Synergistic O$_3$ + OH oxidation pathway to extremely low-volatility dimers revealed in β-pinene secondary organic aerosol

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Dimeric compounds contribute significantly to the formation and growth of atmospheric secondary organic aerosol (SOA) derived from monoterpene oxidation. However, the mechanisms of dimer production, in particular the relevance of gas- vs. particle-phase chemistry, remain unclear. Here, through a combination of mass spectrometric, chromatographic, and synthetic techniques, we identify a suite of dimeric compounds (C$_{15}$-H$_{26}$, C$_{19}$S$_{5}$-1) formed from concerted O$_3$ and OH oxidation of β-pinene (i.e., accretion of O$_2$- and OH-derived products/intermediates). These dimers account for an appreciable fraction (5.9–25.4%) of the β-pinene SOA mass and are designated as extremely low-volatility organic compounds. Certain dimers, characterized as covalent dimer esters, are conclusively shown to form through heterogeneous chemistry, while evidence of dimer production via gas-phase reactions is also presented. The formation of dimers through synergistic O$_3$ + OH oxidation represents a potentially significant, heretofore-unidentified source of low-volatility monoterpene SOA. This reactivity also suggests that the current treatment of SOA formation as a sum of products originating from the isolated oxidation of individual precursors fails to accurately reflect the complexity of oxidation pathways at play in the real atmosphere. Accounting for the role of synergistic oxidation in ambient SOA formation could help to resolve the discrepancy between the measured atmospheric burden of SOA and that predicted by regional air quality and global climate models.

Dimeric compounds | secondary organic aerosol | synergistic oxidation | atmospheric accretion chemistry | dimer formation | monoterpene

The oxidation of monoterpenes (C$_{10}$H$_{16}$) represents a substantial and well-established source of atmospheric secondary organic aerosol (SOA) (1, 2), which constitutes a dominant mass fraction (15–80%) of fine particulate matter (PM$_{2.5}$) (3) and exerts large but uncertain effects on Earth’s radiative balance (4) as well as adverse impacts on regional air quality and human health (5, 6). High-molecular-weight, low-volatility dimeric compounds have been identified as significant components of both ambient (7–11) and laboratory-derived (12–22) monoterpene SOA, and have been implicated as key players in new particle formation and growth (9–14, 23–26), particle viscosity (27), and cloud condensation nuclei (CCN) activity (8, 24, 26).

Accumulating studies of α-pinene SOA indicate that a vast majority of these dimers are formed only through O$_3$- and not OH-initiated oxidation, despite the apparent monomeric building blocks being present in both oxidative systems (11–13). Particle-phase reactions of closed-shell monomers [e.g., α-diol addition/condensation (15–18), (peroxy)hemiacetal/acetal formation (16, 21, 22), esterification (7, 18–21), and gem-diol formation (16, 17)] and gas-phase reactions involving early-stage oxidation products and/or reactive intermediates [e.g., stabilized Criegee intermediates (SCIs), carboxylic acids, and organic peroxy radicals (RO$_2$) (9–14, 23–26)] have been advanced as possible dimer formation pathways. However, the mechanisms underlying dimer production and the relative importance of gas- vs. particle-phase chemistry remain unresolved.

In this work, we investigate the formation, identity, and abundance of molecular products in SOA derived from the O$_3$- and OH-initiated oxidation of β-pinene, the second-most-abundant monoterpene emitted to the atmosphere (global emissions estimated at 19 Tg y$^{-1}$) (28). Through detailed chromatographic and mass spectrometric analysis, coupled with $^{13}$C isotopic labeling and HO/SCI scavenging, we identify a reactive pathway to produce low-volatility dimeric compounds in SOA formed from monoterpene ozonolysis involving reaction of O$_3$-derived products/intermediates/fragments with compounds generated from oxidation by OH produced in situ via vinyl hydroperoxide (VHP) decomposition. We present evidence for formation of these dimers via both gas- and particle-phase processes, underscoring the complexity of atmospheric accretion chemistry. In establishing that O$_3$ and OH can act in concert to form nontrivial yields of dimeric SOA constituents, we highlight the potential significance of synergistic oxidation in ambient aerosol formation.

