Section S1. General unimolecular and bimolecular reactions of RO$_2$•

Autoxidation has been recently identified as the key step leading to rapid formation of highly oxygenated organic molecules (HOM) (11, 19), via successive intramolecular hydrogen shift and O$_2$ addition, as shown in Fig. S1.

![Autoxidation Diagram](image)

**Fig. S1. Autoxidation steps.** Successive intramolecular hydrogen shift and O$_2$-addition to form highly oxygenated organic molecules.

Both unimolecular and bimolecular reactions (18, 37, 78) of RO$_2$• can produce closed-shell products maintaining the C atom number, while gaining one more hydrogen atom, preserving hydrogen atom, or losing one hydrogen atom, as shown below (Fig. S2).
Fig. S2. Termination reactions of \( \text{C}_2\text{H}_y\text{O}_x^\cdot \) peroxy radical to produce closed-shell products maintaining the number of C-atoms. Bimolecular reactions of individual peroxy radical \( \text{C}_2\text{H}_y\text{O}_x^\cdot \) with (A1) \( \text{RO}_2^\cdot \) and (A2) \( \text{HO}_2^\cdot \) lead to closed-shell products gaining one more hydrogen atom as alcohols \( \text{C}_2\text{H}_{y+1}\text{O}_{x-1} \) (ROH) or hydroperoxides \( \text{C}_2\text{H}_{y+1}\text{O}_x \) (ROOH). Organic nitrates \( \text{C}_2\text{H}_y\text{NO}_{x+1} \) (RONO \(_2\)) are closed-shell products that preserve the number of hydrogen atoms, formed from (B) bimolecular reactions of \( \text{C}_2\text{H}_y\text{O}_x^\cdot \) with NO. Closed-shell products losing one hydrogen atom are \( \text{C}_2\text{H}_{y-1}\text{O}_{x-1} \), carbonyls (\( \text{R}=\text{O} \)) formed from (C1) bimolecular reactions of \( \text{C}_2\text{H}_y\text{O}_x^\cdot \) with \( \text{RO}_2^\cdot \) and (C2) self-OH elimination of \( \text{C}_2\text{H}_y\text{O}_x^\cdot \), and epoxides formed from (C3) ring closure.
Section S2. Instrumentation & experimental overview

For gas-phase species, a set of instruments was applied, including a laser-induced fluorescence system (79) to measure concentrations of OH, HO2•, and RO2•, a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik, Austria) for concentrations of α-pinene, as well as a NOx analyzer (Eco Physcis TR480) and an O3 analyzer (Ansyco, model O341M). Their concentrations within the first 15 min reaction time are shown in Fig. S3. Note that concentrations of O3 are under the detection limit (detection limit of 1 ppb and a precision of 0.5 ppb) in both low and high NO experiment and thus cannot be seen in the figure. This low O3 concentrations also ensure that oxidation by OH radicals is overwhelming in our experiments. Further note that in the low NO experiment, the NOx analyzer encountered a technical problem. The NO concentration based on the average concentration in the three other experiments at the same conditions were provided (solid black markers in Fig. S3A), which show good agreement with the NO concentrations (grey line) in Fig. S3A derived from the established methods in the SAPHIR chamber by Rohrer et al. (52). For all the low NO experiments in SAPHIR, a typical background concentration before roof opening is 10-30 ppt NO, which is also included in the Master Chemical Mechanism (MCM) HOM modeling for α-pinene + OH shown in this study. Measurements in the other low NO experiments (solid black markers) and simulated calculations (grey lines) in Fig. S3A showed that NO concentrations increased from 0-30 ppt to ~100 ppt during the first 15 min reaction time in this study.

For the particles, the number and size distribution were measured using a Scanning Mobility Particle Sizer (SMPS, TSI, DMA 3081/CPC 3785), with total number concentrations and surface area concentrations shown in Fig. S3. In both low and high NO experiments, negligible particles were formed during the first 15 min reaction time, with total number concentrations of <40 cm⁻³ at low NO and <20 cm⁻³ at high NO.

The physical parameters including temperature, pressure, relative humidity (RH), and solar irradiation (photolysis frequencies of J values such as JNO2, JOD, JH2O2, and JHONO) were recorded throughout the chamber experimental runs.
Fig. S3. Overview of low NO (30 - ~100 ppt) and high NO (~20 ppb) experimental conditions. Concentrations of gas phase species (α-pinene, NO, and O₃), radicals (OH, HO₂•, and RO₂•), and particles (total number concentrations and total surface area concentrations) within the first 15 min reaction time of (A-C) low NO and (D-F) high NO experiments. Concentrations of O₃ are under the detection limit (detection limit of 1 ppb and a precision of 0.5 ppb) in both low and high NO experiment and thus cannot be seen in the figure. NO(*) in (A) low NO experiment was the average NO concentration of the other three experiments performed at the same conditions, as no direct data was available due to a technical problem of the NOX analyzer during this experiment. NO concentrations due to well-characterized emissions from the chamber wall of our SAPHIR chamber according to Rohrer et al. (52) are also shown (grey, denoted as NO (chamber)). All error bars in the figure represent one standard deviation.
Section S3. Calculations of carbonyls’ contribution to C10H16OX

According to the C10 closed-shell products from unimolecular and bimolecular reactions of the two C10-HOM-RO2• families (C10H15OX• and C10H17OX•, Fig. 1E in the main text and Fig. S2 in the Supplementary Materials), C10H16OX can be carbonyls (R=O) and epoxides from C10H17OX• peroxo radicals, as well as alcohols (ROH) and hydroperoxides (ROOH) from C10H15OX• peroxo radicals. Note that carbonyls and epoxides from C10H17OX• share the same elemental composition and cannot be separated in this study. According to literature and quantum chemical calculations, carbonyls are likely to dominate over epoxides, which thus will not affect the calculations here.

The quotient \( \frac{d[ROH]}{dt} + \frac{d[ROOH]}{dt} }{d[R=O]/dt} \) was used to calculate the contribution of C10H17OX•-related products to C10H16OX, as shown below:

\[
\frac{d[ROH]/dt + d[ROOH]/dt}{d[R=O]/dt} = \frac{\alpha k_{RO2+RO2}[RO2][RO2]^T + k_{RO2+HO2}[RO2][HO2]}{(1-\alpha)k_{RO2+RO2}[RO2]^T + k_{RO2+HO2}[HO2]}
\]

(Eq. S1)

where \([RO2]^T\) is the total concentration of RO2•, and \([HO2•]\) is the concentration of HO2• in the reaction system. Herein \(k_{RO2+RO2}\) and \(k_{RO2+HO2}\) are the rate coefficients of the bimolecular reactions of RO2• with RO2• and HO2•, and \(k_{RO2}\) is the rate coefficient of the unimolecular termination of RO2•. In reactions of RO2• + RO2•, \(\alpha\) represents the carbonyl yield and thus \(1-\alpha\) is the alcohol yield.

We assume the same \(k_{RO2+RO2}, \alpha, k_{RO2+HO2}, \text{ and } k_{RO2}\) for a certain C10H15OX•- and C10H17OX• pair. As a consequence, the ratios of \(\frac{d[ROH]/dt + d[ROOH]/dt}{d[R=O]/dt}\) for C10H15OX•-chemistry (Eq. S2) and C10H17OX•-chemistry (Eq. S3) are the same. By combining Eq. S2 and S3 we obtain Eq. S4 which allows for calculating \([R=O]\)%, the fractional contribution of the carbonyls produced from C10H17OX• to C10H16OX. Wall loss was neglected due to its minor effects on the concentrations of the products (<1%) and derived \([R=O]\)% values (<3%) during the first 15 min reaction time in this study.

\[
\frac{d[ROH]/dt + d[ROOH]/dt}{d[R=O]/dt} = \frac{d[C_{10}H_{16}O_x]}{d[C_{10}H_{16}O_x]_{R=0}} = \frac{d[C_{10}H_{16}O_x]}{d[C_{10}H_{16}O_x]_{R=0}}
\]

(Eq. S2)

\[
\frac{d[ROH]/dt + d[ROOH]/dt}{d[R=O]/dt} = \frac{d[C_{10}H_{16}O_x]}{d[C_{10}H_{14}O_x]_{R=0}} = \frac{d[C_{10}H_{16}O_x]_{R=0}[1-\alpha]}{d[C_{10}H_{14}O_x]}
\]

(Eq. S3)

\[
\frac{d[C_{10}H_{16}O_x]}{d[C_{10}H_{14}O_x]} = \frac{d[C_{10}H_{16}O_x]}{d[C_{10}H_{16}O_x]_{R=0}}
\]

(Eq. S4)

About 97% and 78% of C10H16OX were estimated to be carbonyls from C10H17OX• at low and high NO, respectively. Similar concentration ratios of carbonyl families (C10H14Ox/C10H16Ox) and organic nitrate families (C10H15NOx/C10H17NOx) are obtained, as shown in Fig. 1C, 1D in the...
main text. In C7-HOM, as discussed in Section S5 in the Supplementary Materials, C7H10OX can be carbonyls formed from C7H11Ox•, as well as alcohols and hydroperoxides from C7H9Ox•. Same concentration ratios of carbonyls (C7H8Ox/C7H10Ox) to that of organic nitrates (C7H8NOx/C7H11NOx) were used to separate carbonyls’ contribution to C7H10Ox.
Section S4. Uncertainties of HOM yield

The direct calibration method using HOM standards is not possible so far, mainly due to the difficulty to synthesize pure HOM and unknown chemical structures of many HOM. However, as discussed by Ehn et al. (11), the sensitivity of NO$_3^-$-CIMS to H$_2$SO$_4$ is similar to HOM, and thus the calibration coefficient of H$_2$SO$_4$ is commonly applied to HOM (11, 12, 21, 78). Effective deprotonation of H$_2$SO$_4$ leads to formation of clusters with NO$_3^-$ ions, with rates close to the kinetic collision limit. In this study, most of detected HOM are binding with NO$_3^-$ reagent ions, also near the collision limit as H$_2$SO$_4$. Combining the theoretical calculations (39, 40) and our previous experimental results (41) discussed here and in the main text, we conclude that the sensitivity of NO$_3^-$-CIMS to all HOM is similar to that of H$_2$SO$_4$ in this study and the calibration coefficient of H$_2$SO$_4$ can be applied to all HOM. If the HOM charge at rates lower than the collision limit, the calibration coefficient would be overestimated and the HOM concentrations derived using the calibration factor of H$_2$SO$_4$ thus constitute a lower limit with an uncertainty by a factor of 2 (58).

