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Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds

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Decades of research on the autooxidation of organic compounds have provided fundamental and practical insights into these processes; however, the structure of many key autooxidation intermediates and the reactions leading to their formation still remain unclear. This work provides additional experimental evidence that highly oxygenated intermediates with one or more hydroperoxy groups are prevalent in the autooxidation of various oxygenated (e.g., alcohol, aldehyde, keto compounds, ether, and ester) and nonoxygenated (e.g., normal alkane, branched alkane, and cycloalkane) organic compounds. These findings improve our understanding of autooxidation reaction mechanisms that are routinely used to predict fuel ignition and oxidative stability of liquid hydrocarbons, while also providing insights relevant to the formation mechanisms of tropospheric aerosol building blocks. The direct observation of highly oxygenated intermediates for the autooxidation of alkanes at 500–600 K builds upon prior observations made in atmospheric conditions for the autooxidation of terpenes and other unsaturated hydrocarbons; it shows that highly oxygenated intermediates are stable at conditions above room temperature. These results further reveal that highly oxygenated intermediates are not only accessible by chemical activation but also by thermal activation. Theoretical calculations on H-atom migration reactions are presented to rationalize the relationship between the organic compound’s molecular structure (\(n\)-alkane, branched alkane, and cycloalkane) and its propensity to produce highly oxygenated intermediates via extensive autooxidation of hydroperoxalkylperoxy radicals. Finally, detailed chemical kinetic simulations demonstrate the influence of these additional reaction pathways on the ignition of practical fuels.

Significance

Highly oxygenated molecules are involved in autooxidation reactions leading to the formation of secondary organic aerosols (SOAs); they are also critical intermediates in autooxidation processes for liquid hydrogen degradation and the ignition of fuels in advanced combustion systems. However, these reactions are still poorly understood. In this study, we unveil a generalized reaction mechanism involving the autooxidation of peroxy radicals with at least three stages of sequential \(O_2\) addition. We elucidate important underlying kinetics and structural characterizations of autooxidation processes used for developing new technologies including those aimed at reducing climatically active SOAs and pollutants from fuel combustion. We show that advances can be made by bridging experimental and theoretical methods used by atmospheric and combustion scientists.


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autooxidation | peroxides | ignition | secondary organic aerosol | mass spectrometry

The autooxidation of volatile organic compounds (VOCs) influences the formation of tropospheric ozone (1) and secondary organic aerosols (SOAs) (2, 3), degradation of liquid and gaseous hydrocarbons (4, 5), as well as ignition processes in combustion (6). The chemistry of peroxy radical intermediates plays a significant role in autooxidation processes, because their H-shift and sequential \(O_2\) addition reactions lead to the eventual formation of hydroperoxides, such as those found in liquid-phase hydrocarbon degradation (7, 8). Under atmospheric conditions (e.g., below 400 K), peroxy radical H-shift reactions compete with NO, HO\(_2\), and peroxy radical biomolecular reactions that convert peroxy radicals to alkoxy radicals or closed-shell species such as nitrates, hydroperoxides, or carbonyls and alcohols, respectively (1, 9). Under low NO\(_x\) conditions, peroxy radical H-shift reactions provide a large source of low-volatility SOA in the atmospheric oxidation of monoterpnes (10, 11). At relatively higher temperatures (e.g., 500–800 K), the chemistry of peroxy radicals triggers interesting combustion phenomena such as cool flames (12) and negative temperature-coefficient behavior, leading to reactivity that decreases with increasing temperature (13), and to engine knock (14).

