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Title

Alkylperoxy Radicals are Responsible for the Formation of Oxygenated Primary Organic Aerosol

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Abstract

Organic aerosol (OA) is an air pollutant ubiquitous in urban atmospheres. Urban OA is usually apportioned into primary OA (POA), mostly emitted by mobile sources, and secondary OA (SOA), which forms in the atmosphere due to oxidation of gas-phase precursors from anthropogenic and biogenic sources. By performing coordinated measurements in the particle phase and the gas phase, we show that alkylperoxy radical chemistry that is responsible for low-temperature ignition also leads to the formation of oxygenated POA (OxyPOA). OxyPOA is distinct from POA emitted during high-temperature ignition and is chemically similar to SOA. We present evidence for the prevalence of OxyPOA in emissions of a spark-ignition engine and a next-generation advanced compression-ignition engine, highlighting the importance of understanding OxyPOA for predicting urban air pollution patterns in current and future atmospheres.

Teaser

The discovery of an unexpected source of oxygenated organic aerosol is reported.

MAIN TEXT

Introduction

Atmospheric aerosols exhibit profound impacts on air quality and the climate. Commonly referred to as particulate matter (PM) in the public-health community, aerosols are associated with various health effects and inflict the highest social cost among air pollutants (*1, 2*). Unlike greenhouse gases, which perturb the atmospheric radiative balance via a straightforward mechanism (the greenhouse gas effect), aerosols exhibit complex direct and indirect interactions with atmospheric radiation, rendering them the largest contributor to uncertainty in climate calculations (*3*). Organic aerosol (OA) constitutes the majority of submicron aerosol mass in both urban and rural atmospheres (*4*). A large fraction of OA forms via diverse gas-phase chemical reaction pathways that produce molecules with low volatilities, favoring particle formation via condensation. Such reactions occur during combustion (*5*) leading to the formation of primary organic aerosol (POA), as well as in the atmosphere (*6, 7*) leading to the formation of secondary organic aerosol (SOA). Though OA mass concentrations in the atmosphere can be quantified with relatively high confidence,

detailed speciation of OA is challenging. In response, atmospheric chemists have devised creative techniques that allow grouping OA into different categories and linking these categories to sources (*4*). The most prevalent categorization framework is based on factor analysis applied to aerosol mass spectrometer (AMS) measurements (*8, 9*). Under this framework, hydrocarbon-like OA (HOA) represents OA with low oxygen content (O/C < 0.1), while oxygenated OA (OOA) represents OA with high oxygen content (0.25 < O/C < 1). The current consensus is that OOA is predominantly composed of SOA, while urban POA, emitted from the combustion of hydrocarbon fuels (e.g. vehicle emissions), is HOA (*4*). Here we show that hydrocarbon combustion can emit what we refer to as oxygenated POA (OxyPOA), which retains chemical properties similar to those of SOA. We present results from laboratory experiments that link OxyPOA formation to low-temperature combustion chemistry (*10-12*). We also provide evidence of OxyPOA in emissions from spark-ignition and next-generation advanced compression-ignition engines, illustrating the relevance of elucidating OxyPOA formation to understanding OA pollution in current and future urban atmospheres.

Results

Difference in POA emitted from first-stage and second-stage ignition

Figure 1 shows results from chemical analysis of POA emitted from the controlled combustion of *n*-pentane and *n*-heptane. We distinguish between 'first-stage POA,' which formed at relatively low temperatures (550 K – 650 K) where reactions of peroxy radicals (RO_2) dominate, and 'second-stage POA,' which formed at relatively high temperatures (> 1000 K) (see fig. S1 in the supplementary materials). Traditionally, only second-stage POA has been thought to constitute POA emissions from the combustion of hydrocarbon fuels, whereas first-stage POA was only recently discovered (*13*). Therefore, it is imperative to set the appropriate context for the results. Second-stage POA forms at relatively high temperatures (> 1000 K) and is equivalent to 'incipient soot' in combustion science terminology (*14*). It is comprised of polycyclic aromatic hydrocarbons (PAHs) and aliphatic species (*5*) and therefore falls strictly under HOA (*4*). With further increase in temperature, the organic molecules that comprise second-stage POA transform into mature soot (*14*), which is largely equivalent to black carbon (BC) in atmospheric science terminology (*15*). BC is a strong light-absorber and a leading contributor to global warming (*15*). Second-stage POA can also be light-absorbing and is categorized as brown carbon (BrC) (*16*). For these reasons, the formation and physicochemical properties of second-stage POA have been extensively studied by both combustion scientists and atmospheric scientists (*5, 13, 16, 17*).

Some hydrocarbon fuels, including *n*-pentane and *n*-heptane, exhibit two-stage ignition behavior (*18, 19*), with first-stage ignition occurring at relatively low temperatures (550 K – 750 K). Discovery of first-stage ignition in the mid-twentieth century was motivated by efforts to understand the cause of engine knock in spark-ignition engines (*20, 21*). Furthermore, the importance of first-stage ignition in advanced compression-ignition (ACI) engines that rely on low-temperature combustion (LTC) remains an impetus for unveiling chemical kinetics of RO_2. As part of a complex degenerate chain-branching mechanism, RO_2 isomerization to (carbon-centered) QOOH radicals and subsequent reactions are the focal points for understanding chain-branching reactions in combustion (*12, 22*). However, while the dynamics of two-stage ignition chemistry is known to rely on QOOH-mediated reactions below 1000 K, the concomitant production of organic molecules with volatilities low enough to condense and form OA (i.e. first-stage POA) has only recently been reported (*13*).

The second-stage POA generated in our experiments was detected by laser desorption ionization mass spectrometry (LDI-MS) and exhibited clusters of peaks separated by 12 u (fig. S2 in the supplementary materials), which are characteristic signatures of PAHs. Similar spectra have been reported for POA extracted from flames (*23, 24*) and pyrolysis of hydrocarbons (*25, 26*). The clusters of peaks with 12 u separation have been shown to correspond to two series associated with even carbon numbers (usually major peaks) and odd carbon numbers (usually minor peaks), each separated by 24 u, with 12 u offset between them. At large molecular sizes, the minor peaks become less prominent and can disappear from the spectra (*16, 24, 27*), leaving the major peaks with 24 u separation (Fig. 1). Being non-polar, the second-stage POA molecules were not efficiently ionized by electrospray ionization (ESI) and were thus not detected by ultra-high resolution ESI mass spectrometry (ESI-MS). Conversely, the first-stage POA was transparent to LDI-MS but was detected by ESI-MS, indicating that the first-stage POA did not include PAHs and was comprised of polar compounds that were efficiently ionized by ESI. The first-stage POA had an average O/C of 0.65 and 0.56 for *n*-pentane and *n*-heptane, respectively, and thus falls under OOA, a category previously reserved for SOA (*4, 28, 29*). Furthermore, ESI-MS spectra show repetitive clusters of peaks separated by 14 u, which is indicative of oligomer formation (*30*), another feature usually associated with SOA (*31-33*) and is further explored in the subsequent section. It is possible that the first-stage POA included some reduced species that were not detected by ESI-MS, but the fact that it was completely transparent to LDI-MS indicates that reduced species, if any, did not constitute a substantial fraction.

