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Accretion Product Formation from Ozonolysis and OH Radical Reaction of alpha-Pinene : Mechanistic Insight and the Influence of Isoprene and Ethylene

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2 **Accretion Product Formation from Ozonolysis and OH Radical Reaction of**
3 **α -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene**
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Abstract

α -Pinene, $C_{10}H_{16}$, represents one of the most important biogenic emissions in the atmosphere. Its oxidation products can significantly contribute to the secondary organic aerosol (SOA) formation. Here, we report on the formation mechanism of C_{19} and C_{20} accretion products from α -pinene oxidation, which are believed to be efficient SOA precursors. Measurements have been performed in a free-jet flow system. Detection of RO_2 radicals and accretion products was carried out by recent mass spectrometric techniques using different ionization schemes. Observed C_{10} - RO_2 radicals from α -pinene ozonolysis were $O,O-C_{10}H_{15}(O_2)_xO_2$ with $x = 0, 1, 2, 3$ and from the OH radical reaction $HO-C_{10}H_{16}(O_2)_\alpha O_2$ with $\alpha = 0, 1, 2$. All detected C_{20} accretion products can be explained via the accretion reaction $RO_2 + R'O_2 \rightarrow ROOR' + O_2$ starting from the measured C_{10} - RO_2 radicals. We speculate that C_{19} accretion products are formed in an analogous way assuming CH_2O elimination. Addition of isoprene, C_5H_8 , producing C_5 - RO_2 radicals, leads to C_{15} accretion products formed via cross-reactions with C_{10} - RO_2 radicals. This process is competing with the formation of C_{19}/C_{20} products from the pure α -pinene oxidation. A similar behavior has been observed for ethylene additives that form C_{12} accretion products. In the atmosphere a complex accretion product spectrum from self- and cross-reactions of available RO_2 radicals can be expected. Modeling atmospheric conditions revealed that C_{19}/C_{20} product formation is only reduced by a factor of 1.2 or 3.6 in isoprene-dominated environments assuming a 2-fold or 15-fold isoprene concentration over α -pinene, respectively, as present in different forested areas.

Introduction

Monoterpenes, $C_{10}H_{16}$, are emitted into the atmosphere with a mean global rate of 95×10^6 metric tons of carbon per year. α -Pinene, the main $C_{10}H_{16}$ compound, accounts for about one-third of that.^{1,2} Its atmospheric degradation, starting with the attack of hydroxyl (OH) or nitrate (NO_3) radicals or ozone (O_3) and subsequent O_2 addition, generates different RO_2 radicals as reactive intermediates.³ These RO_2 radicals can undergo isomerization reactions, such as intra-molecular H shifts⁴⁻⁸ or endo-cyclization in the case of unsaturated RO_2 radicals^{7,9,10}, which result in higher oxidized RO_2 radicals after subsequent O_2 addition. Competing bimolecular RO_2 radical reactions with NO, HO_2 or other RO_2 radicals as well as the RO_2 self-reaction represent the main loss processes in the atmosphere.³

It is well established that RO_2 self- and cross-reactions mainly form either the corresponding alkoxy radicals or an alcohol along with a carbonylic substance.¹¹⁻¹³ A third reaction pathway leading to peroxides, pathway (1), has been considered to be minor based on experimental results obtained from small RO_2 radicals such as CH_3O_2 or $C_2H_5O_2$.^{14,15}

In the course of investigations on atmospheric autoxidation processes and associated with the progress of analytical techniques in recent years, high-molecular weight products have been identified that are likely formed via the peroxide route according to pathway (1).^{5-8,16-19} Very recently, universal validity of accretion product formation from the self- and cross-reactions of RO_2 radicals via pathway (1) has been proposed.²⁰

Due to their lower vapor pressure, accretion products $ROOR'$ formed from C_{10} - RO_2 radicals of the α -pinene oxidation are believed to be more efficient aerosol precursors than the corresponding C_{10} closed-shell products.^{21,22} For example, calculated vapor pressures of C_{20} accretion products from the OH + α -pinene reaction were below 10^{-15} atm while those of the corresponding highly oxidized C_{10} closed-shell products were in the range $(0.5 - 8) \times 10^{-10}$ atm.⁷

α -Pinene emissions in forestlands are accompanied by emissions of a series of other hydrocarbons, such as isoprene and ethylene, which are present in large excess over the monoterpenes in some areas.²³⁻²⁵ For instance in the Amazon tropical forest, α -pinene mixing ratios are in the range of 0.05 - 0.15 ppbv, those of isoprene 1.14 - 2.72 ppbv and those of ethylene 0.63 - 1.68 ppbv.²³ It can be supposed that RO_2 radicals arising from the degradation of other hydrocarbons can significantly disturb the formation of pure α -pinene derived accretion products through competitive RO_2 cross-reactions. In this context, rates of early particle growth by organics, as experimentally determined for highly oxidized products from the pure α -pinene oxidation²⁶, do not hold describing field observations in isoprene-dominated forests.²⁷

While different groups consistently observed the formation of C₁₉ and C₂₀ accretion products from α -pinene oxidation up to now^{5-7,18,19,22,26}, the knowledge on the mechanism, the reacting RO₂ radicals and the kinetics of this process is very sparse. Here, we use a free-jet flow system for mechanistic and kinetic studies of accretion product formation from α -pinene oxidation at close to atmospheric conditions. RO₂ radicals and closed-shell products are measured simultaneously applying most recent mass spectrometric techniques that provide a more complete overview of the product distribution. Isoprene and ethylene additives to the reaction gas gave insight into competing RO₂ radical reactions and the resulting modification of the product distribution.