The peak intensities of H$_2$SO$_4$ can be converted to concentrations following Eq. S5.

$$[H_2SO_4] = C \times I$$  \hspace{1cm} (Eq. S5)

where [H$_2$SO$_4$] is the concentration of H$_2$SO$_4$ (molecule cm$^{-3}$), C is the calibration coefficient, and I is peak intensities in the unit of normalized count (nc), i.e. the peak area of H$_2$SO$_4$ divided by total signals. The detailed method deriving the calibration coefficient of H$_2$SO$_4$ can be found in Zhao et al. (76). Briefly, oxidation of SO$_2$ by OH was performed in the SAPHIR chamber to produce in-situ H$_2$SO$_4$, by injecting SO$_2$ (~15 ppb) in the chamber and opening the roof to produce OH radicals from the photolysis of HONO. Additional NO (~20 ppb) was added to enhance OH production. Following the reaction kinetics, concentrations of H$_2$SO$_4$ can be described as:

$$\frac{d[H_2SO_4]}{dt} = k \times [SO_2] \times [OH] - k_{wall\ loss} \times [H_2SO_4] - k_{dilution\ loss} \times [H_2SO_4]$$  \hspace{1cm} (Eq. S6)

where [H$_2$SO$_4$], [SO$_2$], and [OH] are the concentrations of H$_2$SO$_4$, SO$_2$, and OH (molecule cm$^{-3}$), respectively, k is the rate coefficient (1.1×10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, Atkinson et al. (80)) of the OH oxidation reaction of SO$_2$, and $k_{wall\ loss}$ and $k_{dilution\ loss}$ are the wall loss rate (~6.0×10$^{-4}$ s$^{-1}$, Zhao et al. (38)) and dilution loss rate (~1×10$^{-5}$ s$^{-1}$) of H$_2$SO$_4$, respectively. Combining Eq. S5 and Eq. S6, C can be obtained as:

$$C = \frac{k \times [SO_2] \times [OH]}{I_0 \times (k_{wall\ loss} + k_{dilution\ loss}) \times I}$$  \hspace{1cm} (Eq. S7)

where $I_0$ is the peak intensity at the reaction time zero. Based on the uncertainties on SO$_2$ concentration (~7%), OH concentration (~10%), I (~15%), k (Δlogk=±0.3), transmission efficiency (-0%/+14%), and sensitivity (-0%/+100%), the uncertainty of C was estimated to be -52%/+143%. Integrating the uncertainties of HOM peak intensity (~10%) and the α-pinene concentration (~15%), an uncertainty of HOM yield is estimated to be -55%/+144%, following equation 1 in the main text.
Moreover, HOM concentrations were corrected for wall loss and dilution. The value of $6 \times 10^{-4} \text{ s}^{-1}$ and $2.2 \times 10^{-3} \text{ s}^{-1}$ was respectively used for the wall loss correction $k_{\text{wall loss}}$ at low and high NO based on our previous study (38) and our recent updates for different conditions. Acting mixing due to a running fan in our high NO experiments leads to a larger wall loss rate. Although wall loss rates of less oxygenated compounds can change during an experiment (38), in this study, we focus on HOM and short reaction times (0-15 min), therefore HOM yields are not expected to be sensitive to the wall loss rate. Sensitivity analyses showed that variation of the wall loss rate from +100% to -50% led to changes in the molar HOM yield between +28.2% and -13.9% in the low NO experiment and between +76.0% and -36.2% in the high NO experiment. The dilution rate $k_{\text{dilution loss}}$ was derived from a constant dilution flow rate of the chamber, leading to a value of $1.5 \times 10^{-5} \text{ s}^{-1}$. 
Fig. S4. Average mass spectrum of identified HOM from OH oxidation of α-pinene during the first 15 min reaction time at (A) low NO (30 - ~100 ppt) and (B) high NO (~20 ppb), with a resolving power $m/z/\Delta m/z$ of ~3000. Identified HOM are detected as clusters with reagent ion $^{15}\text{NO}_3^-$. Note that background signals (-10 - 0 min reaction time) were subtracted.
Fig. S5. Examples of high-resolution peak fittings of $C_{10}$H$_{15}$O$_x$• and $C_{10}$H$_{17}$O$_x$• related $C_{10}$- and $C_{20}$-HOM. Assignment of representative peroxy radicals, carbonyls, organic nitrates, and accretion products of $C_{10}$H$_{15}$O$_x$• (red) and $C_{10}$H$_{17}$O$_x$• (blue) related $C_{10}$- and $C_{20}$-HOM in high resolution spectra at (A-F and M-O) low NO (30 - ~100 ppt) and (G-L) high NO (~2 ppb).
Fig. S6. Relative abundances of individual products during the first 15 min reaction time at low NO (30 - ~100 ppt, solid bars) and high NO (~20 ppb, patterned bars). Left-hand side: (A) C_{10}H_{15}O• (peroxy radicals, X=6-14) and its related products of (B) C_{10}H_{16}O• (carbonyls, X=6-16) and (C) C_{10}H_{15}NO• (organic nitrates, X=6-15). Right-hand side: (D) C_{10}H_{17}O• (peroxy radicals, X=7-14) and its related products of (E) C_{10}H_{16}O• (carbonyls, X=6-16) and (F) C_{10}H_{17}NO• (organic nitrates, X=6-14). C_{10}H_{15}O•-related C_{10}-HOM are denoted in red while C_{10}H_{15}O•-related C_{10}-HOM are in blue. All products are normalized to the signals of C_{10}H_{14}O_{10}, the most abundant individual product at both low and high NO. Carbonyls C_{10}H_{16}O• were estimated following Section S3.
Fig. S7. Bimolecular loss fate of peroxo radicals. Contribution of RO$_2^•$ loss via the reaction with HO$_2$ (red), NO (blue), and RO$_2^•$ (yellow) to total RO$_2^•$ loss during the first 15 min reaction time at (A) low NO (30 - ~100 ppt) and (B) high NO (~20 ppb), based on measured data. The loss rate of RO$_2^•+$ RO$_2^•$ was estimated using a reaction coefficient of 2.5$x10^{-13}$ molecule$^{-1}$ cm$^3$ s$^{-1}$ (82).
Fig. S8. Time series of lumped product families and representative individual products. Normalized signals of $\text{C}_{10}\text{H}_{15}\text{O}_x$ related $\text{C}_{10}$-HOM (in red colors), including (A-C) $\text{C}_{10}\text{H}_{14}\text{O}_x$ family, $\text{C}_{10}\text{H}_{14}\text{O}_{10}$, $\text{C}_{10}\text{H}_{14}\text{O}_{11}$, and (D-F) $\text{C}_{10}\text{H}_{15}\text{NO}_x$ family, $\text{C}_{10}\text{H}_{15}\text{NO}_{11}$, $\text{C}_{10}\text{H}_{15}\text{NO}_{12}$, and $\text{C}_{10}\text{H}_{17}\text{O}_x$ related $\text{C}_{10}$-HOM (in blue colors), including (G-I) $\text{C}_{10}\text{H}_{16}\text{O}_x$ family, $\text{C}_{10}\text{H}_{16}\text{O}_{10}$, $\text{C}_{10}\text{H}_{16}\text{O}_{11}$, and (J-L) $\text{C}_{10}\text{H}_{17}\text{NO}_x$ family, $\text{C}_{10}\text{H}_{17}\text{NO}_{11}$, $\text{C}_{10}\text{H}_{17}\text{NO}_{12}$, as a function of reaction time during the first 15 min reaction time at low NO (30 - ~100 ppt, solid lines) and high NO (~20 ppb, dashed lines). Note that the error bars (low NO) and error shades (high NO) represent one standard deviations.
Section S6. C₇ HOM

Besides C₁₀-HOM, both C₉-HOM and C<₁₀-HOM were observed, as shown Fig. S9. As discussed in the main text, C₁₀-HOM observations (with C₂₀-HOM as an example) also indicated a chemistry dominated by C₁₀H₁₅Oₓ•. For C<₁₀-HOM, C₇-HOM are the most abundant products in both low and high NO cases. Their detailed formation chemistry of C₇-HOM and their relation to C₁₀-HOM is discussed below.

**Fig. S9. Relative abundance of other HOM.** Relative abundances of C₉-HOM at (A) low NO (30 - ~100 ppt) and (B) high NO (~20 ppb), with carbonyls/alcohols/hydroperoxides in solid, organic nitrates in horizontal stripes, and peroxy radicals in vertical stripes, and C₁₀-HOM (in black boxes) at (C) low and (D) high NO. Their contributions to all observed HOM in low and high NO experiments are denoted in parenthesis. The area of the pie charts are sized proportionally to the relative contributions to the total HOM.
Two families of peroxy radicals, C$_7$H$_9$O$_x$• and C$_7$H$_{11}$O$_x$•, are identified in C$_7$-HOM (Fig. S9), together with their corresponding C$_7$ closed-shell products, carbonyls (C$_7$H$_8$O$_x$ and C$_7$H$_{10}$O$_x$) and organic nitrates (C$_7$H$_9$NO$_x$ and C$_7$H$_{11}$NO$_x$). Higher concentrations of C$_7$H$_9$O$_x$•-related C$_7$ closed-shell products were observed compared to C$_7$H$_{11}$O$_x$•, with concentration ratios of carbonyls (C$_7$H$_8$O$_x$/C$_7$H$_{10}$O$_x$) of 9.8 and 7.1 at low and high NO, respectively, and concentration ratios of organic nitrates (C$_7$H$_9$NO$_x$/C$_7$H$_{11}$NO$_x$) of 5.7 and 8.8 at low and high NO. According to the current master chemical mechanism MCM v.3.3.1 \(^{(48, 83)}\) and calculations by Vereecken and Peeters \(^{(29)}\), C$_7$H$_{11}$O$_x$• are expected to be formed from the decomposition of C$_{10}$H$_{17}$O$_x$• with acetone as a byproduct as shown in Fig. S10A. C$_7$H$_9$O$_x$• are proposed to be produced from decomposition of C$_{10}$H$_{15}$O$_x$•. As shown in Fig. S10, one alkoxy step for R6OO, R9OO, and R10OO (Fig. 2 in the main text) leads to alkoxy radicals R6O, R9O, and R10O, whose subsequent decomposition reaction is expected to form alkyl radicals C$_7$H$_{9}$O$_2$•, acetone. The following autoxidation of successive O$_2$-addition and H-shift is proposed to form highly oxygenated C$_7$H$_9$O$_x$•. Thereby, the C$_7$-HOM product distribution is consistent with C$_{10}$-HOM, further confirming the importance of C$_{10}$H$_{15}$O$_x$• in α-pinene + OH.