Results and Discussion

Dimers in β-Pinene SOA. β-Pinene ozonolysis and photooxidation experiments were carried out in the Caltech dual 24 m$^2$ Teflon Environmental Chambers (CTEC) (Materials and Methods). A significant fraction (25.4%) of the β-pinene SOA mass is assigned to extremely low-volatility organic compounds. Certain dimers, characterized as covalent dimer esters, are conclusively shown to form through heterogeneous chemistry, while evidence of dimer production via gas-phase reactions is also presented. The formation of dimers through synergistic O$_3$ + OH oxidation represents a potentially significant, heretofore-unidentified source of low-volatility monoterpene SOA. This reactivity also suggests that the current treatment of SOA formation as a sum of products originating from the isolated oxidation of individual precursors fails to accurately reflect the complexity of oxidation pathways at play in the real atmosphere. Accounting for the role of synergistic oxidation in ambient SOA formation could help to resolve the discrepancy between the measured atmospheric burden of SOA and that predicted by regional air quality and global climate models.

Significance

Secondary organic aerosol (SOA) is ubiquitous in the atmosphere and plays a pivotal role in climate, air quality, and health. Monoterpenes, emitted in large quantities from forested regions, are a dominant source of SOA globally, with dimers having been identified as key contributors to particle formation and growth. Here, we establish the role of concerted oxidation by O$_3$ and OH as a significant route to dimer formation in SOA generated from β-pinene, the second-most-abundant monoterpene emitted to the atmosphere. Production of this class of dimers is found to occur through both gas- and particle-phase processes. Dimer formation via synergistic O$_3$ + OH oxidation could represent an appreciable source of “missing” SOA not included in current atmospheric models.

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custom-modified particle-into-liquid sampler (PILS) integrated with ultra-performance liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry operated in negative ion mode [UPLC/(−)ESI-Q-TOF-MS] was used to characterize the time-resolved SOA molecular composition (Materials and Methods) (29). Base peak ion (BPI) chromatograms of the O₃- and OH-derived β-pinene SOA are shown in Fig. 1. The chromatographic fingerprint of the O₃ system displays distinct monomeric and dimeric regions. Conversely, while the identities of the monomers in both systems are similar, dimers measurable by PILS + UPLC/(−)ESI-Q-TOF-MS were not formed above the detection limit in the OH system, consistent with previous LC/(−)ESI-MS studies on dimer formation in α-pinene SOA (11–13). The monomers, on average, exhibit higher O/C ratios than the dimers, suggesting that deoxygenation (e.g., condensation) is operative in dimer formation (18, 21). That the dimers in the O₃-derived SOA elute at retention times (RT) distinct from those of the monomers and are undetected in SOA produced from OH oxidation demonstrates that they are authentic β-pinene SOA products rather than ion-source artifacts (e.g., nonvolatile adducts) formed during the (−)ESI process.

The absence of detectable dimers in pinene photooxidation systems has prompted SCIs, specifically reaction of SCIs with first-generation carboxylic acids forming hydroperoxide esters (11, 12, 15), to be implicated as potential drivers of monoterpene accretion chemistry. However, we recently demonstrated that dimers identified in α-pinene SOA using LC/ESI-MS methods do not contain (hydro)peroxide moieties (30). Further, no clear reduction in dimer abundance was observed for SOA generated from β-pinene ozonolysis when either water vapor or formic acid was introduced as an SCI scavenger (SI Appendix, Fig. S1). These findings, together with modest SCI yields (15%) measured for α-pinene ozonolysis (31, 32), experimental and theoretical studies showing thermal unimolecular decay to be a dominant SCI loss process (32–34), and reported increases in dimer concentrations in α-pinene SOA with increasing relative humidity (RH) (11–13) despite the probable role of water vapor as an SCI scavenger, call into question the importance of SCI chemistry in monoterpene dimer production. The lack of peroxide dimers in α-pinene SOA also implies that gas-phase dimers formed via RO₂ self-cross-reactions (RO₂ + RO₂→ ROOR + O₂) (23–26) do not retain their peroxide character (i.e., undergo chemical transformation/decomposition) following condensation to the particle phase, as previously suggested (13, 20, 23).