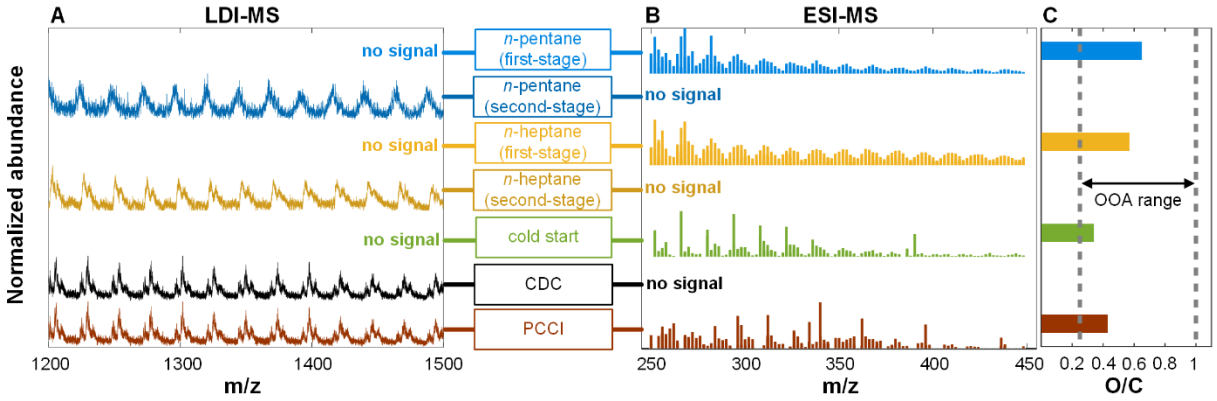

Fig. 1. Mass spectrometry analysis of POA emissions from controlled combustion of *n*-pentane and *n*-heptane, a spark-ignition engine operated at simulated cold-start conditions, and a compression-ignition engine operated at steady-state conditions using either conventional diesel combustion (CDC) strategy or an advanced compression-ignition (ACI) strategy (premixed charge compression ignition – PCCI). The temperature of the *n*-pentane and *n*-heptane combustion was controlled to emit either first-stage POA (550 K – 650 K) or second-stage POA (1100 K – 1300 K) (see supplementary materials). **(A)** Mass spectra obtained using LDI-MS. **(B)** Mass spectra obtained using ESI-MS. **(C)** Average O/C of the molecules detected by ESI-MS. The *n*-heptane first-stage POA was also analyzed using high resolution nanospray desorption electrospray ionization (nano-DESI) mass spectrometry, which yielded mass spectra and average O/C (0.57) consistent with ESI-MS (fig. S3).

These results demonstrate a marked difference in chemical characteristics between first-stage POA and traditional hydrocarbon-combustion POA (i.e., second-stage POA), which necessitates distinction between the two. To facilitate use within the context of atmospheric chemistry, we introduce the term 'oxygenated POA' (OxyPOA) to refer to first-stage POA. OxyPOA communicates the most distinct aspect of first-stage POA, namely high O/C, and maintains the same general terminological character used to describe organic aerosol in atmospheric chemistry literature (POA, SOA, HOA, OOA, etc.). We note that OxyPOA is different from oxidized POA (OPOA), a term used to refer to aged POA that has undergone heterogeneous oxidation in the atmosphere (*34, 35*). We also note that even though first-stage POA, or OxyPOA, is essentially organic particulate combustion emissions, it does not form through the high-temperature soot-formation route (*36*) and therefore should not be subsumed under the term 'incipient soot' (*14*). The formation pathways of OxyPOA, described in the subsequent section, differ from those of furans, which involve incorporation of oxygen into PAH structures in the high-temperature region of hydrocarbon flames (*37*). Furthermore, furans and other oxygenated species that form at high temperatures in flames usually have relatively small O/C (*37*), consistent with HOA (traditional hydrocarbon-combustion POA).

Formation pathways of OxyPOA

Collisionally stabilized alkylperoxy radicals (RO_2) traverse unimolecular reactions on potential energy surfaces that include isomerization to carbon-centered QOOH radicals and concerted elimination of HO_2. The former type of reaction is central to chain-branching and can also produce cyclic ether species, as in Fig. 2, in which 2-pentyl undergoes reaction with O_2 to ultimately form 2-methyltetrahydrofuran, which is one of several isomers formed during *n*-pentane oxidation (*38*). Similar to alkyl radicals, cyclic ethers also undergo complex reactions with O_2 (*39-41*). In addition to unimolecular reactions, however, RO_2 radicals can undergo bimolecular reactions including with other RO_2 radicals (*42*). Figure 2 depicts, as an example, a set of reactions of 2-methyltetrahydrofuran that produce highly oxidized, multi-functional intermediates in sequential steps mediated by organic hydroperoxides (ROOH), which result in species of decreased volatility that can partition to the particle phase and contribute to OxyPOA formation.

2-Methyltetrahydrofuran ($C_5H_{10}O$) and 2-methyltetrahydrofuran-3-one ($C_5H_8O_2$) were detected in the gas phase emissions of first-stage *n*-pentane combustion. Both species had temperature-dependent concentration profiles that exhibited similar trends to that of OxyPOA (fig. S4), signifying their role as OxyPOA precursors. As illustrated in Fig. 2, 2-methyltetrahydrofuran-3-one can undergo two additional oxygen-addition steps leading to the formation of $C_5H_6O_3$ molecules (2-methylfuran-3,4(2*H*,5*H*)-dione and 3-oxotetrahydrofuran-2-carbaldehyde), and ultimately $C_5H_4O_4$ molecules (5-methylfuran-2,3,4(5*H*)-trione and 3,4-dioxotetrahydrofuran-2-carbaldehyde). The intermediate $C_5H_6O_3$ molecules were not detected in the gas phase, which is ascribed to their existence at concentrations below the detection limit of our gas-phase instruments. Furthermore, their volatility is appreciably high such that partitioning to the particle phase is precluded (fig. S5). The $C_5H_4O_4$ molecules, however, have volatilities low enough to partition to the particle phase. The *n*-pentane OxyPOA species detected by ESI-MS included a peak at m/z 128.011 that reflects a molecular formula $C_5H_4O_4$, which coincides with 5-methylfuran-2,3,4(5*H*)-trione and 3,4-dioxotetrahydrofuran-2-carbaldehyde in Fig. 2.

Other pathways to multi-functional species include the formation of dicarbonyls via oxidation of the tertiary radical of *syn*-2,4-dimethyloxetane, another cyclic ether derived from *n*-pentane (*41*). Fig. S7 illustrates the formation of 2,4-pentanedione ($C_5H_8O_2$) (detected in the gas phase of first-stage *n*-pentane combustion), which undergoes further oxidation to form 2,3,4-trioxopentanal and 2,4-dioxopentanedial. Both species have molecular formula $C_5H_4O_4$, which coincides with the m/z 128.011 peak detected in the particle phase.

It is worth noting that the chemical composition of OxyPOA shares some similarity with highly oxygenated organic molecules (HOMs) (*43*) by containing multiple oxygen atoms in a hydrocarbon structure. However, the two are differentiated by the formation mechanisms: OxyPOA arises from QOOH-mediated, cyclic-ether derived reaction pathways during low-temperature combustion, whereas HOMs form via autoxidation involving RO_2 radicals in the atmosphere and are contributors to SOA (*43*).

