atkinson, 2012). RO_2 can also react with NO_2 to form peroxynitrates; 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 higher NO_x concentrations reduced the formation of gas-phase α-pinene HOM-accretion products, leading to a lower SOA particle mass yield. When CO and NOx coexist, oxidant levels and RO_2 reaction pathways are influenced by multiple interacting processes. These interactions contribute to the complexity of the ambient atmosphere. It is therefore important to investigate SOA formation in systems containing multiple trace gases.

3. **The final paragraph of the Introduction has been revised**

Line 96-105:

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 SOA particle mass yields and chemical composition *from α-pinene, 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 ($C_{10}H_{16}$) 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 ($C_{12}H_{26}$) serves as a proxy for anthropogenic intermediate-volatility organic compounds (IVOCs), being widely present in fuels and emitted primarily as a non-combusted hydrocarbon (Zhao et al., 2015). Experiments were conducted in the Manchester Aerosol Chamber (MAC), using online instruments to characterise particle- and gas-phase compounds.*

4. **The description of the FIGAERO cycle was moved from Sect. 2.2 (formerly 2.1) to Sect. 2.4.1 (formerly 2.3.1)**

Line 240-241:

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 (i), corresponding to the completion of particle sampling (Fig. S1).

5. **The description of the advantages of the Vocus PTR-ToF-MS in Sect. 2.3.2 (formerly 2.2.2) was revised**

Line 259-264:

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) consisting of a glass tube that is mounted inside a radio frequency (RF) quadrupole, with an axial electric field applied along the 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).

6. **Parts of the chemical composition description were revised**

Line 351-355:

Within the CHO group, fragments contributed more than 60 %, with a substantial proportion distributed in the C_7–C_9 range (Fig. S11). Monomers accounted for 36 % and 31 % in the absence and presence of CO, 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., $C_{10}H_{15}NO_{7–8}$) (Fig. 2a).

Line 391-393:

In the absence of CO, the most abundant 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.

Line 397-402:

Within the CHON group, 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 $C_{12}H_{23}NO_7$) (Fig. 4a). However, a few exceptions were observed. For example, a series of highly oxygenated C_{13} CHO compounds, such as $C_{13}H_{24}O_9$ and $C_{13}H_{22}O_{10}$, accounted for a higher fraction in the presence of CO, whereas $C_{12}H_{25}NO_5$ accounted for a higher fraction in the absence of CO. Fragments accounted for 30 % and 37 % in the absence and presence of CO, respectively.

Line 434-436:

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.

Line 439-444:

Fragments dominated under both conditions and accounted for 40% of the total signal in each case. Accretion products accounted for 12 % and 11 % in the absence and presence of CO, respectively. Except for C_{15} species, the fractions of C_{13}–C_{24} products decreased slightly in the presence of CO. In addition, the presence of CO resulted in an increased proportion of C_{12} CHO compounds (e.g., $C_{12}H_{26}O_4$ and $C_{12}H_{24}O_5$), and a reduced proportion of C_{10} CHON compounds (e.g., $C_{10}H_{15}NO_7$) (Fig. 5a). Overall, changes in carbon number distribution were less pronounced in the mixed-precursor system than in the single-precursor systems (Fig. S11).

7. **The presentation of product hydrogen atom distributions in Sects. 3.1.2, 3.2.2, and 3.3.2 (formerly Line 294-299, 346-353, and 398-403), as well as the corresponding figure (formerly Fig. S11) in the Supplementary Information, were removed**

8. **The discussion of precursor/NO_x conditions in Sect. 4.1 was revised**

Line 474-483:

The precursor/NO_x ratio is important for determining the chemical regime of O_3 and SOA formation (Chen et al., 2022). 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 O_3 and NO_x differed substantially between the single- and mixed-precursor systems (Figs. 1a and S5). In the α-pinene system, O_3 concentrations peaked after approximately two hours of reaction and subsequently declined, while NO_x levels stabilised. By this point, over 80 % of α-pinene had been consumed, and the SOA particle formation rate began to decline (Figs. 1b–c). These trends may indicate a reduction in RO_2 + NO reactions, which would slow the conversion of NO to NO_2 and thereby limit photochemical O_3 production. In contrast, in the n-dodecane and mixture systems, over 50 % of n-dodecane was still unreacted after two hours, and the SOA particle formation rate continued to increase (Figs. 1b–c), indicating that RO_2 + NO reactions remained active. This sustained reactivity enabled continuous conversion of NO to NO_2 and enhanced photochemical O_3 production.

9. **The x-axis labels in Figures 2a, 4a, and 5a have been revised to include the unit, now shown as "Molecular mass (Da)".**

10. **The titles of Sections 3.1.1, 3.2.1, and 3.3.1 have been revised to "SOA particle mass yields".**

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