Although dimers in pinene SOA seem to form only through O₃- and not OH-initiated oxidation, scavenging of OH radicals produced as a byproduct of the hot Criegee VHP channel during α-pinene ozonolysis has been found to suppress the formation of certain dimeric species (11). To further explore this effect, steady-state β-pinene ozonolysis experiments were conducted in the Caltech Photooxidation Flow Tube (CPOT) in the presence and absence of cyclohexane as an OH scavenger (Materials and Methods). UPLC/(−)ESI-Q-TOF-MS was employed to measure the molecular composition of SOA samples collected on Teflon filters and extracted into H₂O (Materials and Methods). A group of 23 dimeric compounds, also present in the CTEC experiments, was identified whose formation was significantly inhibited (>65%) by introduction of the OH scavenger; four of the dimers are major peaks in the BPI chromatogram (Fig. 2). These dimers, with molecular formulas C₁₅₋₁₉H₂₄₋₂₂O₃₋₁₁ and O/C ratios ranging from 0.26 to 0.61, exhibit saturation mass concentrations (Cₛ) < 3 × 10⁻³ µg m⁻³ and are designated as extremely low-volatility organic compounds (ELVOC) (Table 1). Compounds with accurate masses/molecular formulas corresponding to 20 of the 23 identified dimers have been measured in recent monoterpene SOA formation experiments, and 18 such compounds have been observed in ambient SOA samples from forested regions dominated by monoterpene emissions (SI Appendix, Table S2). The clear conclusion from these experiments is that formation of this particular collection of dimeric species depends on both O₃ and OH oxidation, in either a concurrent or sequential manner.
eliminated following OH addition to β-pinene (36, 37) but prior to reaction with the O3-derived species. The steady-state CPOT experiments enabled collection of sufficient quantities of SOA mass for detailed structural analysis via collision-induced dissociation (CID) (SI Appendix, S3.5). MS/MS spectra of the 13C-labeled dimers and their 13C isotopologues revealed distinct OH-derivated (13C-mass-shifted) and O3-derived (unshifted) fragmentation patterns (SI Appendix, Table S3). A group of eight dimeric compounds (Table 1, type I) was identified with fragmentation patterns and relative peak intensities characteristic of covalent dimer esters, which have been reported to be significant components of monoterpene SOA (7, 10–13, 18–21). Specifically, (i) the elemental composition of the dimers is given by condensation of the O3- and OH-derivated monomeric product ions (M1 + M2 − M1H2O = M1H2O) (7, 16), and (ii) assuming that the principal fragmentation occurs at the ester linkage, producing carboxyl and alkox fragment ions through neutral loss of the alcohol and dehydrated acid moieties, respectively, public fragments and associated daughter ions are more intense than the alkox fragments and their daughter ions (Fig. 3) (20, 21, 38), in line with conventional charge accommodation behavior in (-)ESI-MS. For the remaining 10 dimers (Table 1, types 2 and 3), the O3- and OH-derivated fragmentation patterns were not indicative of known accretion chemistry (e.g., formal addition or condensation), and in most instances a reasonable OH-derivated (13C-mass-shifted) monomeric building block either could not be identified or failed to account for the observed OH-derivated daughter ions (SI Appendix, Table S3). The structures of these dimers were not investigated further.