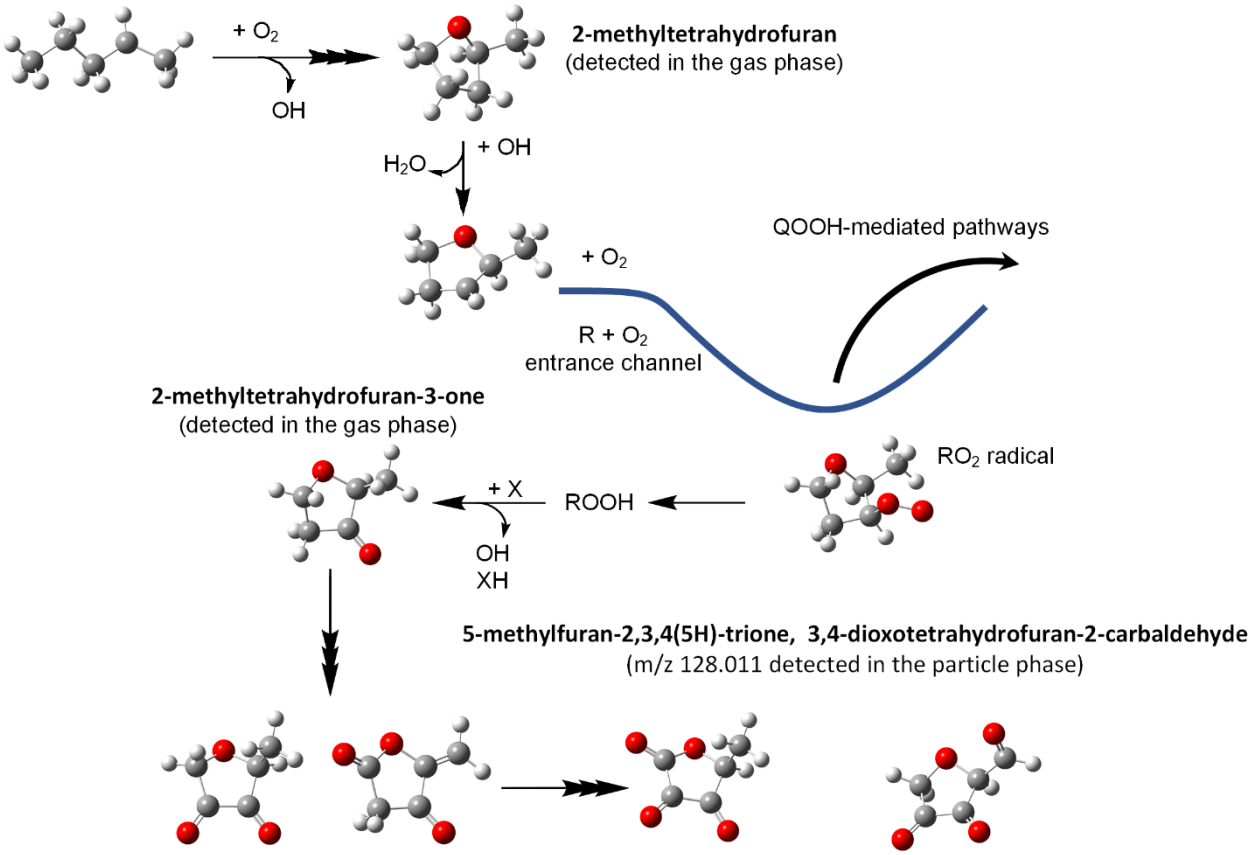

Fig. 2. Pathway for OxyPOA formation from gas-phase precursors produced during first-stage combustion of *n*-pentane. Oxidation of 2-pentyl produces 2-methyltetrahydrofuran, a cyclic ether, via a QOOH-mediated reaction. Subsequent H-abstraction and O_2-addition produces cyclic ether peroxy radicals (RO_2), such as 2-methyl-tetrahydrofuranyl-3-peroxy, which can undergo additional QOOH-mediated reactions or act as a hydrogen abstractor to produce ROOH. Abstraction of tertiary hydrogen from ROOH and barrierless O–O scission of the resultant carbon-centered radical, carbonyl-substituted species are produced coincident with OH in a chain-propagating step (*42*). Subsequent oxidation of species such as 2-methyl-tetrahydrofuran-3-one yields condensable species that form OxyPOA. The RO_2 well-depth, shown arbitrarily submerged, is typically 35 kcal/mol exothermic relative to the R + O_2 entrance channel. X denotes a generic radical and XH denotes a closed-shell hydrogen donor. Fig. S6 in the supplementary materials provides a detailed reaction scheme for other pathways involving RO_2 radicals that occur during low-temperature combustion.

Supported by species detected in the gas phase and particle phase of the *n*-pentane first-stage combustion emissions, the schemes in Fig. 2 and fig. S7 provide viable pathways for OxyPOA formation from gas-phase precursors. However, this alone cannot explain the large molecular sizes observed in the mass spectra of OxyPOA species (Fig. 1 and fig. S3). Limited by the scarcity of small hydrocarbon radicals at LTC conditions, such as vinyl and propargyl, it is unlikely for gas-phase reactions to produce species with carbon numbers larger than that of the parent hydrocarbon. We hypothesize that the critical final step in OxyPOA formation is molecular growth by oligomerization. Formation of oligomers not only renders the molecules in the particle phase less volatile, but also provides a condensation sink for more monomers to condense and oligomerize, thus creating a feedback mechanism that promotes condensational particle growth. We provide two levels of evidence for the prevalence of oligomers in OxyPOA: (i) patterns in the ESI-MS spectra, and (ii) response to perturbation in gas-particle equilibrium partitioning.