**Fig. S10. Example formation pathway of C$_7$ products.** Example formation pathway of (A) C$_7$H$_{11}$O$_x$• alkyl radicals from C$_{10}$H$_{17}$O$_3$• peroxy radicals and (B, C, D) C$_7$H$_9$O$_2$• alkyl radicals from C$_{10}$H$_{15}$O$_4$• peroxy radicals; decomposition rates calculated as described in Vereecken and Peeters \(^{(51)}\). The formation pathway of R6OO, R9OO, and R10OO are shown in Fig. 2 in the main text. Alkoxy steps are marked in red. Note that alkoxy steps in A-D are more likely to occur at high NO.
while unimolecular reactions are more likely at low NO (Fig. S12A for C$_{10}$H$_{17}$O$_3$•; Fig. 2 for R6OO, R9OO, and R10OO).

Moreover, higher concentrations of C$_7$-HOM at high NO (Fig. S9B) than those at low NO (Fig. S9A) are also consistent with more active alkoxy steps at high NO than at low NO, where unimolecular reactions of C$_{10}$-RO$_2$• are more competitive due to the longer lifetime at low NO. Overall, the distributions of C$_7$-HOM at both low and high NO are consistent with the important role of alkoxy radicals in HOM formation, particularly for C$_{10}$H$_{15}$O$_x$• and its related HOM in this study.

Similar to the C$_{10}$-HOM case, more C$_7$H$_{9}$O$_x$•-related HOM (carbonyls C$_7$H$_8$Ox and organic nitrates C$_7$H$_9$NOx) are formed at earlier reaction time in high NO experiments compared to low NO experiments, as shown in Fig. S11. As proposed, C$_7$H$_5$Ox• and C$_7$H$_{11}$Ox• are respectively formed from C$_{10}$H$_{15}$O$_x$• and C$_{10}$H$_{17}$O$_x$•. As discussed in the main text, the formation rate of C$_{10}$H$_{15}$O$_x$• depends on NO concentrations, which does not influence the formation of C$_{10}$H$_{17}$O$_x$•. Concentration ratios of their related C$_7$ closed-shell products (C$_7$H$_8$Ox/C$_7$H$_{10}$Ox and C$_7$H$_9$NOx/C$_{11}$H$_{11}$NOx) reached values of 1, where C$_7$H$_{9}$Ox• chemistry is considered to be equivalent to C$_7$H$_{11}$Ox• at a reaction time of >5 min at low NO and 1-2 min at high NO. This faster appearance of C$_7$H$_{9}$Ox•-dominated chemistry at high NO again agrees with the temporal behavior of C$_{10}$ HOM (Fig. 3 in the main text) and provides additional evidence for the importance of alkoxy steps in this study. Additionally, the formation of C$_7$ HOM is an evident support for the existence of alkoxy steps in α-pinene + OH.
Fig. S11. Time series of C₇ carbonyls and organic nitrates in low NO (30 - ~100 ppt) and high NO (~20 ppb) experiments. The carbonyl family C₇H₈Oₓ (red), C₇H₁₀Oₓ (blue), and their concentration ratio (C₇H₈Oₓ/C₇H₁₀Oₓ, grey dots) during the first 15 min reaction time are shown in (A) low and (C) high NO experiments. Time series of the organic nitrate family, including C₇H₉NOₓ (red), C₇H₁₁NOₓ (blue), and their concentration ratio (C₇H₉NOₓ/C₇H₁₁NOₓ, grey dots), are similarly demonstrated in (B) low and (D) high NO experiments. The horizontal dashed lines represent a concentration ratio of 1, where C₇H₈Oₓ• chemistry is equivalent to C₇H₁₁Oₓ• chemistry. All data are averaged to a time resolution of 1 min. In each panel, error bars of C₇ carbonyls and organic nitrates represent one standard deviation (left axes, peak intensities lower than background signals are not shown) and error bars of concentration ratios (right axes, uncertainties more than 200% are not shown) were calculated using error propagation.
Section S7. Pinonaldehyde production from OH addition channel

For the established OH addition channel, direct autoxidation is expected to occur in channel A in Fig. S12, leading to C_{10}H_{17}O_{x•} (25-27). The branching ratio for this ring-opened RO_{2•} ranges from 7.5% to 22% (MCM v3.3.1 and Peeters et al. (28), respectively). This limited reaction contribution can be one possible reason for the low concentrations of C_{10}H_{17}O_{x•} related HOM observed in this study. Channels B and C lead to a major product pinonaldehyde C_{10}H_{16}O_{2} (84), whose aldehydic hydrogen atom can be readily abstracted by OH radical again, leading to the indirect formation of C_{10}H_{15}O_{x•} via following autoxidation steps (Fig. S12B, S12C). The limited role of hydrogen abstraction from pinonaldehyde for production of C_{10}H_{15}O_{x•} related HOM in this study will be discussed in the following.

Fig. S12. Simplified mechanism of OH addition channel of α-pinene. The formation of (A) C_{10}H_{17}O_{x•} from α-pinene + OH via the addition channel according to the established literature (25-27). The formation of (B, C) C_{10}H_{15}O_{x•} from hydrogen abstraction from pinonaldehyde, the main product after OH addition to α-pinene. Note that autoxidation pathways in channel (A) likely play a more important role at low NO than alkoxy steps (Fig. S10A) which is expected to be more important at high NO.
Compared to the direct hydrogen abstraction from α-pinene, the hydrogen abstraction from pinonaldehyde pathway is expected to occur later since pinonaldehyde must first be formed via OH addition to α-pinene (85). Considering the rapid formation of C_{10}H_{15}O• and related HOM (within 3 min) observed in this study, first-generation peroxy radicals are likely to dominate in C_{10}H_{15}O• formation compared to any second generation peroxy radicals from pinonaldehyde. In order to quantify the relative importance of the two pathways, we calculated the relative reaction rate (Equation S8) of hydrogen abstraction from α-pinene to that of pinonaldehyde by OH radicals, as shown below:

$$\frac{R[AP+OH]_{H\ abstraction}}{R[PINAL+OH]} = \frac{k[AP+OH] \times [AP] \times [OH] \times BR[H\ abstraction]}{k[PINAL+OH] \times [PINAL] \times [OH]} = \frac{k[AP+OH] \times [AP] \times BR[H\ abstraction]}{k[PINAL+OH] \times [AP] \times Y[PINAL]}$$

(Eq. S8)

where $k[AP+OH]$ and $k[PINAL+OH]$ are temperature-dependent reaction rate constants taken from MCM v3.3.1 (48, 83). Here, BR[H-abstraction] is the branching ratio for α-pinene + OH reactions to undergo H-abstraction channel. As the H-abstraction channel is not included in current MCM v3.3.1, we added it with branching ratio of 0.09 (28). Concentrations of α-pinene were measured in the experiments while concentrations of pinonaldehyde were estimated according to their NO-dependent yields ($Y[PINAL]$ in Equation S8), with a range of 0.05-0.13 at low NO and 0.3-0.45 at high NO (85-87). In this study, 0.05 and 0.3 were used for the yield $Y[PINAL]$ in low NO and high NO experiments, respectively. The uncertainties of $\frac{R[AP+OH]_{H\ abstraction}}{R[PINAL+OH]}$ was estimated to be -40%/+168% at low NO and -40%/+71% at high NO, from the uncertainty of α-pinene concentration (~15%), $k[AP+OH]$ ($\Delta \log k = \pm 0.08$), $k[PINAL+OH]$ ($\Delta \log k = \pm 0.15$), and $Y[PINAL]$ (-0%/+160% at low NO and -0%/+50% at high NO) using error propagation.

The relative reaction rate $\frac{R[AP+OH]_{H\ abstraction}}{R[PINAL+OH]}$ along with uncertainties during the first 15 min reaction are shown in Fig. S13. Hydrogen abstraction from α-pinene is more than 70 times faster than that from pinonaldehyde at low NO and more than 8 times at high NO. Note that the concentrations of pinonaldehyde were estimated from consumed α-pinene and yields of pinonaldehyde, thus reflecting only the production. As pinonaldehyde is continuously consumed by OH, its true concentration should be lower, and thus its relative importance is even overestimated using this method. Overall, we thus conclude that pinonaldehyde has only a minor to negligible contribution to HOM formation at early stages of the experiments.
Fig. S13. Relative reaction rate of hydrogen abstraction by OH from α-pinene to that from pinonaldehyde. Data within the first 15 min reaction time of (A) low NO (30 - ~100 ppt) and (B) high NO (~20 ppb) experiments, with dashed lines as the value of 10. Note that the y axes in panel (A) and (B) are different, but both on log scale.
Section S8. Theoretical methodology

The geometries of the intermediates and transition states in the mechanism were first optimized using the M06-2X/cc-pVDZ methodology (88, 89), with an exhaustive characterization of all conformers for each reactant and transition state. All geometries obtained thus were further optimized at the M06-2X-D3/aug-cc-pVTZ level of theory which includes Grimme et al. (90). D3 diffusion corrections (90, 91). Moments of inertia for molecular rotation, and wavenumbers for vibration were obtained at the same level of theory, with a vibrational scaling factor of 0.971 (89, 92). The transition states were validated by IRC calculations and by visual verification of the imaginary frequency vibrational mode. Finally, the relative energies were further improved by single-point calculations at the CCSD(T)/aug-cc-pVTZ level of theory (93, 94); this final level of theory is referred to as CCSD(T)/M06-2X-D3. T1 diagnostics at that level of theory did not reveal high multi-reference character for any of the structures (T1 ≤ 0.028). The expected uncertainty on the reaction barrier heights at this level of theory is ±0.5 kcal mol⁻¹. All quantum chemical calculations were performed using the Gaussian-16 software suite (95). The quantum chemical data underlying the theoretical kinetic calculations can be found as a text file at https://doi.org/10.26165/JUELICH-DATA/GLU9BW.

The rate coefficients for the individual reactions at the high-pressure limit were then calculated using multi-conformer transition state theory, MC-TST (96), incorporating the data for all conformers obtained as described above. Tunneling is accounted for using an asymmetric Eckart barrier correction (97, 98). Based on earlier work at a similar level of theory in comparison with experimental data on H-migration in RO₂• radicals with no or only one oxygenated functionality (50, 99) and available theoretical literature data on ring closure reactions (56), we estimate the thermal rates to be accurate to a factor 2 to 3.
Section S9. Theoretical kinetic study of RO$_2$• radicals after H-abstraction

As already studied in prior literature (28, 29, 33), the dominant H-abstraction sites in $\alpha$-pinene are those that lead to allyl-resonance stabilized alkyl radicals. Under atmospheric conditions, these allyl radicals will undergo O$_2$ addition, which can occur on either side of the ring for endocyclic radical sites. Formally, there are then 7 distinct RO$_2$• radicals that need to be examined (see Fig. S14). Of these, R2OO is expected to be dominant under atmospheric conditions, with an estimated 40:60 syn to anti ratio.