Methods

The investigations were carried out in a free-jet flow system at a temperature of 297 ± 1 K and a pressure of 1 bar purified air that allows experiments for almost wall-free conditions.^{7,20,28} Briefly, the flow system consists of an outer tube (i.d. 16 cm, length of 200 cm) and an inner tube (o.d. 9.5 mm) equipped with a nozzle. The first reactant, usually ozone, premixed with air (5 L min⁻¹ STP) is injected through the inner tube into the main gas stream (95 L min⁻¹ STP), which contains the second reactant, α -pinene and other organics if needed. The chosen flow conditions and the nozzle geometry ensure rapid reactant mixing and the development of a free-jet type gas flow. Gas sampling takes place from the center flow that is fully unaffected by wall interactions. The reaction time was 7.9 s.

Ozone was produced by means of an ozone generator (UVP OG-2). In the case of photolysis experiments, isopropyl nitrite was taken from a gas mixture prepared in a gas-metering unit. Photolysis was carried out downstream the mixing point of the gas streams by means of 8 NARVA 36W Blacklight Blue lamps.

Reactant concentrations were in the range: [O₃] = $(4.6 - 23) \times 10^{11}$, [α -pinene] = $(2.7 - 300) \times 10^{10}$, [isoprene] = $(6.6 - 146) \times 10^{10}$, [isoprene-1-¹³C] = $(6.6 - 145) \times 10^{10}$ and [ethylene] = $(3.65 - 80.3) \times 10^{11}$ molecules cm⁻³. Isopropyl nitrite concentrations in the photolysis experiments were $(1.7 - 31) \times 10^{10}$ molecules cm⁻³.

Detection of RO₂ radicals and accretion products was carried out by means of a CI-APi-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometer (Airmodus, Tofwerk) and a CI3-TOF (chemical ionization time-of-flight) mass spectrometer²⁹ sampling from the center flow of the free-jet flow system with a rate of 10 L min⁻¹ (STP) each. Used reagent ions of the CI-APi-TOF were protonated n-propylamine (C₃H₇NH₃⁺), acetate (CH₃COO⁻) or nitrate (NO₃⁻). The CI3-TOF was running in the ammonium mode (NH₄⁺). Mass spectra are depicted with the mass-to-charge unit Thompson (Th), where 1 Th = 1 u/e. Given concentrations from CI-APi-TOF measurements are lower end values based on calculated calibration factors. The NH₄⁺-CI3-TOF was calibrated using 3-hexanone from a gas standard. More information is given in the Supporting Information (SI).

Results and Discussion

Detection of RO₂ radicals from α -pinene oxidation. First, we focused on the investigation of the formed RO₂ radicals from the combined O₃/OH + α -pinene reaction, which represent the intermediates generating finally the accretion products. Recently, progress has been made for the detection of RO₂ radicals in different reaction systems applying acetate (CH₃COO⁻), ammonium (NH₄⁺) or protonated n-propylamine (C₃H₇NH₃⁺) as the reagent ion instead of the mostly used nitrate.^{7,20,29} Using these reagent ions, detected main RO₂ radicals from the O₃/OH + α -pinene reaction comprise two groups, i.e. the ozonolysis derived RO₂ radicals O,O-C₁₀H₁₅(O₂)_xO₂ with x = 0, 1, 2, 3 and those from the OH radical reaction HO-C₁₀H₁₆(O₂) _{α} O₂ with α = 0, 1, 2 (Figure 1, SI Figure S1).^{5-7,18} Bimolecular RO₂ loss processes were unimportant under the chosen reaction conditions because of the relatively low RO₂ radical concentrations mostly far smaller than 10⁸ molecules cm⁻³, the kinetic limitation of bimolecular RO₂ reactions for the reaction time of 7.9 s, and the absence of efficient reaction partners like HO₂ radicals in excess. The detection of the less oxidized RO₂ radicals with x = 0 and α = 0 is reported here for the first time.

Scheme 1 shows the expected pathways leading to the less oxidized RO₂ radicals with x = 0 and α = 0 based on the knowledge given in the literature.³⁰⁻³³ Ozonolysis of α -pinene leads to two different Criegee intermediates (CI)³⁴, each of which appear in different conformers³⁵. The CIs are formed with excess energy, denoted with an asterisk in the scheme. They can either decompose forming mainly OH radicals and O,O-C₁₀H₁₅ alkyl radicals or they are thermalized by collisions with any gas molecule M forming stabilized Criegee intermediates (sCI). Stabilization accounts for about 15% at atmospheric conditions.^{36,37} Due to the longer sCI lifetime compared to that of non-thermalized CI, also bimolecular sCI reactions with water vapor or trace gases are possible being competing with the decomposition pathway. The isomeric O,O-C₁₀H₁₅ alkyl radicals form the corresponding RO₂ radicals after O₂ addition, O,O-C₁₀H₁₅(O₂)_xO₂ with x = 0. OH radicals from the decomposition of Criegee intermediates react readily with α -pinene in the system forming after O₂ addition the isomeric RO₂ radicals HO-C₁₀H₁₆(O₂) _{α} O₂ with α = 0. Subsequently, repetitive RO₂ radical isomerization followed by O₂ addition may take place forming the higher oxidized RO₂ radicals O,O-C₁₀H₁₅(O₂)_xO₂ with x = 1, 2, 3 and HO-C₁₀H₁₆(O₂) _{α} O₂ with α = 1, 2. The exact chemical nature of these reaction steps and the chemical structures of the resulting RO₂ radicals are uncertain up to now. In ref.7 the variety of pathways and structures of OH-derived RO₂ radicals from α -pinene oxidation is presented as obtained from theoretical calculations. Here, it will be argued in the following with the chemical formulas only.