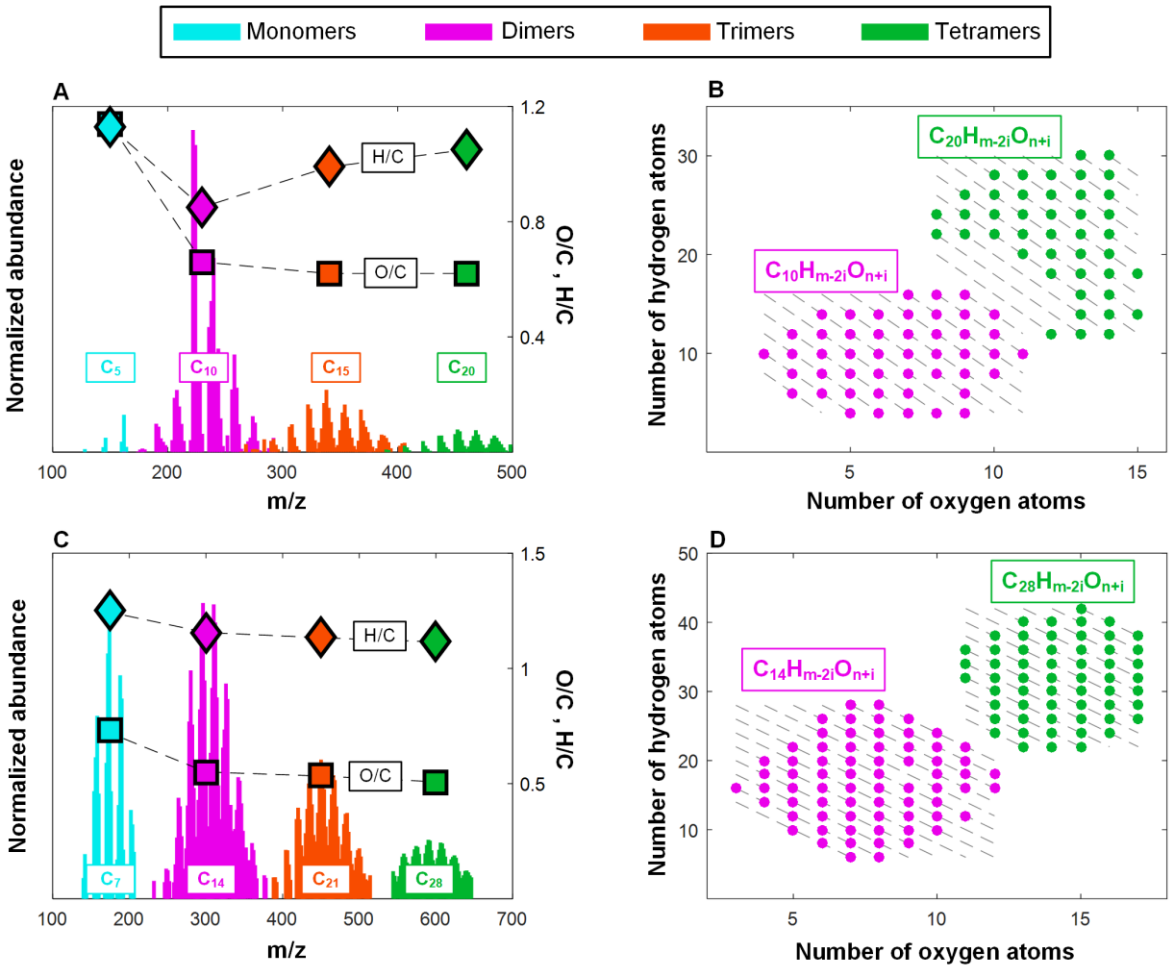

Fig. 3. Evidence for oligomer formation from ESI-MS analysis. (**A** and **C**) ESI-MS spectra of OxyPOA in *n*-pentane and *n*-heptane combustion that isolate C_5 monomers (*n*-pentane, **A**) and C_7 monomers (*n*-heptane, **C**) and oligomers with carbon numbers that are multiples of 5 and 7, respectively. Also shown are the average H/C and O/C of the monomers and the oligomers. (**B** and **D**) Number of hydrogen atoms versus number of oxygen atoms of the dimers and tetramers. (**B**) All the dimers and tetramers in the *n*-pentane OxyPOA belong to families with the general formula $C_{10}H_{m-2i}O_{n+i}$ and $C_{20}H_{m-2i}O_{n+i}$ (dashed gray lines), respectively. (**D**) All the dimers and tetramers in the *n*-heptane OxyPOA belong to families with the general formula $C_{14}H_{m-2i}O_{n+i}$ and $C_{28}H_{m-2i}O_{n+i}$ (dashed gray lines), respectively. Results consistent with those in panels **C** and **D** for *n*-heptane were obtained using nano-DESI mass spectrometry (fig. S3).

Mass spectra of oligomers previously observed in SOA are characterized by broad groupings, with each grouping comprised of clusters of equidistant peaks (*32*). Due to the high diversity of monomer combinations, the broad groupings are not apparent in the OxyPOA ESI-MS spectra (Fig. 1) but can be observed by isolating monomers with a certain carbon number. Representative results are shown in Fig. 3 for C_5 (*n*-pentane) and C_7 (*n*-heptane) monomers and oligomers with carbon numbers that are multiples of 5 and 7, respectively. These monomers form via first-stage functionalization pathways over which the hydrocarbon backbone remains intact during oxidation, resulting in C_5 (for *n*-pentane combustion) and C_7 (for *n*-heptane combustion) molecules with diverse functionality, including carbonyls and cyclic ethers, which are common products of alkane oxidation (*44, 45*). Isolating molecules with carbon numbers C_{5c} and C_{7c} (c = 1, 2, 3, 4) in the ESI-MS spectra of the *n*-pentane OxyPOA (Fig. 3A) and *n*-heptane OxyPOA (Fig. 3C) reveals oligomer signatures similar to those previously reported for SOA (*32*). Oligomer formation is further evidenced by the relatively small change in H/C and O/C with increasing carbon number, which is consistent with growth by monomer association. One exception is noted for the O/C of the C_5 monomers in *n*-pentane OxyPOA being substantially larger than the oligomers. This can be explained as follows: because of the small carbon number, only the highly functionalized C_5 monomers with high O/C have volatilities low enough (*46*) to partition to the particle phase, resulting in the O/C of the C_5 monomers in the OxyPOA sample being skewed high.

The broad groupings of C_{5c} and C_{7c} oligomers exhibit sequences of smaller clusters separated by 14 u. This suggests dominant formation pathways of monomers that include sequential steps with the net result of abstracting two hydrogen atoms and adding one oxygen atom (Fig. 2). Various combinations of these C_5 and C_7 monomers lead to the formation of oligomers with general formulae $C_{5c}H_{m-2i}O_{n+i}$ and $C_{7c}H_{m-2i}O_{n+i}$ (i = 1, 2, 3,…). This is illustrated in Fig. 3B and Fig. 3D, which show that all the dimers and tetramers belong to, respectively, $C_{5c}H_{m-2i}O_{n+i}$ and $C_{7c}H_{m-2i}O_{n+i}$ families (c = 2,4). The various combinations of monomers (with varying carbon numbers) that form through similar hydrogen-abstraction and oxygen-addition pathways manifest as tightly packed oligomer structures separated by 14 u (Fig. 1).

To further confirm the role of oligomerization in OxyPOA formation, we examined the response of *n*-pentane OxyPOA to either dilution with clean air or heating in a thermodenuder. In the absence of oligomers, the extent of evaporation in response to both perturbations would be dictated by internally consistent thermodynamic properties (volatility distribution) of the aerosol components. The presence of oligomers, however, leads to an evaporation response that is limited by the rate of oligomer dissociation, which increases substantially with increasing temperature (*47*). This would manifest as an apparent thermodynamic inconsistency in the aerosol response to the two perturbations: the aerosol would appear more volatile in the thermodenuder perturbation compared to dilution. The dilution perturbation led to minimal evaporation (Fig. 4C), in agreement with equilibrium partitioning calculations using volatility distribution estimated from ESI-MS molecular assignments. This indicates that the estimated volatility distribution, while not meant to be exact, predicted reasonably well the fraction of species that measurably partitioned to the gas phase in response to dilution (intermediate-volatility and semi-volatile compounds). However, equilibrium partitioning calculations using the same volatility distribution severely underestimated the extent of evaporation in the thermodenuder (Fig. 4A). Reproducing the OxyPOA response to the thermodenuder perturbation required substantially shifting the volatility distribution toward higher-volatility components, which would overestimate the extent of evaporation in response to dilution. As we argue above, this seeming thermodynamic inconsistency signifies a prominent role of oligomer dissociation (*47*).