Based on comparison with MS/MS data for commercial standards and/or previously published MS/MS spectra, the O3-derived monomeric building blocks of the dimer esters are attributed to one of three dicarboxylic acids, each a well-characterized pinene oxidation product that has been implicated in dimer formation: cis-pinic acid (C9H16O4; Fig. 3A), cis-norpinic acid (C9H14O4; Fig. 3B), and dipteraxenic acid (C10H16O2; Fig. 3C) (7, 39) (SI Appendix, S6.1). Conversely, the OH-derivated monomeric units are characterized by the ion [M-H]− formulas [C9H15O12-]−, indicative of OH addition to β-pinene (C10H16O) followed by varying degrees of O2 incorporation, isomerization, and bi-molecular radical chemistry (36, 37). The daughter ions of the dicarboxylic acid and [C9H15O10-]− monomeric units are rationalized by successive neutral losses of H2O (18 Da), CO (44 Da), CH3O (30 Da), and CH2O (58 Da), all of which are established CID pathways (40–42). Notably, the loss of 13CH3O (31 Da) from the [C9H15O12-]− fragment is observed in the MS3 spectrum of almost every 13C-labeled dimer ester (Fig. 3 and SI Appendix, Table S3), consistent with the expected major addition of OH to β-pinene (83% of total OH reactivity) at the terminal vinyllic carbon (36). Moreover, while the three dicarboxylic acids implicated as O3-derived precursors were identified as major products in β-pinene SOA formed from ozonolysis (SI Appendix, S6.1), SOA products corresponding to the OH-derivated monomeric building blocks (i.e., C9H10O4, 7 and C9H18O2, 4) were not detected.

To further constrain the structures of the dimer esters, β-pinene SOA filters were extracted into D2O and analyzed via UPLC/(-)ESI-Q-TOF-MS using D2O as the polar eluent (SI Appendix, S5.6).

Table 1. Dimers identified in SOA produced from the O3-initiated oxidation of β-pinene that exhibited a significant decrease in abundance (>65%) due to OH scavenging

<table>
<thead>
<tr>
<th>Dimer type</th>
<th>Observed m/z (–)</th>
<th>RT, min</th>
<th>Molecular formula</th>
<th>Error, ppm</th>
<th>O:C</th>
<th>O2:C</th>
<th>logCt, μg m−3</th>
<th>Exchangeable hydrogens</th>
<th>SOA mass fraction, %</th>
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<td>1</td>
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<td>6.86</td>
<td>C9H16O4</td>
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<td>0.28</td>
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<td>–3.9</td>
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<td>0.04–0.17</td>
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<td>C9H14O4</td>
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<td>0.39</td>
<td>–0.78</td>
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<td>4</td>
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<td>0.33</td>
<td>–1.00</td>
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<td>–0.78</td>
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<td>4</td>
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<td>2.2</td>
<td>0.47</td>
<td>–0.71</td>
<td>–9.1</td>
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Mechanisms of Dimer Formation. To assess the relative contributions of gas- vs. particle-phase chemistry to the formation of dimers derived from concerted O$_3$ and OH oxidation, the temporal evolution of individual products in β-pinene SOA formed from ozonolysis in the CTEC was examined. Shown in Fig. 4A–C are the particle-phase growth profiles of the eight dimer esters (Table 1, type 1) overlaid upon those corresponding to the di- and tetra-carboxylic acid monomers (cis-pinic acid, cis-norpinic acid, and dipteranenic acid) that were implicated as precursors based on detailed MS/MS analysis. The strong correlation between the particle-phase abundances of the dimer esters and their presumed dicarboxylic acid building blocks points toward a mechanism of heterogeneous formation, wherein the semivolatile dicarboxylic acids undergo traditional equilibrium gas-particle partitioning (43) with subsequent reactive uptake of the gas-phase, OH-derived monomers/intermediates on collision with particle surfaces to form ELVOC dimers. A heterogeneous rather than purely particle-phase mechanism is supported by the absence of monomers corresponding to the OH-derived dimer ester precursors in SOA generated from β-pinene ozonolysis. Such heterogeneous/multiphase accretion processes, leading to the production of high-molecular-weight oligomeric products, have recently been shown to contribute significantly to SOA formation in both biogenic and anthropogenic systems (44, 45).