The RO₂ radical primarily formed from ozonolysis with x = 0 was consistently detected with high sensitivity by the C₃H₇NH₃⁺-APi-TOF and the NH₄⁺-CI3-TOF while the CH₃COO⁻-APi-TOF underestimated its concentration by more than three orders of magnitude. Higher oxidized RO₂ radicals with x = 1, 2, 3 were much more efficiently detected by the CH₃COO⁻-APi-TOF caused by the stronger binding of the (RO₂)CH₃COO⁻ clusters.^{38,39} The concentrations of the RO₂ radicals with

x = 1, 2, 3 were measured in reasonable agreement within a factor of about 2 - 3 applying the three ionization schemes, with exception of the RO₂ radical with x = 3 that was not observed by the NH₄⁺-CI3-TOF.

In the case of the different RO₂ radicals from the OH + α-pinene reaction, a similar oxidation-state-dependent behavior of the detection sensitivity for the three ionization schemes has been observed as for the ozonolysis derived RO₂ radicals (Figure 1).

Furthermore, unambiguous identification of a C₉-RO₂ radical, C₉H₁₅O₅, has been achieved by the NH₄⁺-CI3-TOF as well as the C₃H₇NH₃⁺-APi-TOF. The measured C₉H₁₅O₅ concentrations, however, did not exceed 4 × 10⁵ molecules cm⁻³ and the importance of C₉H₁₅O₅ radicals within the reaction system was assumed to be small.

Total ozonolysis products detected by the C₃H₇NH₃⁺-APi-TOF technique, including RO₂ radicals and the closed-shell products C₁₀H₁₆O₂ and C₁₀H₁₆O₃, account for 51 - 60 % of the reacted carbon being close to the attainment of the carbon balance (SI Figure S2). Almost identical results have been obtained using protonated ethylamine or n-butylamine as the reagent ion for the aminium-APi-TOF measurements. In the case of the OH radical reaction, however, the total products measured by the C₃H₇NH₃⁺-APi-TOF account only for 14 - 22 % of the reacted carbon assuming an OH yield of 85 % from α-pinene ozonolysis.⁴⁰ The reason for the seemingly low total sensitivity for OH radical products is not clear at the moment and more precise measurements are needed. The carbon balance obtained by the NH₄⁺-CI3-TOF measurements is similar to the one of the aminium-APi-TOF due to almost the same sensitivity for the main products.

Figure 1. Main RO₂ radicals from the O₃/OH + α-pinene reaction measured by different ionization schemes: **A** C₃H₇NH₃⁺-APi-TOF, **B** CH₃COO⁻-APi-TOF, **C** NH₄⁺-CI3-TOF. OH radicals were formed by the ozonolysis reaction. Depicted are the ozonolysis derived RO₂ radicals O₂O-C₁₀H₁₅(O₂)_xO₂ with x = 0, 1, 2, 3 in red and the OH-reaction derived RO₂ radicals HO-C₁₀H₁₆(O₂)_αO₂ with α = 0, 1, 2 in blue. Reactant concentrations were [O₃] = 6.8 × 10¹¹ and [α-pinene] = (2.7 - 40.5) × 10¹⁰ molecules cm⁻³.

Scheme 1. Reaction scheme for the formation of the first, less oxidized RO₂ radicals **A**: O,O-C₁₀H₁₅O₂ from α -pinene ozonolysis and **B**: HO-C₁₀H₁₆O₂ from the OH + α -pinene reaction. The asterisk indicates the presence of excess energy, M stands for all gas-phase molecules acting as collision partner. The alkyl radical moiety is highlighted by a shaded oval.

Formation of C₁₉/C₂₀ accretion products. Figure 2 shows a mass spectrum from the O₃/OH + α -pinene reaction in the mass range of 380 - 500 Th recorded by the C₃H₇NH₃⁺-APi-TOF. The spectrum of the extended mass range of 500 - 650 Th is given in SI Figure S3. The measurement in the presence of the OH radical scavenger revealed the accretion products that are exclusively formed via reactions of ozonolysis derived RO₂ radicals, see the upper part in red of Figure 2 and SI Figure S3. Additional experiments on the pure OH + α -pinene reaction, forming OH radicals via photolysis of isopropyl nitrite, disclosed the accretion products that solely arise from OH-reaction derived RO₂ radicals, i.e. C₂₀H₃₄O_{4,6,8,10,12} (SI Figure S4). Their C₃H₇NH₃⁺-adduct signals are marked in blue in the given spectra (Figure 2, SI Figure S3).