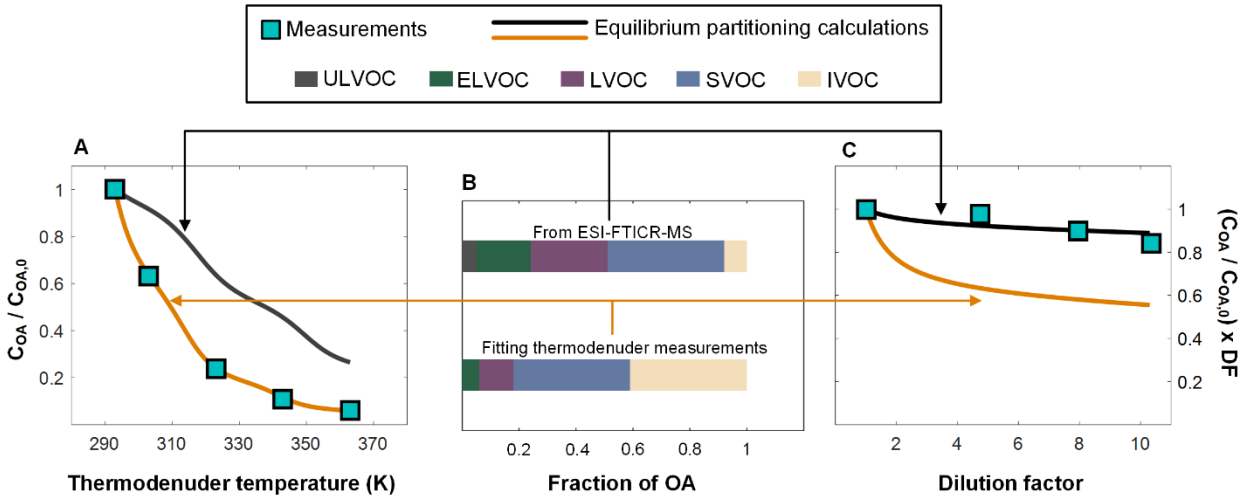

Fig. 4. Evidence for presence of oligomers in OxyPOA from comparing evaporation measurements of *n*-pentane OxyPOA to equilibrium partitioning calculations. (**A**) Thermodenuder measurements showing the aerosol mass concentration at each temperature (C_{OA}) relative to the aerosol mass concentration at the reference temperature ($C_{OA,0}$). Also shown are equilibrium partitioning calculations using volatility distribution obtained from ESI-MS molecular assignments (black line). The brown line corresponds to equilibrium partitioning calculations using a volatility distribution adjusted to reproduce the measurements. (**B**) Volatility distributions obtained from ESI-MS molecular assignments (top bar) and adjusted to reproduce the thermodenuder measurements (bottom bar). The aerosol components are apportioned into intermediate-volatility (IVOC), semi-volatile (SVOC), low-volatility (LVOC), extremely low-volatility (ELVOC), and ultra-low-volatility (ULVOC) organic compounds. (**C**) Dilution measurements showing C_{OA} at a certain dilution factor (DF) relative to no dilution ($C_{OA,0}$). Dilution leads to a decrease in C_{OA} because of dilution itself as well as evaporation. To isolate the effect of evaporation, the y-axis is scaled by DF, such that the case of no evaporation would show as a horizontal line with a value of 1. Also shown are equilibrium partitioning calculations using volatility distribution obtained from ESI-MS molecular assignments (black line) and volatility distribution adjusted to reproduce the thermodenuder measurements (brown line).

Prevalence of OxyPOA in engine emissions

We performed LDI-MS and ESI-MS analysis on POA samples collected from the emissions of a spark-ignition (gasoline) engine operated at a simulated cold-start condition and a compression-ignition (diesel) engine operated at steady state conditions using either conventional diesel combustion (CDC) strategy or an ACI strategy (premixed

charge compression ignition – PCCI). As shown in Fig. 1, the cold-start POA was transparent to LDI-MS but was detected by ESI-MS and exhibited repetitive peaks separated by 14 u with an average O/C within the OOA range. These results indicate that the POA from the simulated cold-start emissions was dominated by OxyPOA. The majority of POA emissions from on-road gasoline vehicles occur during cold-start conditions (*48*), which are especially important in urban settings where a large share of driving consists of short trips at cold engine conditions (*49*). Therefore, we expect OxyPOA to be ubiquitous in urban atmospheres.

Both CDC and PCCI emitted POA with typical soot-formation signatures identified by LDI-MS, signifying the presence of second-stage POA (Fig. 1). ESI-MS detected species in the PCCI POA but not the CDC POA. Similar to the cold-start POA, the PCCI POA species measured by ESI-MS had O/C within the OOA range and the spectra exhibited repetitive peaks, albeit not as prominent as the cold-start POA possibly due to the lower signal. These results suggest that the lower global in-cylinder temperatures in PCCI compared to CDC (*50*) resulted in a portion of the emissions experiencing temperature histories (550 K – 750 K) conducive to the formation of first-stage POA (OxyPOA). Previous studies have reported substantial increase in emissions of POA relative to mature soot for various ACI strategies (*51, 52*). Our results indicate that a fraction of this POA is OxyPOA.

Discussion

The discovery of OxyPOA reported in this study can help solve a long-standing mystery associated with air-quality models persistently predicting lower SOA levels in urban regions compared to observations (*53-56*). SOA formation in air quality models is simulated based on parameterizations derived from smog-chamber experiments that involve oxidizing SOA precursors found in the emissions of various sources, including vehicle emissions. Several culprits have been proposed as possible explanations for the underestimation of SOA formation in these parameterizations, including missing precursors (*53*) and underestimation of SOA yields of precursors in vehicle emissions (*57*). Intermediate-volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs) in vehicle emissions, which have particularly high SOA yields, have been hypothesized to be among the missing SOA precursors (*58*). However, a recent modeling study concluded that accounting for IVOCs and SVOCs played a minor role in closing the gap between modeled and measured SOA over urban areas in southern California (*56*). Another proposed explanation is vapor wall-loss artifacts in smog chamber experiments leading to underestimation of SOA yields in the derived parameterizations (*55, 56*). We provide an alternative explanation: the gap between modeled and measured SOA in urban atmospheres is partly due to overestimation of SOA in atmospheric observations, rather than underestimation in models. Atmospheric measurements equate POA from vehicle emissions to HOA and SOA to OOA. However, our results suggest that OxyPOA constitutes a substantial fraction of urban POA emitted from gasoline vehicles during cold-start. Consequently, OxyPOA would be counted as OOA and misattributed to SOA in atmospheric measurements, leading to overestimation of SOA.

Quantifying the levels of OxyPOA in urban atmospheres, however, requires further investigation. On the atmospheric measurements front, this entails identifying molecular markers and/or factors that distinguish OxyPOA from anthropogenic SOA. Representing OxyPOA in air-quality models requires incorporating it as a separate POA category alongside traditional POA in vehicle emission inventories. This, in turn, requires performing measurements to quantify emission factors of OxyPOA that take into account variables such as emission certification standards, driving conditions, fuel blends, among others.

The detection of OxyPOA in the emissions of the PCCI engine (Fig. 1) suggest a relative increase in OOA compared to HOA in future urban atmospheres if these next-generation ACI strategies are widely adopted. Importantly, quantifying OxyPOA in ACI engine emissions is critical for obtaining a comprehensive understanding of their emission profiles in order to devise control strategies that aid in the development of clean, sustainable transportation energy technologies (*59*).