Fig. S14. Peroxy radicals formed from $\alpha$-pinene H-abstraction. Seven peroxy radicals formed from hydrogen abstraction from $\alpha$-pinene and following O$_2$ addition.
For each of these RO$_2^\cdot$ radicals, we examined all geometrically accessible intramolecular H-migrations; ring closure reactions lead to strained tricyclic structures and are either geometrically not feasible or energetically not competitive even without the additional ring strain of the bicyclic molecular frame (56). The calculated rate coefficients are tabulated below in Table S1. As can be seen, all unimolecular reactions are slow, and not competitive with bimolecular reactions under the experimental conditions, where RO$_2^\cdot$ lifetimes are of the order of 1 minute or less ($\leq 10^2$ s).

**Table S1.** H-migrations in RO$_2^\cdot$ radicals formed from $\alpha$-pinene H-abstraction, listing barrier heights $E_b$ (kcal mol$^{-1}$), rate coefficient $k$ (s$^{-1}$) at 298 K, and parameters for a Kooij equation fit $k(T)=A \times T^n \times \exp(-E_a/T)$ for the temperature range 200-450 K, calculated using the CCSD(T)//M06-2X-D3 level of theory.

| RO$_2^\cdot$ Reaction type | $E_b$ (kcaT) | $k$ (298K) | $A$/s$^{-1}$ | $n$ | $E_a$/K |
|---------------------------|--------------|------------|--------------|-----|---------|
| R12OO 1,7-H-shift         | 23.9         | 5.4$\times$10$^{-4}$ | 1.17E-88     | 31.73 | -4234   |
| R12OO 1,6-H-shift         | 28.2         | 5.9$\times$10$^{-6}$ | 4.16E-111    | 39.57 | -4988   |
| R12OO syn-R13OO 1,7-H-shift| 29.0         | 7.6$\times$10$^{-7}$ | 2.52E-117    | 41.56 | -5258   |
| R12OO syn-R13OO 1,5-H-shift| 25.0         | 2.0$\times$10$^{-4}$ | 9.13E-99     | 35.81 | -3944   |
| R12OO syn-R200 1,6-H-shift | 26.0         | 9.9$\times$10$^{-5}$ | 4.98E-103    | 37.07 | -4529   |
| R12OO syn-R200 1,5-H-shift | 27.4         | 4.7$\times$10$^{-6}$ | 6.12E-111    | 39.63 | -4695   |
| R12OO anti-R100 1,6-H-shift | 26.8         | 2.8$\times$10$^{-3}$ | 1.03E-105    | 37.75 | -4824   |
Section S10. Theoretical kinetic study of RO₂• radicals formed from R1OO and R2OO

Due to the long unimolecular lifetime of the R1OO and R2OO peroxy radicals, they are likely to undergo bimolecular reactions, where reactions with other peroxy radicals or with NO will yield alkoxy radicals in significant fractions (100). The formation routes of RO₂• radicals formed from R1OO and R2OO are shown in Fig. S15. Anti-R2O will readily open the 6-membered ring, \( k \sim 2 \times 10^5 \text{ s}^{-1} \) (28), forming a cyclobutyl radical that reacts with O₂ under atmospheric conditions, forming syn- and anti-R4OO. Syn-R2O is expected to undergo a 1,5-H-migration, \( k \sim 3 \times 10^6 \text{ s}^{-1} \) (28) forming a chemically excited alkyl radical which, due to the ring strain in the 4-membered ring, is expected to undergo ring opening for a large fraction. The resulting cyclo-allyl radical will then add O₂ on either side of the ring, forming syn- and anti-R5OO and syn- and anti-R14OO. The fate of R1O is not discussed in detail. We provide a partial reaction scheme in the main text, and in Fig. S15C, S15D.

Fig. S15. Peroxy radicals formed from R1OO and R2OO. The formation pathway of peroxy radicals from (A) anti-R2OO, (B) syn-R2OO, (C) anti-R1OO, and (D) syn-R1OO with one alkoxy step and subsequent O₂ addition are shown.
We have performed theoretical kinetic calculations on the fate of the R3OO, R4OO, R5OO and R14OO radicals, which can undergo H-migration reactions and ring closure reactions. The calculation results are tabulated in Table S2. As can be seen, only unimolecular reactions in syn-R14OO and the fast 1,8-H-migration in syn-R3OO (included in Fig. 2 in the main text) are competitive against bimolecular reactions under the current reaction conditions with RO2• lifetimes of less than 1 min. The majority of the peroxy radicals are thus expected to undergo bimolecular reactions, which for a significant fraction will yield the corresponding alkoxy radicals (R3O, R4O, R5O, and R14O, shown in Fig. S16). Their fate can be estimated using established structure-activity relationships and available theoretical work (51, 101, 102). The dominant loss process for R3O and R4O radicals will be the opening of the 4-membered ring, forming R6OO and R10OO molecules, respectively, after reaction with O2 (see Fig. S16). Similarly, R14O radicals will instantly open the 6-membered ring, forming an α-OH alkyl radical that reacts readily with O2 to form a ketone + HO2•, terminating the radical chain. For R5O radicals we estimate that the ring structure will hamper H-migration and ring closure reactions, leaving the favorable opening of the 6-membered ring as the dominant fate, forming R11OO after O2 addition.

Fig. S16. The ring cleavage of alkoxy radicals. The radical chain propagation of alkoxy radicals of (A) R3O, (B) R4O, and (C) R5O, and radical termination pathway of alkoxy radical (D) anti-R14O. Reaction rates calculated as described in Vereecken and Peeters (51).
Table S2. H-migrations in RO₂• radicals formed from α-pinene H-abstraction after a first alkoxy stage, listing barrier heights $E_b$ (kcal mol$^{-1}$), rate coefficient $k$ (s$^{-1}$) at 298 K, and parameters for a Kooij equation fit $k(T)=A×T^n×\exp(-E_a/T)$ for the temperature range 200-450 K, calculated using the CCSD(T)//M06-2X-D3 level of theory.

| RO₂•  | Reaction type | $E_b$  | $k(298\text{K})$  | $A / \text{s}^{-1}$ | $n$ | $E_a / \text{K}$ |
|-------|---------------|--------|-------------------|---------------------|-----|-----------------|
| syn-R4OO | 1,5-H-shift (prim.) | 23.5 | $6.9×10^{-4}$ | 1.97E-92 | 33.52 | -3852 |
|         | 1,9-H-shift (vinoxy) | 29.8 | $4.1×10^{-8}$ | 2.81E-114 | 39.64 | -5554 |
|         | 6-ring closure | 21.7 | $6.0×10^{-5}$ | 9.98E2 | 2.51 | 9223 |
|         | 7-ring closure | 30.4 | $4.8×10^{-12}$ | 3.03E+07 | 0.84 | 14326 |
| anti-R4OO | 1,5-H-shift (prim.) | 24.1 | $2.1×10^{-3}$ | 3.89E-90 | 32.95 | -3586 |
|         | 1,5-H-shift (tert.) | 31.8 | $2.9×10^{-6}$ | 1.33E-102 | 35.97 | -5034 |
| syn-R3OO | 1,5-H-shift (prim.) | 23.4 | $1.7×10^{-4}$ | 1.06E-91 | 33.60 | -3504 |
|         | 1,7-H-shift (allyl) | 26.3 | $6.8×10^{-5}$ | 1.58E-93 | 33.09 | -4638 |
|         | 1,8-H-shift (aldch.) | 19.8 | $2.8×10^{-1}$ | 3.86E-68 | 25.21 | -3084 |
|         | 6-ring closure | 26.1 | $2.5×10^{-8}$ | 2.98E-09 | 6.40 | 10242 |
|         | 7-ring closure | 30.0 | $4.2×10^{-11}$ | 1.87E+08 | 0.93 | 14384 |
| anti-R3OO | 1,5-H-shift (prim.) | 23.3 | $1.7×10^{-4}$ | 1.95E-88 | 32.51 | -3372 |
|         | 1,5-H-shift (tert.) | 30.1 | $4.6×10^{-6}$ | 7.48E-107 | 37.67 | -5208 |
| syn-R5OO | 6-ring closure | 19.8 | $1.9×10^{-4}$ | 4.16E-01 | 3.56 | 8340 |
|         | 7-ring closure | 18.8 | $3.8×10^{-3}$ | 1.08E+07 | 1.20 | 8521 |
|         | 1,7-H-shift (allyl) | 22.3 | $4.0×10^{-3}$ | 9.17E-80 | 28.75 | -3788 |
| anti-R5OO | 1,5-H-shift (tert.) | 232 | $7.1×10^{-3}$ | 1.69E-84 | 30.90 | -3566 |
|         | 1,7-H-shift (prim) | 34.1 | $2.6×10^{-10}$ | 6.37E-139 | 48.21 | -6406 |
| syn-R14OO | 6-ring closure | 16.9 | $3.3×10^{-2}$ | 3.55E+05 | 1.51 | 7390 |
|         | 7-ring closure | 17.8 | $1.8×10^{-2}$ | 4.71E+09 | 0.28 | 8312 |
|         | 1,7-H-shift (allyl) | 20.5 | $2.7×10^{-2}$ | 4.30E-71 | 25.88 | -3274 |
| anti-R14OO | 1,5-H-shift (prim.) | 25.3 | $1.2×10^{-4}$ | 4.15E-101 | 36.48 | -4267 |
|         | 1,5-H-shift (tert.) | 23.2 | $7.8×10^{-3}$ | 5.78E-88 | 32.04 | -4028 |
Section S11. Procedure for constructing oxidation schemes after ring opening

Explicit theoretical calculations on the intermediates get increasingly costly as more oxygen atoms are added. At this time, we chose not to do such calculations for intermediates where both rings are opened. Instead, we anticipate that in the absence of ring strain the rate of reactions can be fairly well described based on structure-activity relationships (SARs).