Starting from the 7 main C₁₀-RO₂ radicals generated by the combined O₃/OH + α -pinene reaction (Figure 1), all possible C₂₀ accretion products from RO₂ self- and cross-reactions according to pathway (1) have been observed. These are C₂₀H₃₀O_{6,8,10,12,14,16,18} formed solely from ozonolysis derived RO₂ radicals O,O-C₁₀H₁₅(O₂)_xO₂ with x = 0, 1, 2, 3, C₂₀H₃₄O_{4,6,8,10,12} from OH-reaction derived RO₂ radicals HO-C₁₀H₁₆(O₂)_αO₂ with α = 0, 1, 2 and C₂₀H₃₂O_{5,7,9,11,13,15} from the mixed reactions of both types of RO₂ radicals. The larger number of remaining accretion product signals in the spectra can be explained in a similar way according to pathway (1) but with an involvement of a formal CH₂O elimination. Accordingly, C₁₉H₂₈O_{5,7,9,11,13} can be formed from ozonolysis derived RO₂ radicals and

$C_{19}H_{30}O_{6,8,10,12,14}$ from the mixed reactions of both types of RO_2 radicals. No C_{19} accretion products have been observed as a result of the pure OH + α -pinene reaction. It should be noted, that there is no experimental evidence for a CH_2O release and we cannot state a possible mechanistic explanation for that at the moment. It is just a suggestion that helps to describe the experimental findings. Determination of the exact accretion product masses supports the proposed chemical composition of the accretion products (SI Table S1).

Figure 2. Accretion products from the $O_3/OH + \alpha$ -pinene reaction in the mass range 390 - 500 Th measured by $C_3H_7NH_3^+$ -APi-TOF, the upper part in red is obtained in the presence of the OH radical scavenger propane, the lower spectrum “w/o α -pinene” characterizes the background. Reactant concentrations were $[O_3] = 2.3 \times 10^{12}$, $[\alpha\text{-pinene}] = 1.2 \times 10^{12}$ and $[\text{propane}] = 2.5 \times 10^{16}$ molecules cm^{-3} . Given numbers are nominal masses of the $C_3H_7NH_3^+$ -adducts with the accretion products. Color coding of $ROOR'$ formation via pathway (1):
red: $C_{20}H_{30}O_{6,8,10}$ via $O,O\text{-}C_{10}H_{15}(O_2)_{x_1}O_2 + O,O\text{-}C_{10}H_{15}(O_2)_{x_2}O_2$ for $x_1 + x_2 = 0, 1, 2$ (For example: $C_{20}H_{30}O_{10}$ can be formed from RO_2 radicals with $x_1 = 0$ and $x_2 = 2$ or $x_1 = 1$ and $x_2 = 1$, etc.); red italic bold: $C_{19}H_{28}O_{5,7,9,11}$ via $O,O\text{-}C_{10}H_{15}(O_2)_{x_1}O_2 + O,O\text{-}C_{10}H_{15}(O_2)_{x_2}O_2$ for $x_1 + x_2 = 0, 1, 2, 3$ incl. CH_2O release; blue: $C_{20}H_{34}O_{4,6,8,10}$ via $HO\text{-}C_{10}H_{16}(O_2)_{\alpha_1}O_2 + HO\text{-}C_{10}H_{16}(O_2)_{\alpha_2}O_2$ for $\alpha_1 + \alpha_2 = 0, 1, 2, 3$; black: $C_{20}H_{32}O_{5,7,9}$ via $O,O\text{-}C_{10}H_{15}(O_2)_xO_2 + HO\text{-}C_{10}H_{16}(O_2)_\alpha O_2$ for $x + \alpha = 0, 1, 2$; black italic bold: $C_{19}H_{30}O_{6,8,10}$ via $O,O\text{-}C_{10}H_{15}(O_2)_xO_2 + HO\text{-}C_{10}H_{16}(O_2)_\alpha O_2$ for $x + \alpha = 1, 2, 3$ incl. CH_2O release.

We tested for unwanted processes in the ion-molecule reaction (IMR) region of the CI-APi-TOF that could affect the detected signals of the accretion products. To do so, measurements with increased reactant concentrations have been conducted sampling either the undiluted reactions gas or after dilution by a factor of 8.^{7,20} The measured accretion product signals decreased by a factor of 6.3 - 8.5

after dilution being in line with the dilution factor within the experimental uncertainty. That confirms that the product formation predominantly takes part in the flow system and not in the IMR region (SI Figure S5).

Accretion product spectra were also recorded applying the mostly used NO_3^- -APi-TOF technique⁵⁻⁷ (SI Figure S6). The spectra are qualitatively in good agreement with the results from the $\text{C}_3\text{H}_7\text{NH}_3^+$ -APi-TOF for accretion products with 8 - 9 O atoms or more. For ROOR' with lower oxygen content, however, the NO_3^- -APi-TOF is less sensitive or totally fails to detect them. This behavior is obviously due to missing functional groups in the less oxidized products that prevent sufficient strong binding with the NO_3^- ion.^{38,41} Nevertheless, the detectable accretion products by the NO_3^- -APi-TOF conclusively support the proposed assignment of ROOR' products to the reacting RO_2 precursors. Accretion products with 4 or 5 O atoms, not detectable by the NO_3^- -APi-TOF, were observed by the NH_4^+ -CI3-TOF and the $\text{C}_3\text{H}_7\text{NH}_3^+$ -APi-TOF in good agreement including $\text{C}_{20}\text{H}_{30}\text{O}_4$ and $\text{C}_{20}\text{H}_{30}\text{O}_5$ with relatively low concentrations (SI Figure S7). Formation paths leading to $\text{C}_{20}\text{H}_{30}\text{O}_4$ and $\text{C}_{20}\text{H}_{30}\text{O}_5$ are not understood at the moment.