The growth dynamics of the dimer esters can be contrasted against those shown in Fig. 4D for another group of dimers (Table 1, type 2) also produced from coupled O$_3$ and OH oxidation. These dimers achieve essentially their maximum, steady-state SOA concentrations after ~2 h of reaction, whereas within the same time frame the dimer esters reach only ~60% of their highest measured particle-phase abundances. Prompt formation and rapid particle-phase growth of the dimers in Fig. 4D, at rates faster than those observed for the monomers (Fig. 4A–C), indicate production via gas-phase reactions of first-generation oxidation products/intermediates followed by irreversible condensation of the resulting ELVOC dimers onto particle surfaces. As the formation of these dimers was not significantly inhibited by introduction of SCI scavengers (SI Appendix, Fig. S1), they likely originate from closed-shell/radical species unique to the hot Creigee VHP channel. Although the identified dimers were found not to contain (hydro)peroxide functionalities (SI Appendix, S3.7), production of the dimers in Fig. 4D may be explained by gas-phase RO$_2$ self-cross-reactions (23–26, 46) with subsequent particle-phase decomposition leading to nonperoxide species (13, 20). Fast formation of particle-bound dimers during monoterpene ozonolysis has been reported in several recent studies (10–13, 20) and, together with their estimated low volatility, has been advanced to explain nucleation and initial growth of monoterpene SOA, both in laboratory studies without seed aerosol and in regions, such as the boreal forest, dominated by biogenic emissions (47).

This approach facilitated deuterium substitution (H → D) of labile hydrogens (e.g., –OH, –OOH, and –COOH) in the SOA constituents while preserving chromatographic separation, enabling quantification of the number of exchangeable hydrogens in the identified dimer molecules based on systematic shifts in m/z due to H/D exchange (Table 1 and SI Appendix, Fig. S4). Additionally, using our recently developed iodometry-assisted LC/ESI-MS assay for the molecular-level identification of organic peroxides (30), it was established that the 23 identified dimers do not contain hydroperoxide (ROOH) or organic peroxide (ROOR) functionalities (SI Appendix, S3.7). On the basis of these supporting experiments, the accurate mass (MS) and fragmentation (MS/MS) data, the inferred dicarboxylic acid structures of the O$_3$-derived monomers, and the prevailing mechanism of β-pinene photooxidation (36, 37), tentative molecular structures and fragmentation pathways for the dimer esters are proposed in SI Appendix, Table S4 and Fig. S10, respectively (SI Appendix, S6.1).