For most H-migrations in RO$_2^*$ radicals, we base ourselves on the SAR by Vereecken and Nozière (50); this SAR was reported to reproduce the scarce experimental data within a factor of 2, but for multi-functionalized species such as studied in this work the scatter on the data within each SAR category reaches an order of magnitude. For those reaction classes that are not covered by the SAR, we attempt to extrapolate the reactivity trends in that SAR. For example: to estimate the rate of a 1,8-H-migration of an aldehyde H-atom (not covered by the SAR), we could (a) use the rate of an alkyl-1,8-H-migration, augmented by the typical enhancement for an aldehyde H-atom; (b) use the rate of an aldehyde-1,7-H-shift reduced by the difference in rate between an alkyl-1,7- and alkyl-1,8-H-shift; or (c) do both these extrapolations and average the predictions. Such extrapolations are not overly accurate and imply a certain level of arbitrariness in how the extrapolation is done; the expected uncertainty increases by at least an order of magnitude as no reliable data is available to validate the extrapolation. In most cases, however, this is sufficient to determine whether the reaction can contribute or not, as reaction rates typically differ by several orders of magnitude and the SAR covers the most common and favorable reaction classes explicitly. For H-migrations in cycloperoxides, we additionally rely on the systematic study by Vereecken et al. (56), who explicitly calculated rate coefficients for peroxy radicals formed after RO$_2^*$ ring closure reactions. For ring closure reactions in unsaturated RO$_2^*$ we rely on the SAR by Vereecken et al. (56). We assume that the rate of ring closure is not affected by the presence of another cycloperoxide ring; this approximation is unlikely to be accurate, but insufficient data is available to improve the estimates.

In assessing the fate of an RO$_2^*$ radical with one or more -OOH groups, we account for the possibility of H-atom scrambling, as described extensively in the literature (53-55, 99, 103). The H-migrations between the -OO• and -OOH groups often allow for additional pathways, and are typically much faster than other unimolecular channels, such that the scrambling leads to a fast equilibration among all accessible OOH-substituted RO$_2^*$ radicals, and the dominant channel is chosen among those available to the pool of RO$_2^*$ radicals. We refer to Vereecken and Nozière (50) for a more detailed description of this feature.

In the Fig. S17, we show some explicit examples on how this approach work. For each intermediate, we examine all possible unimolecular reaction channels, estimate its rate coefficient, and select the dominant pathway (shown in bold) as the reactive channel. Following these examples, autoxidation pathways subsequent to R6OO, R9OO, R10OO, and R11OO (Fig. 2 in the main text) were determined and shown in Fig. S18.
**Fig. S17. Determination of the unimolecular reactions of peroxy radical intermediates.** Two explicit examples to show the determination approach of the unimolecular reactions for (A) R11OO and (B) R10OO. All possible unimolecular reaction channels of each peroxy intermediates are listed and the dominant pathway is highlighted in bold. The details of how rate coefficients are determined can be referred to the text in the page above (Section S11).
Fig. S18. Subsequent autoxidation pathways of $\text{C}_{10}\text{H}_{15}\text{O}_x\cdot$. Example autoxidation pathways of (A) R6OO, (B) R9OO, (C) R10OO, and (D) R11OO. The formation pathway of R6OO, R9OO, R10OO, and R11OO are shown in Fig. 2 in the main text. The chemical formulas of peroxy radicals are denoted on the left side of the figure. Note that alkoxy steps are not included in the figure. All of the rate coefficients shown in this figure were derived from SARs, as described in Section S11.
Section S12. Incorporation of the hydrogen abstraction channel in MCM

The hydrogen abstraction channel is not included in the α-pinene + OH chemistry in the current MCM v3.3.1 (48). Based on the calculated reaction rates and mechanism in Fig. 2 in the main text, we added the hydrogen abstraction channel to the MCM (http://mcm.york.ac.uk/home.htt), with detailed reactions and rate coefficients listed in Table S3, which account for the site- and stereospecific data from the theoretical study described above. In the initial step of α-pinene + OH, a branching ratio of 0.09 is applied to the hydrogen abstraction channel (reactions 4-7 in Table S3) and the branching ratio of OH addition channel is also updated (reactions 1-3 in Table S3). The main loss of RO2• radical is assigned to bimolecular reactions with NO to produce organic nitrates (10%) and alkoxy radicals (90%). Bimolecular reactions of RO2• + HO2• are also included, but bimolecular reactions of RO2• + RO2• and OH elimination by unimolecular RO2• reactions are not included. Reactions for the hydrogen abstraction channel start at α-pinene (C10H16) + OH and include the formation of peroxy radicals containing up to ten oxygen atoms (C10H15O10•). Besides the RO2• autoxidation reactions shown in Fig. 2 in the main text and Fig. S18, all other reactions with rate coefficients more than 1×10^{-3} s^{-1} are also included for completeness. While we do not have theoretical calculations for syn-R1OO/syn-R1O, which accounts for about 20% of the hydrogen abstraction channel, similar chemistry is assumed for syn-R1O to syn-R2O, shown as reactions of 33-34 and 49-50 in Table S3. Totally, 139 reactions were included for calculations, including peroxy radicals from R1OO to R29OO in this study.

The MCM simulations were calculated using an open access program iChamber (104). Production and photolysis of HONO were also incorporated into the calculations according to Rohrer et al. (52). Physical parameters, including JHONO, JNO2, temperature, and relative humidity, were constrained to measured data with a time resolution of 10 s. In both low and high NO experiments, initial concentrations of α-pinene were set as 20 ppb. Initial concentrations of NO were set as 0 ppb at low NO and 20 ppb at high NO. A reaction period of 15 min was calculated for both low NO and high NO using the above settings. Condensation sink of HOM to particles is negligible due to the absence of nucleation in this time frame. The wall loss rate of 6×10^{-4} s^{-1} (low NO) and 2.2×10^{-3} s^{-1} (high NO) were applied to HOM with six and more oxygen atoms, and a dilution rate of 1.5×10^{-5} s^{-1} was applied to all compounds in our MCM calculations.

The closed-shell product C_{10}H_{15}NO_{9} is used to compare our calculated results to the observations (CIMS data). These C_{10}H_{15}NO_{9} species are formed from C_{10}H_{15}O_{8}•. The rate coefficients of RO2• + NO → RONO2 are known, and organic nitrate formation is included in our calculations. Moreover, in both low and high NO experiments, the observed concentrations of C_{10}H_{15}NO_{9} are sufficiently high for comparison, with an abundance of 11.3% (low NO) and 27.0% (high NO) relative to the highest closed-shell products C_{10}H_{14}O_{10}. In our calculations, C_{10}H_{15}NO_{9} are formed in reactions 115, 118, 999, 127, 130, and 139 as listed in Table S3. Their calculated time series and CIMS data at low and high NO are shown in Fig. S19. Our simulations agree within the uncertainties with the observations at both low and high NO. The formation of C_{10}H_{15}NO_{9}
accelerates after around 5 min reaction time at low NO, while \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) formation starts after about 2 min reaction time at high NO. Note that as mentioned in Section S2, some background NO concentration was present in the low NO experiments; thus a sensitivity test of initial NO concentrations of 0-30 ppt was also conducted for low NO experiment, with dashed lines shown in Fig. S19A. With each increase in the initial NO concentration, it takes less time to accelerate the formation of \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \). This is consistent with the expectation that higher NO concentrations promote the production of alkoxy radicals. As shown in Fig. S19A, all simulated \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) (with an initial NO concentration from 0-30 ppt) are within the standard errors of the observations. The background NO concentrations have negligible influence on our experiments.

The alkoxy production rate was estimated based on the reaction of \( \text{RO}_2^\bullet + \text{NO} \rightarrow \text{RO}^\bullet + \text{NO}_2 \) in this study, as shown in Fig. S20. Concentrations of \( \text{RO}_2^\bullet \) and NO were derived from our MCM simulations and a uniform rate constant of \( k_{\text{RO}_2^\bullet + \text{NO}} \) was used. The organic nitrate yield is assumed to be 0.1. Overall, a lower alkoxy production rate was observed in low NO than in high NO. Also, as expected, the formation of alkoxy radicals is slow at the beginning of the low NO experiment while immediate formation of alkoxy radicals is observed at high NO. This again emphasizes the requirement for ring opening, and NO dependence in the HOM formation from H-abstraction channel in \( \alpha \)-pinene + OH reactions in this study.

We also examined the sensitivity of the model results to the model parameters. Two sets of the rate coefficients were applied, including one set derived from explicit calculations in this study (as discussed above), and the other set assigned as fixed values (50, 56), as shown in Table S3. Calculated time series of \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) using explicit and fixed rate coefficients are shown in Fig. S19. Overall, no significant difference is observed in concentrations of \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) using explicit and fixed values, and the delayed \( \text{C}_{10}\text{H}_{15}\text{NO}_9 \) formation in low NO are both observed using explicit and fixed values. Hence, the model results are not overly sensitive to the rate coefficients used. However, without knowing reaction pathways and chemical structures, which are still derived from explicit calculations, the fixed values cannot be assigned. In this case, it is essential to determine the reaction pathways based on explicit calculations to simulate product formation in the MCM. Further work is needed to incorporate more detailed H-abstraction channel in MCM.

To further compare \( \text{C}_{10}\text{H}_{15}\text{O}_X^\bullet \) and \( \text{C}_{10}\text{H}_{17}\text{O}_X^\bullet \) chemistry in the HOM formation from OH oxidation of \( \alpha \)-pinene, autoxidation pathway of \( \text{C}_{10}\text{H}_{17}\text{O}_X^\bullet \) was added to the MCM calculations, with reactions in Table S4 following Xu et al. (27). In OH addition channel, autoxidation is expected to only occur in the ring-opened \( \text{RO}_2^\bullet \) (\( \text{C}_{10}\text{H}_{17}\text{O}_5^\bullet \), Fig. S12A). Reactions after the ring-opened \( \text{RO}_2^\bullet \) (\( >1\times10^{-3} \text{ s}^{-1} \)), from \( \text{C}_{10}\text{H}_{15}\text{O}_3^\bullet \) to \( \text{C}_{10}\text{H}_{17}\text{O}_{11}^\bullet \), were incorporated into the calculations, including Scheme 2, 3, and 5 in Xu et al. (27). Note that reactions leading to low oxygenated termination products (\( \text{O}<6 \)), such as P2 in their Scheme 2, are not included to simplify the model. For rate coefficients or branching ratios missing in Xu et al. (27), uniform values were applied. For example, Scheme 5 in their paper, only \( \text{anti-C}_{10}\text{H}_{17}\text{O}_3^\bullet \) can undergo subsequent rapid autoxidation. A stereospecific branching ratio of 50% was applied to \( \alpha \)-pinene+OH, as shown
reactions 1 and 2 in Table S4. The rate coefficients of RO₂• H-shifts were estimated from Vereecken and Nozière (50). Rate coefficients of ring-closure, H scrambling, RO• decomposition, and RO• H-shift, were given as 1 s⁻¹, 1×10² s⁻¹, KDEC (1×10⁶ s⁻¹), and 1×10⁵ s⁻¹ according to empirical knowledge from literature (54-56). Organic nitrate C₁₀H₁₇NO₈ was used to compare our calculated results to the observations, as shown in Fig. S21. Overall, our calculation results agree within the uncertainties with the observations at both low and high NO. Similar time series were observed at low NO and high NO and no delay was observed at low NO. This is consistent with independence of C₁₀H₁₇Oₓ• formation pathway on NO.