Materials and Methods

n-Pentane and *n*-heptane controlled combustion experiments

The setup used to generate first-stage and second-stage primary organic aerosol (POA) from the controlled combustion of *n*-pentane and *n*-heptane is shown in fig. S8 and is described in detail in previous studies (*13, 16, 60-62*). Briefly, fuel oxidation was temperature-initiated in a 0.24 L custom-built cylindrical quartz chamber enclosed in an insulated heater (Thermcraft Inc., NC, USA). Temperature was controlled to within 1 K using a PID controller (OMEGA, CNi3244) utilizing a high-temperature K-type thermocouple located at the center of the chamber. Fuel was introduced via a bubbler system using a mass flow controller (DAKOTA, 6AGC1AL55-09AB) to direct a stream of ultra-high purity N_2 (NI UHP300, Airgas) into a bubbler containing the fuel. The bubbler dimensions were designed to ensure that the N_2 stream was fully saturated with the fuel vapor at the exit of the bubbler, as verified by mass transfer calculations confirming that the residence time of a bubble rising in the bubbler is greater than the time required to saturate it with the fuel vapor (*61*). This allowed us to calculate the flowrate of the fuel entering the combustion chamber based on the fuel saturation pressure and N_2 flowrate. The fuel-saturated N_2 stream was then mixed with a controlled stream of clean dry air and N_2 to maintain an equivalence ratio (ϕ) of 2.3 and O_2/N_2 of 0.06.

The total flowrate into the combustion chamber was 0.75 SLPM, resulting in average residence time of approximately 19 seconds. The combustion emissions were then diluted in a 4 L glass dilution chamber with 12 SLPM of clean dry air prior to POA sampling. To observe first-stage and second-stage POA formation, the temperature of the combustion chamber was varied between 500 K and 1300 K and the size distributions of the POA emissions were continuously monitored at 90-second time resolution using a scanning mobility particle sizer (SMPS, TSI model 3088). The size distributions were integrated using a particle effective density of 1.3 g/cm^3, estimated using tandem differential mobility analyzer – aerosol particle mass analyzer (tandem DMA-APM) technique (*13, 63*), to obtain temperature-dependent POA mass concentration profiles. As shown in fig. S1, both *n*-pentane and *n*-heptane exhibited two-stage aerosol formation. The first-stage POA peak emission was at 583 K and 563 K for *n*-pentane and *n*-heptane, respectively.

We collected POA samples on 47 mm polytetrafluoroethylene (PTFE) filters (0.2 μm pore size, Whatman) for the chemical analyses described below. The collection flowrate was 5 SLPM and the targeted mass loading was 300 μg in order to avoid filter clogging which occurs at ~350 μg. Filters were stored at -15° C pending analysis. First-stage POA samples were collected at combustion temperature of 583 K and 563 K for *n*-pentane and *n*-heptane, respectively. Second-stage POA samples were collected at combustion temperature of 1123 K and 1308 K for *n*-pentane and *n*-heptane, respectively.

We also collected samples from *n*-pentane combustion for gas-phase chemical analysis (described below) using a 1-gallon (3.8 L) stainless steel double ended sample cylinder (304L-HDF4-1GAL, Swagelok) fitted with ¼ inch needle valves on both ends (fig. S8). The combustion emissions were sampled directly into the cylinder from the combustion chamber (without dilution) at a flowrate of 0.5 SLPM, and the valves at the inlet and outlet of the cylinder were closed once steady state conditions were achieved. The POA was removed from the emissions using a PTFE filter prior to entering the cylinder. In order to compare the temperature-dependent concentration profiles of gas-phase species emitted during first-stage combustion to that of first-stage POA, we collected gas-phase samples at five temperature points: 543 K, 563 K, 598 K, 658 K, and 743 K. The second-stage gas-phase samples were collected at 1143 K.

Cold-start spark-ignition engine experiments

A single cylinder version of a GM LNF 2.0L direct-injected (DI) spark-ignited (SI) 4-cylinder engine was used for these experiments, wherein 3 of the cylinders were disabled by grinding off the cam lobes to prevent valve actuation as well as by drilling holes in the pistons to prevent compression. More details of the engine setup, instrumentation, and cold-start operation are available in previous studies on this engine (*64, 65*). Briefly, the firing cylinder was maintained in stock configuration, wherein the compression ratio, combustion chamber geometry, fuel injector, cam lobe profiles, and cam phasing capabilities were all stock. The engine was fueled with a 9-component surrogate fuel blend known as PACE20 that was designed by the Partnership to Advance Combustion Engines (PACE) consortium to closely mimic the fuel properties such as boiling range and octane rating, as well as engine emissions parameters such as sooting propensity of a market-representative 87 anti-knock index (AKI) E10 fuel while eliminating fuel composition uncertainties from chemical-kinetics modeling. The fuel composition and properties are detailed elsewhere (*65*). Cold-start operation was simulated by operating the engine at 1300 RPM and 2 bar net indicated mean effective pressure (NIMEP) stoichiometric operation while the engine out coolant and oil temperature were controlled to 20°C. For this study, spark timing was used as the engine control parameter to study engine emissions under normal and cold-start conditions. For the data presented in this study, the spark timing was fixed at 25 degrees after-top-dead-center-firing (dATDCf) and the exhaust gas was sampled 35mm downstream of the exhaust port.

Compression-ignition engine experiments

The conventional diesel combustion (CDC) and a premixed charge compression ignition (PCCI) samples were collected from the exhaust of a single-cylinder medium-duty diesel engine. A complete description of the engine and mode operation has been previously described (*66*). Briefly, a 6.7 L Cummins 6-cylinder ISB engine was modified to single cylinder operation by deactivating 5 cylinders and run for these samples on certified ultra-low-sulfur diesel no. ULSD #2 fuel. The same engine was operated in both the CDC and PCCI modes to collect filters samples of aerosol emissions. A similar dilution tunnel set-up as that described for the cold-start experiments was used to collect aerosol samples on PTFE filters. Both samples were collected at 1200 rpm but the PCCI samples was at low load (1.8 bar) and the CDC sample was at high load (3.2 bar) (*67*).

POA chemical analysis using laser desorption ionization mass spectrometry

The POA samples shown in Fig. 1 were analyzed using laser desorption ionization mass spectrometry (LDI-MS) at the University of Georgia proteomics and mass spectrometry core facility. LDI-MS is efficient at detecting incipient soot and has been extensively employed to study soot formation from various combustion sources (*17, 68, 69*). We extracted the POA filter samples by sonicating in 2 ml of dichloromethane (DCM) for 40 minutes. The solutions were then concentrated to 1 ml by evaporation using a gentle stream of ultra-high purity N2. The solutions were then spotted onto a stainless-steel grid for LDI-MS analysis in 250 μL batches, allowing the DCM to evaporate after each batch. Based on our experience (*13, 16, 27*) and in concordance with previous studies (*23, 69-71*), we chose DCM as

a solvent for LDI-MS analysis due to its efficacy at extracting large-molecular-size polycyclic aromatic hydrocarbons (PAHs) that constitute incipient soot. LDI-MS analysis was performed on a Bruker Autoflex III in reflectron mode using AutoXecute. Calibration was performed using 2,5 dihydroxybenzoic acid (MH+ = 255.0 m/z; monoisotopic mass), reserpine (609.3 m/z; monoisotopic mass), angiotensin (MH+ = 1296.7 m/z; monoisotopic mass), and insulin (5734.5 m/z; average mass). The instrument uses a 337 nm Nitrogen laser in positive mode. The ion source was set to 19 kV and the reflector voltage to 20 kV. Random walk with the raster was set to 2 shots per spot with a total of 100 laser shots. The samples were analyzed within two molecular size ranges, 100-1000 m/z and 1000-2000 m/z. The instrument sensitivity was set just below saturating the largest signal within each range in order to detect the large-molecular-size PAHs (Fig. 1A), which would otherwise go undetected if the same sensitivity were applied for the full range (100-2000 m/z).