Some studies in the literature point to accretion product formation from ozonolysis experiments based on sCI reactions.^{42,43} However, rapid unimolecular decomposition as well as the effective water vapor reactions result in low steady-state sCI concentrations from α -pinene ozonolysis⁴⁴ making an efficient sCI contribution to the accretion product formation questionable, at least for close to atmospheric reactant conditions. We tested for possible sCI reactions forming accretion products by adding acetic acid as sCI scavenger. Acetic acid additive of 5.0×10^{12} molecules cm^{-3} results in an additional sCI loss rate of 10^3 s^{-1} assuming a $\text{CH}_3\text{COOH} + \text{sCI}$ rate coefficient of $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴⁵ The addition of acetic acid yielded a measureable lowering of the RO_2 radical concentrations in the range of 11 - 17% due to suppression of the unimolecular sCI decomposition, that forms the precursors of the RO_2 radicals $\text{O}_3\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_x\text{O}_2$ and $\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_\alpha\text{O}_2$ to some extent, see Scheme 1. It is to be noted, that a new, very strong signal appeared, which is consistent with an addition product of $\text{CH}_3\text{COOH} + \text{sCI}$. The comparison of the accretion product spectrum in the presence of acetic acid, upper part, with that in absence of the addition is depicted in Figure 3. In the whole spectrum, accretion product signals from the sCI scavenger experiment were about 20 - 30% lower compared to the basis spectrum. This behavior reflects the square dependence of RO_2 concentrations for the ROOR' formation kinetics according to pathway (1). Reduction of RO_2 concentrations by 11 - 17% should theoretical lead to a lowering of the ROOR' concentrations by 21 - 31%. Thus, as a result of the sCI scavenger experiments there were no indications for sCI-driven accretion product formation. The finding is supported by the outcome of the pure $\text{OH} + \alpha$ -pinene reaction in total absence of Criegee intermediates, that also gave rise to the five possible ROOR' products, $\text{C}_{20}\text{H}_{34}\text{O}_{4,6,8,10,12}$, from $\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_\alpha\text{O}_2$ with $\alpha = 0, 1, 2$ (SI Figure S4).

Moreover, also any heterogeneous process for accretion product formation⁴⁶ is highly unlikely because wall interactions are strongly suppressed in the used flow system.

Figure 3. Accretion products from the $\text{O}_3/\text{OH} + \alpha\text{-pinene}$ reaction in the mass range 390 - 500 Th measured by $\text{C}_3\text{H}_7\text{NH}_3^+$ -APi-TOF, the upper part in red is obtained in the presence of the sCI scavenger. Reactant concentrations were $[\text{O}_3] = 2.3 \times 10^{12}$, $[\alpha\text{-pinene}] = 1.2 \times 10^{12}$ and $[\text{acetic acid}] = 5.0 \times 10^{12}$ molecules cm^{-3} . Stated nominal masses of the $\text{C}_3\text{H}_7\text{NH}_3^+$ -adducts with ROOR' belong to $\text{C}_{20}\text{H}_{30}\text{O}_{6,8,10}$ (in red) formed from ozonolysis derived RO_2 radicals and $\text{C}_{20}\text{H}_{34}\text{O}_{4,6,8,10}$ (in blue) from OH-reaction derived RO_2 radicals.

Kinetics of accretion product formation. The free-jet flow system allows conducting the experiments with negligible wall interactions. Particles were not present in the purified feed gas and new particle formation did not take place due to the low reactant conversion and the short reaction time. Thus, RO_2 radical and accretion product concentrations were not influenced by unwanted wall losses or gas/particle partitioning, which admits the determination of rate coefficients based on measured reactant and product concentrations. The $\text{C}_{19}/\text{C}_{20}$ product concentrations, ROOR', showed a square dependence regarding increasing $\alpha\text{-pinene}$ concentrations for constant O_3 (Figure 4), i.e. a slope of about 2 for $\log([\text{ROOR}'])$ vs. $\log([\alpha\text{-pinene}])$, that also stands for a square dependence with respect to reacted $\alpha\text{-pinene}$. The RO_2 radicals increased almost linearly with rising $\alpha\text{-pinene}$ conversion (Figure 1, SI Figure S8). This behavior is in line with the 2nd order kinetics of accretion product formation according to pathway (1) starting from the respective RO_2 radicals.

Figure 4. A series of C₁₉/C₂₀ accretion products, ROOR', from the O₃/OH + α-pinene reaction as a function of the α-pinene concentration for constant O₃ measured by C₃H₇NH₃⁺-APi-TOF. The dashed line represents the slope of 2 for log([ROOR']) vs. log([α-pinene]). Reactant concentrations were [O₃] = 6.4 × 10¹¹ and [α-pinene] = (1.08 - 12.1) × 10¹¹ molecules cm⁻³. The respective measurements of RO₂ radicals are given in SI Figure S8.