Existing kinetic models for gas-phase hydrocarbon combustion assume that one or two \(O_2\) molecules add sequentially to the hydrocarbon radical, leading to intermediates with two or three \(O\) atoms on the hydrocarbon backbone (e.g., hydroperoxides, keto hydroperoxides, etc.), which ultimately dissociate to smaller species (15). However, recent work indicates that partially oxidized alkylperoxy radicals may undergo further sequential additions with \(O_2\), thereby leading to more highly oxygenated intermediates (16, 17). Previous work on ozonolysis or \(OH\)-radical-initiated autooxidation of unsaturated hydrocarbons has identified the formation of highly oxygenated molecules from extensive autooxidation (EA) of peroxy radicals by abstraction of \(H\) atoms from C–H connected to...
oxygenated functional groups (OH and C=O), allylic sites, and other weakly bound H atoms (10, 18–21). Under atmospheric conditions, Jokinen et al. (22) stated that intramolecular H-shift reactions are important only if relatively weak C–H bonds are available. Crounse et al. (23) also showed that functionalized species with carbonyl, alcohol, or alkene moieties are needed to facilitate H-shift reactions at room temperature.

Here, we detect highly oxygenated intermediates involved in the autooxidation of alkanes at 500–600 K. This temperature range and class of hydrocarbons are rarely investigated in atmospheric studies. We build on experimental and theoretical advances in atmospheric autooxidation chemistry research to study related processes under combustion conditions. Isotopic labeling methods demonstrated in atmospheric studies (10, 18–20) are combined with photoionization and high-resolution mass spectrometry methods in combustion research (24) to unravel the complex structure of autooxidation intermediates. We show the presence of at least three O₂ molecules adding sequentially to hydrocarbon/oxygenated radicals during gas-phase oxidation in the temperature range 500–600 K; the oxygen-containing functional groups in the highly oxygenated intermediates are also identified. These findings complement previous atmospheric autooxidation chemistry research, while extending our understanding of autooxidation processes and the prevailing reaction mechanisms used to numerically simulate fuel autoignition.

The gas-phase autooxidation of 15 VOCs was systematically examined to study the key autooxidation intermediates. Ten compounds were drawn from the four major hydrocarbon classes (i.e., normal, branched, and cyclo alkanes and aromatics): an additional five compounds have oxygen-containing functional groups (25) (1-decanol, decanal, 2-decanone, dipentyl ether, and methyl decanoate). The species were selected to represent VOCs present in tropospheric and fuel/energy oxidation environments. Autooxidation studies were carried out in two separate fused-silica jet-stirred reactors (JSR), operating at a mean residence time of 2 s, near atmospheric pressure and temperatures from 500 to 600 K. JSR-1 was coupled to a molecular beam time-of-flight mass spectrometer (MBMS), combined with synchrotron vacuum UV (SVUV) radiation from a third-generation synchrotron source as the photoionization (PI) source (26, 27). The gas-phase products from JSR-2 were analyzed by a high-resolution atmospheric pressure chemical ionization-Orbitrap mass spectrometer (APCI-OTMS) (28–30) (SI Appendix, section 1.1, Fig. S1, and Table S1).