Fig. 4. Temporal profiles of molecular products in SOA produced from the O$_3$-initiated oxidation of β-pinene in the CTEC (SI Appendix, Table S1), Exp. 1), measured by PILS + UPLC/ESI-Q-TOF-MS. Profiles are plotted as the particle-phase abundances of each species, normalized to the highest abundance observed over 4 h of reaction, as a function of reaction time. Discrete data points (5-min resolution) are presented as lines to aid the eye. Numbers correspond to nominal m/z values of [M–H]$^-$ ions; molecular formulas are given in parentheses. (A–C) Profiles of dimer esters (Table 1, type 1) and dicarboxylic acids implicated as precursors based on MS/MS analysis: (A) cis-pinic acid (m/z 185; C$_6$H$_8$O$_4$), RT 4.33), (B) cis-norpinic acid (m/z 171; C$_7$H$_9$O$_4$, RT 4.06), and (C) dipteranenic acid (m/z 189; C$_{12}$H$_{15}$O$_4$, RT 3.32). (D) Profiles of dimers (Table 1, type 2) characterized by almost immediate formation and rapid particle-phase growth. Dashed lines (0 h, 0.6 abundance) are drawn to aid in comparison between growth profiles in A–C and D.
As a means of evaluating the hypothesized mechanism of heterogeneous dimer ester formation, β-pinene photooxidation experiments were conducted in the CTEC in the presence of seed aerosol composed of varying mass ratios of ammonium sulfate [(NH₄)₂SO₄] and cis-pinic acid, the only commercially available pinene-derived dicarboxylic acid (Materials and Methods). Consistent with the idea that introducing the O₃-derived dimer ester precursors into the particle phase of the OH system should promote otherwise negligible heterogeneous dimerization, the presence of cis-pinic acid in the (NH₄)₂SO₄ seed resulted in significant formation, proportional to the mass ratio of cis-pinic acid to (NH₄)₂SO₄, of the major dimer ester at m/z 337 (C₉H₈O₃) (Fig. 3), corroborating the indirect MS/MS (Fig. 34) and kinetic (Fig. 44) evidence for production from particle-bound cis-pinic acid. That the dimer ester at m/z 337 was not observed in OH-initiated β-pinene SOA, with pure (NH₄)₂SO₄ seed, collected on a Teflon filter coated with cis-pinic acid excludes the possibility of dimer formation via accretion of condensed monomers, either on the filter or during the extraction process (SI Appendix, Fig. S11). Although the details of the mechanism forming the ester linkage remain unclear, the observed increase in dimer ester abundance at elevated RH (SI Appendix, Fig. S1) argues against production via conventional esterification (i.e., carboxylic acid + alcohol). Overall, these findings conclusively demonstrate the role of heterogeneous accretion chemistry in monoterpenic SOA formation (SI Appendix, S6.2).

Surprisingly, these experiments also imply that a simple mass limitation of monomeric precursors in the particle phase is responsible for the absence of dimer esters in β-pinene SOA formed from OH-initiated oxidation. However, increased mass fractions of cis-pinic acid in SOA from α-pinene ozonolysis, relative to photooxidation, have been observed in a number of previous studies and have been invoked as a possible explanation for the lack of dimers containing cis-pinic acid in α-pinene photooxidation experiments (7, 12, 48). Indeed, in this study cis-pinic acid was found to comprise a much higher fraction of β-pinene SOA mass when formed from O₃ (13.4 ± 3.1%) rather than OH-initiated (1.7 ± 0.4%) oxidation (see m/z 185; RT 4.33 in Fig. 1), while significant but less pronounced disparities in SOA mass fraction between ozonolysis and photooxidation experiments were observed for cis-norpinic acid (1.4 ± 0.3% vs. 0.24 ± 0.06%) and diaterpenylic acid (0.71 ± 0.16% vs. 0.28 ± 0.06%) (SI Appendix, S7).

Although also suggested to arise from heterogeneous reaction of particle-phase cis-pinic acid (Fig. 4A), neither the prominent dimer ester at m/z 369 (C₁₇H₁₇O₇) nor the minor dimer ester at m/z 351 (C₁₇H₁₆O₈) was detected in the photooxidation experiments carried out with cis-pinic acid and (NH₄)₂SO₄ seed. One plausible explanation for the absence of these dimers is that the high HO₂ concentrations (~10¹⁰ molecules cm⁻³) inherent in the use of H₂O₂ as an OH precursor (SI Appendix, S1.1) produce an oxidative environment in which the OH-derived RO₂ isomerization and bimolecular reaction channels are vastly different from those operative in the comparatively low-HO₂ (~10¹⁰ molecules cm⁻³) ozonolysis system (SI Appendix, S4) that form the [C₉H₈O₃]⁺ and [C₉H₇O₄]⁺ building blocks of the dimer esters at m/z 369 and 351, respectively (SI Appendix, Table S3).