For the chosen experimental conditions, RO₂ radical concentrations increased linearly with time and RO₂ consuming reaction steps did not significantly influence their concentrations (SI Figure S9). Hence, the rate coefficients k_1 of accretion product formation via pathway (1) can be estimated in a simple manner according to equation (I) using the measured concentrations of ROOR' and RO₂ radicals at the reaction time t , see Supporting Information (SI):

$$k_1 = \frac{[\text{ROOR'}]_t}{[\text{RO}_2]_t \times [\text{R'O}_2]_t} \frac{3}{t} \quad (\text{I})$$

It is assumed that the highest oxidized RO₂ radicals, O,O-C₁₀H₁₅(O₂)_xO₂ with $x = 3$ and HO-C₁₀H₁₆(O₂)_αO₂ with $\alpha = 2$ are detected with close to maximum sensitivity by the C₃H₇NH₃⁺-APi-TOF due to the expected high content of oxygen-containing moieties and the strong binding with the reagent ion. High sensitivity detection can also be assumed for O,O-C₁₀H₁₅O₂, the predominant RO₂ radical from ozonolysis, because of the carbon balance of ozonolysis products of up to 60%. That justifies selection of their reactions for the estimation of rate coefficients of ROOR' formation. Accretion products according to pathway (1), which can be attributed to reactions of the chosen RO₂ radicals with reasonable certainty, are C₂₀H₃₀O₁₈, C₂₀H₃₄O₁₂ and C₂₀H₃₀O₆ from the respective self-reactions and C₂₀H₃₂O₁₅ from the cross-reaction of O,O-C₁₀H₁₅(O₂)₃O₂ with HO-C₁₀H₁₆(O₂)₂O₂. The

kinetic analysis based on equation (I) revealed the expected linear dependence $[\text{ROOR}']_t$ vs. $[\text{RO}_2]_t \times [\text{R}'\text{O}_2]_t$ properly (SI Figure S10). The corresponding rate coefficients are in the range $(9.7 - 79) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with an assumed uncertainty being not higher than a factor of 3 (Table 1). Additionally, rate coefficients of the RO_2 self-reactions with respect to ROOR' formation of $\text{C}_6\text{H}_{13}\text{O}_2$, $\text{HO-C}_5\text{H}_8\text{O}_2$ and $\text{HO-C}_9\text{H}_{12}(\text{O}_2)\text{O}_2$ from the OH radical reaction with n-hexane, isoprene and mesitylene (1,3,5-trimethylbenzene), respectively, are shown in Table 1 for comparison.²⁰ The rate coefficients cover a range of more than three orders of magnitude. The RO_2 reactivity in the process of accretion product formation increases with rising functionalization of the RO_2 radicals²⁰ and probably with the RO_2 size as well. Comprehensive experimental studies, including theoretical investigations, are needed to get a deeper insight into the ROOR' formation process on molecular level.

Table 1. Selected rate coefficients of accretion product formation via $\text{RO}_2 + \text{R}'\text{O}_2 \rightarrow \text{ROOR}' + \text{O}_2$ from the $\text{O}_3/\text{OH} + \alpha$ -pinene reaction and comparison with data from a former study²⁰. $T = 297 \pm 1 \text{ K}$

RO_2	$\text{R}'\text{O}_2$	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{O},\text{O-C}_{10}\text{H}_{15}\text{O}_2$	$\text{O},\text{O-C}_{10}\text{H}_{15}\text{O}_2$	9.7×10^{-12}
$\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_2\text{O}_2$	$\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_2\text{O}_2$	3.7×10^{-11}
$\text{O},\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_3\text{O}_2$	$\text{O},\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_3\text{O}_2$	4.8×10^{-11}
$\text{HO-C}_{10}\text{H}_{16}(\text{O}_2)_2\text{O}_2$	$\text{O},\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_3\text{O}_2$	7.9×10^{-11}
^a $\text{HO-C}_5\text{H}_8\text{O}_2$	$\text{O},\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_x\text{O}_2 \quad x = 0 - 3$	$(1.3 - 2.3) \times 10^{-11}$
^b $\text{HO-C}_2\text{H}_4\text{O}_2$	$\text{O},\text{O-C}_{10}\text{H}_{15}(\text{O}_2)_x\text{O}_2 \quad x = 0 - 3$	$(1.2 - 3.6) \times 10^{-11}$
^c $\text{C}_6\text{H}_{13}\text{O}_2$ (from OH + n-hexane)	$\text{C}_6\text{H}_{13}\text{O}_2$	9.2×10^{-14}
^c $\text{HO-C}_5\text{H}_8\text{O}_2$ (from OH + isoprene)	$\text{HO-C}_5\text{H}_8\text{O}_2$	6.0×10^{-13}
^c $\text{HO-C}_9\text{H}_{12}(\text{O}_2)\text{O}_2$ (from OH + mesitylene)	$\text{HO-C}_9\text{H}_{12}(\text{O}_2)\text{O}_2$	$(1.4 - 2.5) \times 10^{-10} \text{ }^d$

^a from experiments with isoprene addition

^b from experiments with ethylene addition

^c ref.²⁰

^d results from different reaction conditions

Addition of isoprene or ethylene. Experiments in the presence of isoprene, C₅H₈, or ethylene, C₂H₄, demonstrate how additional RO₂ radicals, i.e. HO-C₅H₈O₂ or HO-C₂H₄O₂, modify the accretion product formation in the O₃/OH + α -pinene system.