Results and Discussion
Many autooxidation intermediates were measured from the autooxidation of the 15 VOCs (i.e., C₅H₁₀O₂) in the SVUV-PI-MBMS and APCI-OTMS experiments. Autooxidation products, with the general molecular formula CₓHᵧ₋₂Oₖ₊ₙ (n = 0–5) and CₓHᵧ₋₂O₂₊ₙ (n = 4), were consistently observed, with only a few exceptions for CₓHᵧ₋₂O₂₊ₙ (n = 4) due to low signal intensity (SI Appendix, Figs. S2–S8). Here, x equals the carbon number of the organic compounds; y is equal to 2x + 2 for alkanes, alcohols, and ethers; 2x for cycloalkanes, aldehydes, ketone compounds, and esters; z is equal to 0 for hydrocarbons, 1 for alcohols, aldehydes, ketone compounds, and ethers, and 2 for esters. A glossary of species discussed in the text is provided in SI Appendix, section 1.3. Fig. 1 shows a generalized peroxy radical oxidation mechanism comprising sequential oxygen addition and radical isomerization reactions that lead to the formation of various intermediates. The specific mechanism diagrams of 2,7-dimethyloctane and n-butylcyclohexane are shown in SI Appendix, section 1.4 and Schemes S1 and S2. The intermediates CₓHᵧ₋₂O₂₊ₙ (n = 0–1) and CₓHᵧ₋₂O₂₊ₙ (n = 2–3) derive from the first and second oxygen addition reactions, a reaction mechanism established in the 1980s (6) and widely adopted in combustion modeling (15). CₓHᵧ₋₂O₂₊ₙ (n = 4–5) intermediates are the result of third oxygen addition reactions, and these reaction pathways are labeled in red in Fig. 1. CₓHᵧ₋₂O₂₊ₙ (n = 3) are also formed from these reactions, but the resulting structures are different from those formed from the second oxygen addition reactions. Details of the reaction mechanism will be described after discussing the elemental composition and structure of the measured intermediates. At 500–600 K, peroxy radical isomerization reactions compete with bimolecular reactions (e.g., cross-combination and recombination of RO₂) and formation of dimer compounds (1, 18). For example, the rate constant of RO₂ + RO₂ (e.g., CₓHᵧOₓ + CₓHᵧOₓ) is on the order of 10¹⁵ cm³ mol⁻¹ s⁻¹ at 298 K and has a weak negative temperature dependence (31), while the intramolecular H-atom abstraction of the RO₂ radical via a six-membered-ring transition state is on the order of 10⁻¹⁸ cm³ mol⁻¹ s⁻¹ at 298 K (23). However, the intramolecular H-atom abstraction is strongly temperature dependent and its rate is on the order of 10⁻¹⁴ s⁻¹ at 550 K (32). This is one feature of alkane autooxidation in the low-temperature combustion environment that is distinct from ozonolysis and/or OH-radical-initiated autooxidation of unsaturated hydrocarbons in which dimer compounds were observed to be important (10, 18, 19).

Elemental C/H/O Composition of Highly Oxygenated Intermediates
Initially, the elemental C/H/O composition of highly oxygenated intermediates was confirmed to have the same carbon number as the VOC reactant with three to five additional oxygen atoms. To enhance molecular information within the instrument’s mass resolution, unambiguous elemental composition was obtained via isotope labeling, using both ¹⁸O₂ and then ³²O₂ as the oxidizers in autooxidation of 2,7-dimethyltetrahydrofuran and cyclohexane. Fig. 2a for 2,7-dimethyltetrahydrofuran (C₁₀H₁₈₂O₂) shows that replacing ¹⁶O₂ by ¹⁸O₂ increases the mass-to-charge ratio, m/z, of highly oxygenated intermediates CₓHᵧOₓO₂, CₓHᵧOₓO₄, CₓHᵧOₓO₃, and CₓHᵧOₓO₂ by 6, 8, 8, and 10, respectively. Similarly, features featuring 3, 4, or 5 oxygen atoms were identified in the case of cyclohexane autooxidation using isotopically labeled O₂ (SI Appendix, Fig. S9). The formation of highly oxygenated intermediates was further corroborated for both VOCs by the high-resolution APCI-OTMS experiment, which observed the protonated molecular
peaks of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, C_{10}H_{20}O_{4}, and C_{10}H_{22}O_{5} (accuracy < 5 ppm, Fig. 2B) for 2,7-dimethylcyclohexane and analogous highly oxygenated intermediates for cyclohexane (SI Appendix, Fig. S9). Similar oxygenated hydrocarbon species have been detected from the atmospheric ozonolysis and autooxidation of monoterpenes and their surrogates under low concentration of NO (10, 11, 18), which establishes the relevance of the present findings with atmospheric chemical processes.