As only part of the C₁₀H₁₅Oₓ• (X≤10) and C₁₀H₁₇Oₓ• (X≤11) chemistry was incorporated into the MCM calculations, C₁₀H₁₇NO₈ and C₁₀H₁₅NO₉ are used as an example to compare C₁₀H₁₅OX• and C₁₀H₁₇OX• chemistry in the HOM formation from OH oxidation of α-pinene. They are formed via similar formation pathway, i.e., two autoxidation steps and following bimolecular reactions with NO. Their concentration ratios from MCM calculations are shown in Fig. S22. At low NO, concentration ratios of C₁₀H₁₅NO₉ to C₁₀H₁₇NO₈ increased with reaction time. This is expected as a result of an accelerated C₁₀H₁₅Oₓ• chemistry and C₁₀H₁₇Oₓ• chemistry independent of NO as reaction proceeds, with increasing NO from HONO photolysis. Higher initial NO concentration leads to higher concentration ratio of C₁₀H₁₅NO₉ to C₁₀H₁₇NO₈, also supporting the acceleration of C₁₀H₁₅Oₓ• chemistry by NO. At high NO, concentration ratio of C₁₀H₁₅NO₉ to C₁₀H₁₇NO₈ is relatively stable, with a quick rise at the start of the reaction and a slight decrease over later reaction times. As high NO concentrations lead to rapid alkoxy steps, C₁₀H₁₅Oₓ• chemistry is expected to dominate over C₁₀H₁₇Oₓ• chemistry and to lead to a relatively stable concentration ratio of C₁₀H₁₅NO₉ to C₁₀H₁₇NO₈. This time series pattern is similar to the observed time series of C₁₀H₁₅NOₓ and C₁₀H₁₇NOₓ (Fig. 3B, 3D), with an increasing concentration ratio of C₁₀H₁₅NOₓ to C₁₀H₁₇NOₓ at low NO and stabilization at low NO. However, it takes more time for observed concentration ratios (~5 min) to achieve stabilization than in MCM calculations (almost immediately after the reactions). This difference may be attributed to the incomplete mechanism of C₁₀H₁₅Oₓ• chemistry, particularly for different chemistry of various isomers as only the most likely pathway is proposed in this study, and to incomplete C₁₀H₁₇Oₓ• chemistry where only example pathways are available in the literature (27) and included in MCM. Part of the difference can also attribute to large uncertainties of observed concentration ratios (Fig. 3). Further studies are warranted for more detailed H-abstraction channel in OH oxidation of α-pinene.
Fig. S19. Time series of calculated C$_{10}$H$_{15}$NO$_9$ concentration and measured one using CIMS. Based on our modified MCM mechanism of α-pinene + OH, time series of C$_{10}$H$_{15}$NO$_9$ are calculated in (A) low NO (with an initial NO concentration of 0 ppb, 0.01 ppb, 0.02 ppb, and 0.03 ppb) and (B) high NO experiments (with an initial NO concentration of 20 ppb). Calculations using explicit reaction rates for individual peroxy radical are red lines; calculations using fixed reaction rates are green lines. CIMS data of C$_{10}$H$_{15}$NO$_9$ are denoted as black markers with one standard deviation as error bars.
Fig. S20. Production rate of alkoxy radicals at low and high NO experiments. Based on reaction of RO\textsuperscript{2−} + NO → RO• + NO\textsubscript{2}, the production rate of alkoxy radicals is estimated in (A) low NO and (B) high NO experiments, using organic nitrate yields (0.1) and concentrations of RO\textsuperscript{2−} and NO from MCM results. Note that the vertical axes of the two panels are on the linear scale with a range of 0-2.0×10\textsuperscript{7} molecule cm\textsuperscript{-3} s\textsuperscript{-1}. 
Fig. S21. Time series of calculated C\textsubscript{10}H\textsubscript{17}NO\textsubscript{8} concentration and measured one using CIMS. Based on our MCM mechanism of α-pinene + OH following Xu et al. (27), time series of C\textsubscript{10}H\textsubscript{17}NO\textsubscript{8} are calculated in (A) low NO (with an initial NO concentration of 0 ppb, 0.01 ppb, 0.02 ppb, and 0.03 ppb) and (B) high NO experiments (with an initial NO concentration of 20 ppb). CIMS data of C\textsubscript{10}H\textsubscript{17}NO\textsubscript{8} are denoted as black markers with one standard deviations as error bars.
Fig. S22. Time series of calculated concentration ratio of $\text{C}_{10}\text{H}_{15}\text{NO}_9/\text{C}_{10}\text{H}_{17}\text{NO}_8$. Based on our MCM mechanism of $\alpha$-pinene + OH following Xu et al. (27), time series of concentration ratio of $\text{C}_{10}\text{H}_{15}\text{NO}_9/\text{C}_{10}\text{H}_{17}\text{NO}_8$ are calculated in (A) low NO (with an initial NO concentration of 0 ppb, 0.01 ppb, 0.02 ppb, and 0.03 ppb) and (B) high NO experiments (with an initial NO concentration of 20 ppb).
Table S3. Hydrogen abstraction mechanism added to α-pinene + OH subset of MCM. Incorporated reactions and rate coefficients in the default α-pinene + OH subset of MCM mechanism. Two sets of rate coefficients were used, including one set of values derived from explicit calculations in this study and another one assigned as fixed values.