Figure 5 shows the measured RO₂ radical concentrations from a series with rising isoprene addition and otherwise constant reaction conditions. Increasing isoprene concentrations led to lowering of the steady-state OH radical concentration due to enhanced OH consumption by the OH + isoprene reaction, see calculated OH radical concentration “OH calc.”. Accordingly, concentrations of OH-reaction derived RO₂ radicals, HO-C₁₀H₁₆(O₂) _{α} O₂ with α = 1, 2 shown in Figure 5, decreased while HO-C₅H₈O₂ radical concentrations grew up nearing a maximum level for [isoprene] / [α -pinene] > 3 with more than 85% OH consumption by isoprene, $k(\text{OH}+\text{isoprene}, 298 \text{ K}) = 1.0 \times 10^{-10}$ and $k(\text{OH}+\alpha\text{-pinene}, 298 \text{ K}) = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴⁷ The measured HO-C₅H₈O₂ concentrations were within a factor of 2 of the calculated values. Moreover, a signal appeared at the nominal product mass of 101 Th that was attributed to the RO₂ radical C₄H₅(O)O₂ formed most likely from the C₄ Criegee intermediate of isoprene ozonolysis.⁴⁸ Within the present study, no effort was undertaken for the identification of products of C₄H₅(O)O₂ due to its low concentration and the expected small importance for product formation. The formation and the resulting concentrations of ozonolysis derived RO₂ radicals, O,O-C₁₀H₁₅(O₂) _{x} O₂ with x = 0 and 2 given in Figure 5, were not influenced by the isoprene addition due to the unchanged ozone concentration and the small importance of RO₂ radical consuming reactions for the RO₂ radical concentrations.

Figure 5. RO₂ radicals from the O₃/OH + α -pinene reaction for increasing isoprene addition and otherwise constant reactant conditions. HO-C₅H₈O₂ and C₄H₅(O)O₂ formed from isoprene have been measured by the NH₄⁺-CI₃-TOF, the C₁₀-RO₂ radicals by the C₃H₇NH₃⁺-APi-TOF. Concentrations of ozonolysis derived RO₂ radicals are depicted in red and the OH-reaction derived RO₂ radicals in blue. “HO-C₅H₈O₂ calcs.” and “OH calcs.” were obtained by modeling. Reactant concentrations were [O₃] = 2.0 × 10¹², [α -pinene] = 3.9 × 10¹¹ and [isoprene] = (0 - 1.46) × 10¹² molecules cm⁻³.

Concentrations of the accretion products strictly followed the behavior of their RO₂ radical precursors with rising isoprene addition according to the kinetics of the respective RO₂ self- and cross-reactions via pathway (1) (Figure 6). Hence, accretion products ROOR' arising solely from ozonolysis derived RO₂ radicals were unaffected by the isoprene additives due to the unaffected concentrations of ozonolysis derived RO₂ radicals, e.g. C₁₉H₂₈O₇ and C₁₉H₂₈O₁₁ in Figure 6A. Concentrations of ROOR' formed from cross-reactions of OH-reaction derived and ozonolysis derived RO₂ radicals dropped down in parallel to the declining OH level in the experiment, see C₁₉H₃₀O₈ and C₂₀H₃₂O₉ in Figure 6A. A steeper decrease than the declining OH level was detected for ROOR' that are formed from two OH-reaction derived RO₂ radicals, again in line with the expected behavior, see C₂₀H₃₄O₈ in Figure 6A. Generally, the experiments with additional RO₂ radicals, here shown for HO-C₅H₈O₂ radicals, confirmed the attribution of the reacting C₁₀-RO₂ radicals to the observed C₁₉/C₂₀ accretion products as described before.

With increasing isoprene addition, rising signals of C₁₅ accretion products from the reaction of HO-C₅H₈O₂ radicals with C₁₀-RO₂ radicals emerged in the spectrum. Figure 6B shows the occurrence of the 4 possible ROOR' products, C₁₅H₂₄O_{5,7,9,11}, from the reaction of HO-C₅H₈O₂ radicals with O₂-C₁₀H₁₅(O₂)_xO₂ radicals with x = 0, 1, 2, 3. Experiments with isoprene-1-¹³C confirmed the signal assignment. Kinetic analysis of the accretion product formation according to pathway (1) led to rate coefficients in the range of $(1.3 - 2.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the C₁₅ products (Table 1, SI Figure S11). It should be noted that also the signal of C₁₀H₁₈O₄ from the HO-C₅H₈O₂ radical self-reaction via pathway (1) was detected in line with the finding of a former study.²⁰

Figure 6. Accretion product formation from the O₃/OH + α-pinene reaction as a function of increasing isoprene addition. **A:** C₁₉/C₂₀ products solely formed from ozonolysis derived RO₂ radicals in red, solely from OH-reaction derived RO₂ radicals in blue and those from both types of RO₂ radicals in black. **B:** C₁₅ products from the reaction of HO-C₅H₈O₂ radicals with O₃-C₁₀H₁₅(O₂)_xO₂ radicals with x = 0, 1, 2, 3. All products have been measured by the C₃H₇NH₃⁺-APi-TOF. Reaction conditions are stated in the caption of Figure 5.