H/D Exchange Reactions. The signal profiles for C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, C_{10}H_{20}O_{4}, and C_{10}H_{22}O_{5} from 2,7-dimethylcyclohexane are typical of hydroperoxides formed during hydrocarbon oxidation (SI Appendix, Fig. S10); they are produced in early stages of oxidation and consumed rapidly at higher temperatures because of the low O–OH bond dissociation energy in the hydroperoxy group (8). Hydroperoxides are important in controlling hydrocarbon reactivity during autooxidation (15, 33).

The presence of hydroperoxy functional groups was confirmed by H/D exchange reactions using D_{2}O in JSR-1 coupled with SVUV-PI-MBMS. H/D exchange reactions have been used in the field of atmospheric chemistry to identify -OH/-OOH functional groups (10, 18–20). However, it was unclear if H atoms in other functional groups could participate in exchange reactions with D_{2}O at higher temperature (e.g., 500–600 K). Therefore, we confirmed that only H atoms in -OH and -OOH functional groups (i.e., acidic H atoms) participate in H/D exchange reactions for the selected conditions by reacting D_{2}O with 2,7-dimethylcyclohexane, as well as ethanol, propanal, acetone, tetrahydrofuran, methyl peroxide, and hydrogen peroxide (SI Appendix, section 1.7 and Fig. S11). Products resulting from the autooxidation of 2,7-dimethylcyclohexane with D_{2}O further supported the finding that only acidic H atoms participated in H/D exchange reactions. The mass spectra obtained for 2,7-dimethylcyclohexane autooxidation in Fig. 3 A–C show the signal intensities for C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5}, with and without the addition of ~50,000 ppm D_{2}O to the reactants. A clear indication for H/D exchange upon D_{2}O addition is seen from the decreasing signal intensity of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5}, and appearance of C_{10}H_{21}DO_{3}, C_{10}H_{21}DO_{4}, C_{10}H_{21}DO_{5}, and C_{10}H_{21}D_{2}O_{5}. We note that a weak signal near m/z 190 is the isotopic peak of C_{10}H_{19}DO_{3}. Further evidence is provided in Fig. 3 D–F, which shows the photoionization efficiency spectra of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5} and the corresponding deuterated compounds, C_{10}H_{21}DO_{3}, C_{10}H_{21}DO_{4}, C_{10}H_{21}DO_{5}, and C_{10}H_{21}D_{2}O_{5}. Photoionization efficiency spectra were obtained by scanning photon energy, and the relationship between structure and photoionization behavior was used for species identification (24, 34). The applicability of this methodology is limited for high-molecular-weight hydrocarbons due to the large number of possible isomers (34). Fig. 3 D–F shows that both hydrogenated and deuterated compounds contribute to the observed spectra, and their near-identical photoionization efficiency spectra indicate their identical structures. Current knowledge of hydrocarbon autooxidation mechanisms would suggest that bimolecular reactions of peroxy radicals, as well as bimolecular reactions of allyl radicals, lead to oxygenated intermediates with –OH functional groups (7, 35). However, these oxygenates do not correspond to the highly oxygenated intermediates observed in this work. Thus, the exchange experiments conclude that the detected intermediate C_{10}H_{20}O_{3} contains one –OOH group, C_{10}H_{22}O_{4} contains one –OOH group, and C_{10}H_{24}O_{6} contains two –OOH groups. The H/D exchange reaction between C_{10}H_{20}O_{3} and D_{2}O also produces C_{10}H_{21}DO_{3} (a smaller peak than that of C_{10}H_{21}DO_{4}), as shown in Fig. 3 B and E. These results indicate that C_{10}H_{20}O_{3} may contain isomers with two –OOH groups (e.g., dienes with two –OOH groups).