| No. | Reactions                                      | Explicit rate coefficients | Fixed rate coefficients |
|-----|-----------------------------------------------|----------------------------|-------------------------|
|     |                                              | (1st order reactions: s⁻¹) | (1st order reactions: s⁻¹) |
|     |                                              | 2nd order reactions: cm³ molecule⁻¹ s⁻¹ | 2nd order reactions: cm³ molecule⁻¹ s⁻¹ |
| 1   | APINENE + OH = APINAO₂                        | 1.2E-11*EXP(440/TEMP)*0.91*0.572 | 1.2E-11*EXP(440/TEMP)*0.91*0.572 |
| 2   | APINENE + OH = APINBO₂                        | 1.2E-11*EXP(440/TEMP)*0.91*0.353 | 1.2E-11*EXP(440/TEMP)*0.91*0.353 |
| 3   | APINENE + OH = APINCO₂                        | 1.2E-11*EXP(440/TEMP)*0.91*0.075 | 1.2E-11*EXP(440/TEMP)*0.91*0.075 |
| 4   | APINENE + OH = syn-R1OO                       | 1.2E-11*EXP(440/TEMP)*0.09*0.4*0.5 | 1.2E-11*EXP(440/TEMP)*0.09*0.4*0.5 |
| 5   | APINENE + OH = anti-R1OO                      | 1.2E-11*EXP(440/TEMP)*0.09*0.4*0.5 | 1.2E-11*EXP(440/TEMP)*0.09*0.4*0.5 |
| 6   | APINENE + OH = syn-R2OO                       | 1.2E-11*EXP(440/TEMP)*0.09*0.6*0.4 | 1.2E-11*EXP(440/TEMP)*0.09*0.6*0.4 |
| 7   | APINENE + OH = anti-R2OO                      | 1.2E-11*EXP(440/TEMP)*0.09*0.6*0.6 | 1.2E-11*EXP(440/TEMP)*0.09*0.6*0.6 |
| 8   | anti-R1O = syn-R3OO                           | 6.3E+06*0.5                 | KDEC*0.5                |
| 9   | anti-R1O = anti-R3OO                          | 6.3E+06*0.5                 | KDEC*0.5                |
| 10  | anti-R3O = anti-R3OO-Others                  | 1.3E-01 (1,5-H-shift)       | 1.0E-02                 |
| 11  | syn-R3O = R6OO                               | 6.7E+12                     | KDEC                    |
| 12  | anti-R3O = R6OO                              | 6.7E+12                     | KDEC                    |
| 13  | R6OO = R15OO                                 | 3.3E+02                     | 1.0E+00                 |
| 14  | R15OO = R16OO                                | 1.7E-01                     | 5.0E-01                 |
| 15  | R16OO = R17OO                                | 1.1E+03                     | 1.0E+02                 |
| 16  | R17OO = R18OO                                | 5.8E-02                     | 1.0E-02                 |
| 17  | syn-R3OO = R7OO                              | 1.3E-01                     | 5.0E-01                 |
| 18  | R7OO = R8OO                                  | 1.6E+01                     | 1.0E+02                 |
| 19  | R8O = R9OO                                   | 6.7E+12                     | KDEC                    |
| 20  | R9OO = R19OO                                 | 3.3E+02                     | 1.0E+00                 |
| 21  | R19OO = R20OO                                | 1.7E-01                     | 5.0E-01                 |
| 22  | anti-R2O = syn-R4OO                           | 2.9E+08*0.5                 | KDEC*0.5                |
| 23  | anti-R2O = anti-R4OO                          | 2.9E+08*0.5                 | KDEC*0.5                |
| 24  | anti-R4OO = anti-R4OO-Others                 | 2.1E+03 (1,5-H-shift)       | 1.0E-02                 |
| 25  | syn-R4O = R10OO                              | 6.7E+12                     | KDEC                    |
| 26  | anti-R4O = R10OO                             | 6.7E+12                     | KDEC                    |
| 27  | R10OO = R21OO                                | 8.7E+02                     | 1.0E+00                 |
|     |                                              | 2.8E-01 (1,5-H-shift)       | 5.0E-01                 |
| 28  | R10OO = R10OO-Others                         | 2.4E+01 (6-ring closure)    | 1.0E+00                 |
| 29  | R21OO = R22OO                                | 1.7E-01                     | 5.0E-01                 |
| 30  | R21OO = R21OO-Others                         | 5.8E-02 (1,5-H-shift)       | 1.0E-02                 |
| 31  | R22OO = R23OO                                | 2.7E+04                     | 1.0E+02                 |
| 32  | R23OO = R24OO                                | 5.8E-02                     | 1.0E-02                 |
33 syn-R1O = syn-R5OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
34 syn-R1O = anti-R5OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
35 syn-R2O = syn-R5OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
36 syn-R2O = anti-R5OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
37 syn-R5OO = syn-R5OO-Others 3.8E-03 (7-ring closure) 1.0E+00
4.0E-03 (1,7-H-shift) 1.0E-02
38 anti-R5OO = anti-R5OO-Others 7.1E-03 (1,5-H-shift) 1.0E-02
39 syn-R5O = R11OO 1.6E+06 KDEC
40 anti-R5O = R11OO 1.6E+06 KDEC
41 R11OO = R25OO 4.0E+03 5.0E-01
5.6E-01 (7-ring closure) 1.0E+00
1.0E+01 (6-ring closure) 1.0E+00
42 R11OO = R11OO-Others 4.3E-02 (6-ring closure) 1.0E+00
5.2E+01 (5-ring closure) 1.0E+00
3.0E-02 (1,6-H-shift) 1.0E-02
43 R25OO = R26OO 1.6E+01 1.0E+02
6.0E-03 (1,7-H-shift) 1.0E-02
44 R25OO = R25OO-Others 1.5E-01 (9-ring closure) 1.0E+00
2.6E-02 (8-ring closure) 1.0E+00
45 R26OO = R27OO 5.2E+01 1.0E+00
46 R27OO = R28OO 2.7E-02 1.0E+00
47 R27OO = R29OO 4.5E-02 1.0E+00
48 R27OO = R27OO-Others 1.8E-03 (1,5-H-shift) 3.5E-02
1.2E-02 (1,6-H-shift) 8.8E-04
49 syn-R1O = syn-R14OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
50 syn-R1O = anti-R14OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
51 syn-R2O = syn-R14OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
52 syn-R2O = anti-R14OO 3.0E+06*0.5*0.5 KDEC*0.5*0.5
53 syn-R14OO = syn-R14OO-Others 3.3E-02 (6-ring closure) 1.0E+00
1.8E-02 (7-ring closure) 1.0E+00
2.7E-02 (1,7-H-shift) 1.0E-02
54 syn-R14O = R14HO + HO2 1.0E+12 KDEC
55 anti-R14O = R14HO + HO2 1.0E+12 KDEC
56 syn-R1OO + HO2 = syn-R10OH KRO2HO2 KRO2HO2
57 syn-R1OO + NO = syn-R1O + NO2 KRO2NO*0.9 KRO2NO*0.9
58 syn-R1OO + NO = syn-R1NO2 KRO2NO*0.1 KRO2NO*0.1
59 anti-R1OO + HO2 = anti-R1OOH KRO2HO2 KRO2HO2
60 anti-R1OO + NO = anti-R1O + NO2 KRO2NO*0.9 KRO2NO*0.9
61 anti-R1OO + NO = anti-R1NO2 KRO2NO*0.1 KRO2NO*0.1
62 syn-R2OO + HO2 = syn-R2OOH KRO2HO2 KRO2HO2
63 syn-R2OO + NO = syn-R2O + NO2 KRO2NO*0.9 KRO2NO*0.9
64 syn-R2OO + NO = syn-R2ONO2 KRO2NO*0.1 KRO2NO*0.1
65 anti-R2OO + HO2 = anti-R2OOH KRO2HO2 KRO2HO2
66 anti-R2OO + NO = anti-R2O + NO2 KRO2NO*0.9 KRO2NO*0.9
67 anti-R2OO + NO = anti-R2ONO2 KRO2NO*0.1 KRO2NO*0.1
68 syn-R3OO + HO2 = syn-R3OOH KRO2HO2 KRO2HO2
69 syn-R3OO + NO = syn-R3O + NO2 KRO2NO*0.9 KRO2NO*0.9
70 syn-R3OO + NO = syn-R3ONO2 KRO2NO*0.1 KRO2NO*0.1
71 anti-R3OO + HO2 = anti-R3OOH KRO2HO2 KRO2HO2
72 anti-R3OO + NO = anti-R3O + NO2 KRO2NO*0.9 KRO2NO*0.9
73 anti-R3OO + NO = anti-R3ONO2 KRO2NO*0.1 KRO2NO*0.1
74 syn-R4OO + HO2 = syn-R4OOH KRO2HO2 KRO2HO2
75 syn-R4OO + NO = syn-R4O + NO2 KRO2NO*0.9 KRO2NO*0.9
76 syn-R4OO + NO = syn-R4ONO2 KRO2NO*0.1 KRO2NO*0.1
77 anti-R4OO + HO2 = anti-R4OOH KRO2HO2 KRO2HO2
78 anti-R4OO + NO = anti-R4O + NO2 KRO2NO*0.9 KRO2NO*0.9
79 anti-R4OO + NO = anti-R4ONO2 KRO2NO*0.1 KRO2NO*0.1
80 syn-R5OO + HO2 = syn-R5OOH KRO2HO2 KRO2HO2
81 syn-R5OO + NO = syn-R5O + NO2 KRO2NO*0.9 KRO2NO*0.9
82 syn-R5OO + NO = syn-R5ONO2 KRO2NO*0.1 KRO2NO*0.1
83 anti-R5OO + HO2 = anti-R5OOH KRO2HO2 KRO2HO2
84 anti-R5OO + NO = anti-R5O + NO2 KRO2NO*0.9 KRO2NO*0.9
85 anti-R5OO + NO = anti-R5ONO2 KRO2NO*0.1 KRO2NO*0.1
86 R6OO + HO2 = R6OOH KRO2HO2 KRO2HO2
87 R6OO + NO = R6O + NO2 KRO2NO*0.9 KRO2NO*0.9
88 R6OO + NO = R6ONO2 KRO2NO*0.1 KRO2NO*0.1
89 R7OO + HO2 = R7OOH KRO2HO2 KRO2HO2
90 R7OO + NO = R7O + NO2 KRO2NO*0.9 KRO2NO*0.9
91 R7OO + NO = R7ONO2 KRO2NO*0.1 KRO2NO*0.1
92 R8OO + HO2 = R8OOH KRO2HO2 KRO2HO2
93 R8OO + NO = R8O + NO2 KRO2NO*0.9 KRO2NO*0.9
94 R8OO + NO = R8ONO2 KRO2NO*0.1 KRO2NO*0.1
95 R9OO + HO2 = R9OOH KRO2HO2 KRO2HO2
96 R9OO + NO = R9O + NO2 KRO2NO*0.9 KRO2NO*0.9
97 R9OO + NO = R9ONO2 KRO2NO*0.1 KRO2NO*0.1
98 R10OO + HO2 = R10OOH KRO2HO2 KRO2HO2
99 R10OO + NO = R10O + NO2 KRO2NO*0.9 KRO2NO*0.9
100 R10OO + NO = R10ONO2 KRO2NO*0.1 KRO2NO*0.1
101 R11OO + HO2 = R11OOH KRO2HO2 KRO2HO2
102 R11OO + NO = R11O + NO2 KRO2NO*0.9 KRO2NO*0.9
103 R11OO + NO = R11ONO2 KRO2NO*0.1 KRO2NO*0.1
104 syn-R14OO + HO2 = syn-R14OOH KRO2HO2 KRO2HO2
105 syn-R14OO + NO = syn-R14O + NO2
106 syn-R14OO + NO = syn-R14ONO2
107 anti-R14OO + HO2 = anti-R14OOH
108 anti-R14OO + NO = anti-R14O + NO2
109 anti-R14OO + NO = anti-R14ONO2
110 R150O + HO2 = R15OOH
111 R150O + NO = R15O + NO2
112 R150O + NO = R15ONO2
113 R16OO + HO2 = R16OOH
114 R16OO + NO = R16O + NO2
115 R16OO + NO = R16ONO2
116 R170O + HO2 = R17OOH
117 R170O + NO = R17O + NO2
118 R170O + NO = R17ONO2
119 R190O + HO2 = R19OOH
120 R190O + NO = R19O + NO2
121 R190O + NO = R19ONO2
122 R210O + HO2 = R21OOH
123 R210O + NO = R21O + NO2
124 R210O + NO = R21ONO2
125 R220O + HO2 = R22OOH
126 R220O + NO = R22O + NO2
127 R220O + NO = R22ONO2
128 R230O + HO2 = R23OOH
129 R230O + NO = R23O + NO2
130 R230O + NO = R23ONO2
131 R250O + HO2 = R25OOH
132 R250O + NO = R25O + NO2
133 R250O + NO = R25ONO2
134 R260O + HO2 = R26OOH
135 R260O + NO = R26O + NO2
136 R260O + NO = R26ONO2
137 R270O + HO2 = R27OOH
138 R270O + NO = R27O + NO2
139 R270O + NO = R27ONO2
Table S4. OH addition mechanism added to α-pinene + OH subset of MCM. Incorporated reactions and rate coefficients (following Xu et al. (27) in the default α-pinene + OH subset of MCM mechanism.