POA chemical analysis using electrospray ionization mass spectrometry

The POA samples shown in Fig. 1 were analyzed using electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry (ESI-FTIRC-MS) at the University of Georgia proteomics and mass spectrometry core facility. ESI-MS is efficient at detecting relatively polar molecules (*72-74*) and has been previously employed to perform chemical analysis on various types of organic aerosol (OA) samples, including biomass-burning OA (*74-76*), secondary OA (SOA) (*77-79*), and urban OA (*80, 81*).

For ESI-FTIRC-MS analysis, the POA filters were extracted using the same procedure described above for LDI-MS analysis, but using acetonitrile as a solvent because of its efficacy at extracting polar compounds (*79, 82, 83*). An extraction blank with a clean PTFE filter was also prepared following the same steps and was used for background correction. Analysis was performed on a Bruker SolariX 12T FTICR mass spectrometer (Bruker Daltonik, GmbH, Bremen, Germany) in negative ion mode. Mass spectra were collected between 75-1000 m/z with 2M data points length and a 0.4194 second transient. Time of flight was set at 0.8 ms. Samples were infused at a rate of 2.0 µL/min. The capillary voltage was set to 4500 V with a -800 V end plate offset. The nebulizer gas was set to 0.5 bar, and the dry gas was set to 4.0 L/min with a dry temperature of 200° C. Ion accumulation time was 0.005 seconds. Calibration was performed with sodium trifluoroacetate (Sigma-Aldrich) (0.1 mg/mL in 50:50 methanol:water). Spectra were collected in triplicate by doing three injections of 10 µL of sample. Prior to introducing samples to the instrument, methanol and extraction blanks were acquired.

For data analysis, 48 scans per injection per sample were averaged using Bruker Compass Data Analysis software (Version 5.3). Background subtraction was performed using Xpose mode with a retention time window of 0.0083s and a ratio of 5 in order to minimize noise signals and signals that were detected in the extraction blanks. MFAssignR (*84*), an open source R package, was used to analyze the data according to component molecular formulae. Assignments were internally recalibrated, and subjected to the following restrictions: CxHyOz, $0.3 \leq H/C \leq 3$, $0 \leq O/C \leq 2.5$, and a maximum allowable error ≤ 1 ppm. The final peak list that represents each sample is composed of molecular formulae that are common across the three injections. The number of molecular assignments was 1014 for *n*-pentane first-stage POA, 1525 for *n*-heptane first-stage POA, 206 for the cold-start spark-ignition engine POA, and 185 for the PCCI engine POA. The *n*-pentane second-stage POA, *n*-heptane second-stage POA, and CDC POA had no signal. Average O/C values shown in Fig. 1C were calculated as signal-weighted averages of O/C values of the individual molecules identified in the ESI-MS spectra.

POA chemical analysis using nanospray desorption electrospray ionization mass spectrometry

In addition to ESI-FTIRC-MS, the *n*-heptane first-stage POA was also analyzed at the Pacific Northwest National Laboratory (PNNL) Environmental Molecular Sciences Laboratory (EMSL) using nanospray desorption electrospray ionization (nano-DESI) high resolution mass spectrometry.

The design of the nano-DESI high resolution mass spectrometry (HRMS) interface has been previously described in (*85, 86*). Briefly, a 7/3 v/v acetonitrile/water solvent mixture (Optima LC-MS grade; Fisher Chemical, Hampton USA) was flowed at 0.5 µL/min through a capillary assembly formed by two fused silica capillaries aligned at ~90° (Polymicro Technologies, Phoenix, USA; primary capillary: 150 µm O.D., 50 µm I.D.; secondary capillary: 150 µm O.D., 20 µm I.D. with etched terminus (*87*)). This junction was brought sufficiently close to the PTFE filter samples such that a liquid junction formed and scanned along the XY plane at 35 µm/s, allowing for continuous and direct sampling from the filters. -3.5 kV was applied via the solvent syringe needle, and the nano-DESI capillary assembly was positioned ~1 mm from the inlet of a high-resolution LTQ Velos Orbitrap mass spectrometer (Thermo Scientific, Waltham). The MS inlet was maintained at 275°C. All samples were analyzed in negative ion mode via MS1 (m/z 100 – 1000) with an automatic gain control (AGC) target of 5 x 105, maximum ion injection time of 500 ms, and mass resolution of 100k at m/z 400.

For data analysis, 100 scans were averaged per sample within Xcalibur (Thermo Scientific) and exported as a .csv peak list (5 decimal points per m/z). MFAssignR was used for component molecular formulae assignment. For features with S/N > 6, assignments were internally recalibrated, and subjected to the following restrictions: CxHyOz; $0.3 \leq H/C \leq 3$; $O/C \leq 2.5$; $-20 \leq DBE\text{-}O \leq 25$ (DBE-O: double bond equivalents minus oxygen count). Datasets were blank subtracted such that molecular formulae detected in both a solvent blank and sample list were removed from the final sample list if they were present in the sample at 3x or lower the level found in the blank. Final datasets were

manually inspected/cleaned for outlier assignments (*86*). The final peak list used in the interpretations for each sample is composed of only molecular formulae commonly detected across each of three replicates. The number of molecular assignments was 1895 for *n*-heptane first-stage POA.

Gas-phase chemical analysis using electron-impact mass spectrometry and vacuum ultraviolet absorption spectroscopy

Using a filtration system to remove particles, gas-phase samples were collected for offline analysis from the controlled combustion of *n*-pentane. In order to compare the temperature-dependent concentration profiles of gas-phase species emitted during first-stage combustion to that of first-stage POA, we collected gas-phase samples at five temperature points: 543 K, 563 K, 598 K, 658 K, and 743 K. The second-stage samples were collected at 1143 K. Gas-phase samples were compressed in an inert-coated chamber and then introduced into a valving system connected to a gas chromatograph (GC), which collects 500 µL of the sample. The 500-µL volume was then introduced via the GC to three different detectors. First, the sample was directed through a 5Å molecular-sieve which separates CO, CO_2, H_2, O_2, and CH_4, for analysis via a thermal conductivity detector (TCD) using Ar as reference gas. The filtered sample was then split into two volumes of 250 µL which are injected sequentially onto two identical PONA columns of 100 m length, 250 µm inner diameter, and 0.50 µm film thickness. The two columns follow the same temperature programming which begins with holding at 40 °C for 5 minutes, increasing to 110 °C at 5 °C/min, holding at 110 °C for 5 minutes, increasing to 280 °C at 5 °C/min, and holding at 280 °C for 5 minutes.