Experiments with ethylene addition revealed the same behavior for the C₁₀-RO₂ radicals and C₁₉/C₂₀ accretion products as observed in the case of runs with isoprene addition. Due to its lower OH reactivity, ethylene was applied in a larger excess over α-pinene than isoprene, $k(\text{OH} + \text{ethylene}, 298 \text{ K}) = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴⁷ Cross-reactions of HO-C₂H₄O₂ radicals with C₁₀-RO₂ radicals formed the corresponding C₁₂ accretion products. SI Figure S12 shows the concentrations of C₁₂H₂₀O_{5,7,9,11} from the reaction with O₃-C₁₀H₁₅(O₂)_xO₂ radicals with x = 0, 1, 2, 3. The corresponding rate coefficients were in the range of $(1.2 - 3.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table 1, SI Figure S13).

Moreover, also the OH radical scavenger experiments with propane have been analyzed with respect to new accretion product formation. Presence of high propane concentrations leads to the formation of propyl peroxy radicals, C₃H₇O₂, instead of HO-C₁₀H₁₆(O₂)_xO₂ radicals. The C₃H₇O₂ radicals formed C₁₃ accretion products from the reaction with ozonolysis derived C₁₀-RO₂ radicals O₃-C₁₀H₁₅(O₂)_xO₂ according to pathway (1) (SI Figure S14). This finding further supports the

universal validity of accretion product formation from all RO₂ radical combinations in a reaction system.

Atmospheric implications. The measurements showed that C₂₀ accretion products according to pathway (1) have been formed from all possible combinations of the 7 main C₁₀-RO₂ radicals. Additionally, C₁₉ accretion products occurred whose formation can be tentatively explained in an analogous way assuming CH₂O elimination. With that, almost the whole accretion product distribution can be mechanistically explained. Obtained rate coefficients of RO₂ radical self- and cross-reaction according to pathway (1) are in the range $(9.7 - 79) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ being similar or slightly higher than the k-values of $(5 - 20) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ generally applied for the major RO₂ loss reactions with NO or HO₂ radicals.¹¹⁻¹³ The relatively high rate coefficients of C₁₀-RO₂ radical cross-reactions with HO-C₅H₈O₂ or HO-C₂H₄O₂ (Table 1) suggest that effective accretion product formation is possible with a number of other RO₂ radicals present in the atmospheric reaction system, such as those generated from other alkenes or aromatics.²³⁻²⁵ Thus, a complex accretion product spectrum can be expected as already proposed from an experimental study with a series of model RO₂ radicals.²⁰ A reasoned evaluation of the role of RO₂ radical self- and cross-reaction according to pathway (1) for different situations in the atmosphere is possible based on the rate coefficients obtained in this study and from the former study²⁰.

In atmospheric science the mechanistic explanation of early particle growth suppression in isoprene-dominated forestlands^{27,49} is still an open question. In a recent field study carried out in a mixed deciduous forest in Alabama, no growth of sub-2 nm particles was observed while C₉ and C₁₀ low-volatility oxygenated products (HOMs) from α -pinene oxidation were measured with mixing ratios of 20 - 30 pptv.²⁷ This behavior stands in stark contrast to the expected growth rates by HOMs from pure α -pinene oxidation as deduced from a chamber study.²⁶ Moreover, suppression of particle formation by isoprene was reported as a result of a plant chamber experiment, which was simply explained by lowering of the OH radical level in the system due to the isoprene additive.⁵⁰ In the atmosphere, however, the OH radical concentration is not lowered in isoprene-dominated areas calling a direct application of the plant chamber findings to the atmosphere into question.⁵¹

We suppose that probably the C₁₉/C₂₀ accretion products play a critical role for the early particle growth, rather than the C₉/C₁₀ HOMs, and performed modeling calculations for atmospheric daytime conditions with different isoprene / α -pinene ratios. The modeling considered constant oxidant concentrations of OH radicals and ozone of 2×10^6 and $7.5 \times 10^{11} \text{ molecules cm}^{-3}$, respectively, and constant concentrations of HO₂ radicals and NO that are defining the main loss reactions of the RO₂ radicals. Rate coefficients for accretion product formation were taken from the present study, see Supporting Information (SI). 2-fold isoprene excess over α -pinene, representing the Alabama conditions, led to a reduction of the C₁₀-RO₂ radical concentration of about 10% and in the case of a

15-fold isoprene excess, as present in the Amazon forest, to a reduction of 48% (SI Figure S15).^{23,27} Consequently, the concentrations of the C₁₉/C₂₀ accretion products dropped down by a factor of 1.2 and 3.6, respectively. Concentrations of the C₁₅ products substantially increased with rising isoprene excess. As a result of the modeling, it is difficult to assume that C₁₉/C₂₀ product reduction of only ~20 % for the Alabama case can explain early growth suppression by isoprene. Further studies are needed in order to discover reasons for early growth suppression in isoprene-dominated forestlands, such as in Alabama or in the Amazon forest.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at ...

Additional Information regarding instrumental analysis, kinetic analysis and other materials are shown in Figures S1 - S15 and Table S1.

Notes

The authors declare no competing financial interest.

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