| No. | Reactions | Rate coefficients |
|-----|-----------|--------------------|
|     |           | (1st order reactions: s\(^{-1}\)) | (2nd order reactions: cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) |
| 1   | APINENE + OH = anti-APINCO2 | 1.2E-11*EXP(440/TEMP)*0.91*0.075*0.5 |
| 2   | APINENE + OH = syn-APINCO2 | 1.2E-11*EXP(440/TEMP)*0.91*0.075*0.5 |
| 3   | APINCOOH + OH = anti-APINCO2 | 1.03E-10*0.5 |
| 4   | APINCOOH + OH = syn-APINCO2 | 1.03E-10*0.5 |
| 5   | anti-APINCO2 + HO2 = APINCOOH | KRO2HO2*0.914 |
| 6   | anti-APINCO2 + NO = APINCNO3 | KRO2NO*0.125 |
| 7   | anti-APINCO2 + NO = APINCO + NO2 | KRO2NO*0.875 |
| 8   | anti-APINCO2 + NO3 = APINCO + NO2 | KRO2NO3 |
| 9   | anti-APINCO2 = APINCO | 6.70E-15*RO2*0.7 |
| 10  | anti-APINCO2 = APINCOH | 6.70E-15*RO2*0.3 |
| 11  | syn-APINCO2 + HO2 = APINCOOH | KRO2HO2*0.914 |
| 12  | syn-APINCO2 + NO = APINCNO3 | KRO2NO*0.125 |
| 13  | syn-APINCO2 + NO = APINCO + NO2 | KRO2NO*0.875 |
| 14  | syn-APINCO2 + NO3 = APINCO + NO2 | KRO2NO3 |
| 15  | syn-APINCO2 = APINCO | 6.70E-15*RO2*0.7 |
| 16  | syn-APINCO2 = APINCOH | 6.70E-15*RO2*0.3 |
| 17  | anti-APINCO2 = anti-R4 | 1.1*0.5 |
| 18  | anti-R4 + NO = P4 | KRO2NO*0.1 |
| 19  | anti-R4 + NO = R7 | KRO2NO*0.9 |
| 20  | anti-R4 + HO2 = R4-ROOH | KRO2HO2 |
| 21  | anti-R4 = R4-C10H17O5-RO2 | 1.0E+02 |
| 22  | R4-C10H17O5-RO2 = R4-C10H16O5 | 0.1 |
| 23  | R4-C10H17O5-RO2 + NO = R4-C10H17O5-RONO2 | KRO2NO*0.1 |
| 24  | R4-C10H17O5-RO2 + NO = R4-C10H17O5-RO | KRO2NO*0.9 |
| 25  | R4-C10H17O5-RO2 + HO2 = R4-C10H17O5-ROOH | KRO2HO2 |
| 26  | R4-C10H17O5-RO2 = R4-C10H17O5-RO2-endo-A | 1.0E+00 |
| 27  | R4-C10H17O7-RO2-endo-A + NO = R4-C10H17O7-RONO2-endo-A | KRO2NO*0.1 |
| 28  | R4-C10H17O7-RO2-endo-A + NO = R4-C10H17O7-RO-endO-A + NO2 | KRO2NO*0.9 |
| 29  | R4-C10H17O7-RO2-endo-A + HO2 = R4-C10H17O7-ROOH-endo-A | KRO2HO2 |
| 30  | R4-C10H17O7-RO2-endo-A = R4-C10H17O7-RO2-endo-B | 1.0E+02 |
| 31  | R4-C10H17O7-RO2-endo-B + NO = R4-C10H17O7-RONO2-endo-B | KRO2NO*0.1 |
| 32  | R4-C10H17O7-RO2-endo-B + NO = R4-C10H17O7-RO-endO-B + NO2 | KRO2NO*0.9 |
| 33  | R4-C10H17O7-RO2-endo-B + HO2 = R4-C10H17O7-ROOH-endo-B | KRO2HO2 |
| 34  | R4-C10H17O5-RO2 = R13 | 2.96E+01*0.5 |
| 35  | R4-C10H17O5-RO2 = R4-C10H17O7-RO2 | 2.96E+01*0.5 |
36 $R4-C10H17O7-RO2 + NO = R4-C10H17O7-RONO2$  \[ KRO2NO*0.1 \]
37 $R4-C10H17O7-RO2 + NO = R4-C10H17O7-RO + NO2$  \[ KRO2NO*0.9 \]
38 $R4-C10H17O7-RO2 + HO2 = R4-C10H17O7-ROOH$  \[ KRO2HO2 \]
39 $R4-C10H17O7-RO2 = R4-C10H17O9-RO2-endo$  \[ 1.0E+00 \]
40 $R4-C10H17O9-RO2-endo + NO = R4-C10H17O9-RONO2-endo$  \[ KRO2NO*0.1 \]
41 $R4-C10H17O9-RO2-endo + NO = R4-C10H17O9-RO-endo + NO2$  \[ KRO2NO*0.9 \]
42 $R4-C10H17O9-RO2-endo + HO2 = R4-C10H17O9-ROOH-endo$  \[ KRO2HO2 \]
43 $\text{anti-} R4 = R11$  \[ 1.0E+05 \]
44 $R11 + NO = R11-RONO2$  \[ KRO2NO*0.1 \]
45 $R11 + NO = R11-RO$  \[ KRO2NO*0.9 \]
46 $R11 + HO2 = R11-ROOH$  \[ KRO2HO2 \]
47 $R11 = R12$  \[ 1.00E-01 \]
48 $R12 = R13$  \[ 1.00E+06 \]
49 $R13 + NO = R13-RONO2$  \[ KRO2NO*0.1 \]
50 $R13 + NO = R13-RO$  \[ KRO2NO*0.9 \]
51 $R13 + HO2 = R13-ROOH$  \[ KRO2HO2 \]
52 $R13 = R14$  \[ 1.00E+03 \]
53 $R14 + NO = R14-RONO2$  \[ KRO2NO*0.1 \]
54 $R14 + NO = R14-RO$  \[ KRO2NO*0.9 \]
55 $R14 + HO2 = R14-ROOH$  \[ KRO2HO2 \]
56 $R14 = R15$  \[ 1.00E-01 \]
57 $R15 = R16$  \[ 1.00E+06 \]
58 $R16 + NO = R16-RONO2$  \[ KRO2NO*0.1 \]
59 $R16 + NO = R16-RO$  \[ KRO2NO*0.9 \]
60 $R16 + HO2 = R16-ROOH$  \[ KRO2HO2 \]
61 $R16 = R17$  \[ 1.00E+06 \]
62 $R17 = R18$  \[ 1.00E+06 \]
63 $R18 + NO = R18-RONO2$  \[ KRO2NO*0.1 \]
64 $R18 + NO = R18-RO$  \[ KRO2NO*0.9 \]
65 $R18 + HO2 = R18-ROOH$  \[ KRO2HO2 \]
66 $R18 = R19$  \[ 1.00E+05 \]
67 $R19 + NO = R19-RONO2$  \[ KRO2NO*0.1 \]
68 $R19 + NO = R19-RO$  \[ KRO2NO*0.9 \]
69 $R19 + HO2 = R19-ROOH$  \[ KRO2HO2 \]
70 $R19 = C10H16O10$  \[ 1.00E-01 \]
71 $R7 = R7-C10H17O4-RO2$  \[ 1.00E+05 \]
72 $R7 = R7-C10H17O4-endo$  \[ 1.00E+00 \]
73 $R7 = R7-C10H17O6-RO2$  \[ KDEC \]
74 $R7-C10H17O6-RO2 + HO2 = R7-C10H17O6-ROOH$  \[ KRO2HO2 \]
75 $R7-C10H17O6-RO2 + NO = R7-C10H17O6-RONO2$  \[ KRO2NO*0.1 \]
76 $R7-C10H17O6-RO2 + NO = R7-C10H17O6-RO$  \[ KRO2NO*0.9 \]
R7-C10H17O6-RO = R7-C10H17O7-RO 5.00E-01
R7-C10H17O7-RO + NO = R7-C10H17O7-RONO2 KRO2NO*0.1
R7-C10H17O7-RO + NO = R7-C10H17O7-RO 1.00E-01
R7-C10H17O6-RO = R7-C7 + ACETONE KDEC
R7-C10H17O7-RO2 + NO = R7-C10H17O7-ROOH KRO2NO*0.1
R7-C10H17O7-RO2 + NO = R7-C10H17O7-RO 1.00E-01
R7-C10H17O7-RO2 + NO = R7-C10H17O7-RONO2 KRO2NO*0.1
R7-C10H17O8-RO2 + NO = R7-C10H17O8-RO + NO2 KRO2NO*0.9
R7-C10H17O6-RO2 = R7-C10H17O6-RO2-A 1.00E+02
R7-C10H17O6-RO2-A + NO = R7-C10H17O6-RONO2-A KRO2NO*0.1
R7-C10H17O6-RO2-A + NO = R7-C10H17O6-RO-A KRO2NO*0.9
R5-C10H17O7-RONO2-end + NO = R5-C10H17O7-RONO2-end KRO2NO*0.9
R5-C10H17O7-RONO2-end + NO = R5-C10H17O7-RONO2-end KRO2NO*0.1
R5-C10H17O7-RONO2-end + NO = R5-C10H17O7-RONO2-end KRO2NO*0.9
R5-C10H17O7-RONO2-end + NO = R5-C10H17O7-RONO2-end KRO2NO*0.1
R5-C10H17O7-RONO2-end + NO = R5-C10H17O7-RONO2-end KRO2NO*0.9
Table S5. Reported products and their molar yields from α-pinene + OH and α-pinene + O3 using different ionizations. Note that molar yields that are not from direct measurements are marked with asterisks (*).

| Reaction          | Molar yield | Products                                                                 | Ionization |
|-------------------|-------------|--------------------------------------------------------------------------|------------|
| α-pinene + OH     | ≤0.01 (17) * | Nitrate                                                                  |            |
|                   | 0.0044 (-50%/+100%) (21) * | Selected products: C10H16(O2)XO2 • (X=2) | Nitrate    |
|                   | 0.012 (-60%/+100%) (12) | C8,10H14,16O6,12,14                                                      | Nitrate    |
|                   | 0.00052 (-50%/+100%) (26) | C10H21(OO)(OOH)O2                                                       | Nitrate    |
|                   | 0.024 (-50%/+100%) (26) | HO-C10H15(OO)(OOH)O2                                                    | Acetate    |
|                   | 0.75-0.81 (-58%/+104%) (25) | HO-C10H15O2,6*                                                          | Ethylaminium Iodide |
|                   | 0.42-0.45 (-58%/+104%) (25) | C10H16O2•                                                                | Ethylaminium Iodide |
|                   | 0.17-0.19 (-58%/+104%) (25) | C10H16O2•                                                                | Ethylaminium |
|                   | 0.076 (-50%/+100%) (65) | HO-C10H15O2xO2* (X=2)                                                   | Methylaminium |
|                   | 0.076 (-50%/+100%) (65) | HO-C10H15O2xO2* (X=2)                                                   | Ethylaminium |
|                   | 0.0484 (-50%/+100%) (65) | HO-C10H15O2xO2* (X=2)                                                   | n-propylaminium |
|                   | 0.008-0.011 (-55%/+144%) (this study) | C10H16O10•                                                               | Nitrate    |
|                   | 0.021 (-50%/+100%) (26) | O,O-C10H15(O2)XO2• (X=1 - 4)                                            | Pyruvate   |
|                   | 0.024 (-50%/+100%) (26) | O,O-C10H15(O2)XO2• (X=1 - 4)                                            | Acetate    |
|                   | 0.024 (-50%/+100%) (26) | O,O-C10H15(O2)XO2• (X=1 - 4)                                            | Lactate    |
|                   | 0.034 (-50%/+100%) (26) | O,O-C10H15(O2)XO2• (X=1 - 4)                                            | Methyaminium |
|                   | 0.055 (-50%/+100%) (65) | O,O-C10H15(O2)XO2• (X=2, 3)                                             | Ethylaminium |
|                   | 0.056 (-50%/+100%) (65) | O,O-C10H15(O2)XO2• (X=2, 3)                                             | Ethylaminium |
|                   | 0.0365 (-50%/+100%) (65) | O,O-C10H15(O2)XO2• (X=2, 3)                                             | N-propylaminium |

Example products:
C10H14,16O2,11
C10H14,16O2,18
C10H21,28,30O6,14
C10H21,28,30O6,18

"Fingerprints" products:
C10H21,28,30O6,14
C10H21,28,30O6,18
C10H21,28,30O6,18
C10H21,28,30O6,18

Selected products:
O,O-C10H15(O2)XO2• (X=1 - 4)
O,O-C10H15(O2)XO2• (X=1 - 4)
O,O-C10H15(O2)XO2• (X=1 - 4)
O,O-C10H15(O2)XO2• (X=1 - 4)
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