That RO₂ + HO₂ rate coefficients are typically order(s) of magnitude larger than those for RO₂ + RO₂ reactions (49) further compounds the disparity between these two RO₂ regimes. Conversely, for the dimer ester at m/z 337, although the structure of the [C₉H₈O₃]⁺ building block is tentative (SI Appendix, Fig. S10 and Table S3), theoretical studies indicate that this monomer is able to form under both ozonolysis and photooxidation conditions from the C₉H₈O₃ hydroxy peroxy radical, produced from OH and subsequent O₂ addition to β-pinene, either via traditional RO₂ + RO₂ chemistry or through an OH-recycling pathway in the reaction with HO₂ (36, 50).

**Atmospheric Implications.** The production of dimeric compounds (Table 1, types 1–3) through concerted O₃ and OH oxidation accounts for an appreciable, heretofore-unidentified fraction (5.9–25.4%) of the total mass of β-pinene SOA derived from ozonolysis under the conditions employed in this work (Table 1). Although specifically revealed in SOA formation from β-pinene, this reactive pathway represents a potentially significant source of high-molecular-weight ELVOC to the atmosphere that is expected to be broadly applicable to other monoterpens (SI Appendix, S8).

Through detailed molecular composition and kinetic analysis, certain dimers are definitively shown to form through heterogeneous processes, while indirect evidence for dimer formation via gas-phase routes is also presented. The importance of both gas- and particle-phase reactions to the formation of dimeric SOA constituents demonstrated in the current work underscores the complexity of atmospheric accretion chemistry, as well as the significant shortcomings in scientific understanding that preclude adequate characterization of its impact.

The O₃ + OH reactivity elucidated in β-pinene SOA also highlights the importance of understanding and accounting for the likely role of oxidative synergism in ambient aerosol formation, where SOA precursors are susceptible to concurrent oxidation by O₃ and OH. At present, SOA formation in atmospheric models is treated as an additive combination of products originating from the isolated oxidation of individual precursors (e.g., α-pinene + O₃ or isoprene + OH). In establishing that oxidants can act in concert to produce extremely low-volatility dimers in nontrivial yields, however, this study suggests that the tendency of current atmospheric models to systematically underpredict ambient SOA mass (1) may be due in part to the fact that discrete SOA formation mechanisms, parameterized by laboratory experiments that typically feature only one oxidant and a single SOA precursor, do not accurately reflect the intricate oxidation pathways at play in the real atmosphere. Revising the chemistry of monoterpene SOA formation in regional air quality and global climate models to account for the role of synergistic oxidation could help to resolve the discrepancy between model predictions and ambient measurements. However, parameterization of this reactivity requires additional work.

**Materials and Methods.** β-Pinene ozonolysis and photooxidation experiments were carried out in the CTEC and CPOAT at ambient temperature (~295 K) and atmospheric pressure (~1 atm), under dry conditions (~10% RH), in the presence of (NH₄)₂SO₄ seed aerosol, and at mixing ratios of NOₓ, typical of the pristine atmosphere (~0.5 ppb). CTEC experiments were designed to mimic oxidation in ambient air, while those in the CPOAT were used to elucidate dimer structures and formation mechanisms. For CTEC experiments with ~4-h duration, β-pinene (~120 ppb) was oxidized by O₃ (~200 ppb) in the absence of an OH scavenger or OH (~2 × 10⁸ molecules cm⁻³). Select photooxidation experiments were performed with mixed (NH₄)₂SO₄ and cis-pinic acid seed. For steady-state CPOAT experiments, oxidation of 30–150 ppb by ~10⁻⁵ Torr of O₃ (~4-h duration) in the presence and absence of scavengers for both OH (cyclohexane) and SO₂ (water vapor and formic acid). In certain CPOAT experiments, ¹³C-C₃-pinenone, synthesized from ¹³C-cis-dimethane and nopine, via Wittig olefination...