One PONA column leads to a 70-eV electron-impact mass-spectrometer (EI-MS), while the other leads to a vacuum-ultraviolet (VUV) absorption cell which is held at 50 °C and 795 ± 2 torr. Species quantification was achieved through fitting of measured absorption spectra to reference spectra at photon energies with high signal-to-noise ratios lying within the full-scale range of 5.17 – 9.92 eV. Prior to quantification, reference spectra were created from injection of reference gas samples, typically at 1000 ppm. VUV spectra of the detected species are shown in fig. S9-S17.

Gas-particle partitioning perturbation experiments

In order to assess the effect of oligomer dissociation on the evaporation behavior of OxyPOA, we subjected the OxyPOA emissions from *n*-pentane combustion to two perturbations: (i) dilution with clean air at room temperature, and (ii) heating in a thermodenuder at temperatures ranging between 303 K and 363 K. Both dilution and heating perturb the gas-particle equilibrium partitioning and force the particles to evaporate in order to reestablish equilibrium. If the particle phase contains oligomers, the perturbation induces not only physical evaporation (i.e. partitioning of molecules from the particle phase to the gas phase), but also oligomer dissociation (*47*). The reason is that monomers evaporate more readily than the oligomers due to their smaller molecular size, thus higher volatility. This perturbs the monomer-oligomer equilibrium in the particle phase, leading to oligomer dissociation to reestablish equilibrium. Quantifying the equilibrium composition of monomers and oligomers is not straightforward. However, the dissociation rate constant is known to increase substantially more than the association rate constant with increase in temperature (*47*). In other words, the monomer-oligomer equilibrium composition shifts toward higher fraction of monomers as temperature increases, making the aerosol more volatile because monomers are more volatile than oligomers. Consequently, the effect of oligomer dissociation would be more prominent if the aerosol is heated in a thermodenuder compared to dilution at room temperature. Here, we probe this temperature-dependent oligomer dissociation effect by comparing the apparent volatility of the OxyPOA, namely saturation concentration (C_{sat}), needed to explain the extent of evaporation in the dilution versus thermodenuder perturbations. If higher C_{sat} values are required to reproduce the observed evaporation in the thermodenuder measurements compared to dilution, this would be evidence that the OxyPOA contains oligomers.

In both the dilution and thermodenuder experiments, the combustion chamber temperature was set to 583 K, corresponding to the peak OxyPOA emissions (fig. S1). The thermodenuder experiments involved diluting the combustion emissions (0.75 SLPM) with 12 SLPM of clean air and then alternating between measuring the baseline aerosol mass concentration at room temperature ($C_{OA,0}$) by sampling through the bypass and measuring the aerosol mass concentration (C_{OA}) at 303 K, 323 K, 343 K, and 363 K by sampling through the thermodenuder (fig. S8). The thermodenuder consisted of a stainless-steel tube wrapped with heating tape and insulation. The temperature was controlled using a PID controller (OMEGA, CNi3244). The thermodenuder has a volume of 0.5 L (diameter = 2.54 cm, length = 1 m) and the aerosol flow was 1 SLPM, yielding an average residence time of 30 seconds. In the dilution experiments, we first obtained a baseline aerosol mass concentration ($C_{OA,0}$) by mixing the combustion emissions (0.75 SLPM) with 3 SLPM of clean air in the dilution chamber (fig. S8). We then applied three dilution factors (DFs) of approximately 5, 8, and 10, and measured the aerosol mass concentration (C_{OA}) at each DF. The aerosol emissions in the dilution experiment were also sampled through the thermodenuder, but without heating, to allow for ample time for evaporation.

We performed gas-particle equilibrium calculations (*88*) to interpret the observed OxyPOA evaporation at the dilution and thermodenuder experimental conditions. We first calculated the reference saturation concentration at 300 K ($C_{sat,ref}$) of the each of the assigned molecules (see above for molecular assignments) based on the parameterization of Li *et al.* (*89*):

$$\log_{10}(C_{\mathrm{sat,ref}}) = (n_{\mathrm{C}}^{0} - n_{\mathrm{C}})\, b_{\mathrm{C}} - n_{\mathrm{O}}\, b_{\mathrm{O}} - 2\,\frac{n_{\mathrm{C}}\, n_{\mathrm{O}}}{n_{\mathrm{C}} + n_{\mathrm{O}}}\, b_{\mathrm{CO}} \quad (1)$$

Where, n_{C} is the number of carbon atoms, n_{O} is the number of oxygen atoms, $n_{\mathrm{C}}^{0} = 22.6$, $b_{\mathrm{C}} = 0.4481$, $b_{\mathrm{O}} = 1.656$, and $b_{\mathrm{CO}} = -0.779$.

The molecules were then grouped into five volatility bins that correspond to:

1. Intermediate-volatility organic compounds (IVOCs): $C_{\mathrm{sat,ref}} > 300$ μg/m^3.
2. Semi-volatile organic compounds (SVOCs): 0.3 μg/m^3 < $C_{\mathrm{sat,ref}}$ < 300 μg/m^3.
3. Low-volatility organic compounds (LVOCs): 3 x 10^{-4} μg/m^3 < $C_{\mathrm{sat,ref}}$ < 0.3 μg/m^3.
4. Extremely low volatility organic compounds (ELVOCs): 3 x 10^{-9} μg/m^3 < $C_{\mathrm{sat,ref}}$ < 3 x 10^{-4} μg/m^3.
5. Ultra-low volatility organic compounds (ULVOCs): $C_{\mathrm{sat,ref}}$ < 3 x 10^{-9} μg/m^3.

We then assigned $C_{\mathrm{sat,ref}}$ value for each bin, calculated as the average $C_{\mathrm{sat,ref}}$ of the components in the bin. We calculated C_{sat} values at different temperatures (C_{sat}(T)) using the Clausius-Clapeyron relation:

$$C_{\mathrm{sat}}(T) = C_{\mathrm{sat,ref}}\,\frac{T_{\mathrm{ref}}}{T}\,\exp\left(\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \quad (2)$$

Where, T_{ref} is the reference temperature (300 K), R is the universal gas constant, and ΔH is the enthalpy of vaporization, estimated using the parameterization of Epstein *et al.* (*90*):

$$\Delta H\ [\mathrm{kJ/mol}] = -11\log_{10}(C_{\mathrm{sat,ref}}) + 129 \quad (3)$$

We then employed an iterative solution to calculate C_{OA} at each experimental condition (for both dilution and thermodenuder experiments) following Donahue *et al*. (*88*):

$$z_{\mathrm{i}} = \left(1 + \frac{C_{\mathrm{sat,i}}}{C_{\mathrm{OA}}}\right)^{-1};\ C_{\mathrm{OA}} = \sum_{\mathrm{i}} C_{\mathrm{i}}\ z_{\mathrm{i}} \quad (4)$$

Where, the subscript 'i' refers to a specific volatility bin, z is the portioning coefficient between the particle phase and the gas phase, and C is the total concentration in both phases.

The equilibrium-partitioning C_{OA} values calculated using the volatility distribution obtained from molecular assignments correspond to the black lines in Fig. 4A and Fig. 4C. We also obtained a volatility distribution that yields equilibrium-partitioning C_{OA} values that fit the thermodenuder measurements by adjusting the mass fractions in the volatility bins. These equilibrium-partitioning C_{OA} values correspond to the brown lines in Fig. 4A and Fig. 4C.

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