The presence of hydroperoxy functional groups in these oxygenates is further supported by both the nature and the similar temperature-dependent behavior of their fragments (SI Appendix, Fig. S10). The ions C_{10}H_{20}O_{4}^{+} and C_{10}H_{22}O_{5}^{+} (SI Appendix, Fig. S104) are plausible fragments of the primary ion C_{10}H_{23}O_{5}^{+}, after elimination of –O–OH and through dissociation of the O–O–OH bond in the hydroperoxy group, respectively. Similarly, C_{10}H_{19}O_{4}^{+} and C_{10}H_{18}O_{3}^{+} (SI Appendix, Fig. S10 B and D) are likely the

Fig. 2. Mass spectra of highly oxygenated intermediates recorded in 2,7-dimethylcyclohexane autooxidation. (A) SVUV-PI-MBMS results at photon energy of 9.5 eV with ^{16}O_{2} (green line) and ^{18}O_{2} (black line) as the oxidizer. (B) APCI-OTMS results with ^{16}O_{2} as oxidizer. Protonated molecular ion peaks C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5} multiplied by 10, 100, and 100, respectively, for clarity.

Fig. 3. Photoionization mass spectra and photoionization efficiency spectra of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5} with and without D_{2}O addition. (A–C) Mass spectra of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5} with (dashed red line) and without D_{2}O addition (black line) at 530 K and 9.5 eV. (D–F) Photoionization efficiency spectra of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, and C_{10}H_{22}O_{5} (open symbols) and their corresponding deuterated species (lines) at 530 K. Signal of C_{10}H_{20}O_{3} in F multiplied by 2.3.
products of the primary ions C_{9}H_{11}O_{4}^{+} and C_{9}H_{12}O_{5}^{+} after elimination of -OOH.

**Autooxidation Mechanism Involving Sequential Oxygen Addition.** Similar distributions of autooxidation intermediates (SI Appendix, Figs. S2-S8) and their fragments (SI Appendix, Table S2) were observed during oxidation of the other 12 VOCs in the SVUV-PL-MBMS experiment. This information on autooxidation intermediates motivates us to establish a general mechanistic understanding of their formation and destruction. Specifically, the reactions involving the first, second, and third sequential O₂ addition steps are addressed in the oxidation of VOCs with the general formula C_{n}H_{2n+1}O_{x} [i.e., reactions involved in the formation of autooxidation intermediates with the general formula C_{n}H_{2n+1}O_{x+4} (n = 0–5)]. Fig. 1 illustrates a generalized reaction mechanism and the pertinent processes for 2,7-dimethyloctane autooxidation.

**First and second oxygen addition.** The reaction sequence starts with H-atom abstraction from the parent organic molecule (i.e., C_{9}H_{12}O, C_{7}H_{7}O) to produce a radical R (C_{n}H_{2n+1}O, C_{n}H_{2n+2}O). Ionicized text within parentheses denotes intermediate species in 2,7-dimethyloctane oxidation. H-atom abstraction occurs at primary, secondary, and tertiary carbon sites of 2,7-dimethyloctane. Fig. 1 shows the structure of the probable intermediates from the autooxidation of R with the radical site at the primary carbon. Intramolecular H-atom abstraction of ROO, OOOOOH, and OO(POOH)₂ radicals, via a six-membered-ring transition state (TS), is considered. Three sequential steps of O₂ addition (solid arrows in Fig. 1) lead to highly oxygenated intermediates [i.e., C_{n}H_{2n}O_{x+5} + x (n = 3–5), C_{n}H_{2n+1}O_{x+6}, C_{n}H_{2n+2}O_{x+6}, and C_{n}H_{2n+3}O_{x+7}]. The first O₂ addition to the radical R produces an alkylperoxy radical (ROO, C_{n}H_{2n+1}O), which may isomerize to a hydroperoxy radical (36) (OOO, C_{n}H_{2n+2}OOH). A second O₂ addition to OOO OH yields a hydroperoxalkylperoxy radical (OOOOGOH, OOC_{n}H_{2n+2}OOH). Intramolecular H-atom abstraction of the C=H alpha to the -OOH group in OOOOH, with subsequent β-O-O scission, forms highly oxygenated intermediates C_{n}H_{2n}O_{x+5} (with one C=O and one -OOH) and one OH radical. Here, the intramolecular H-atom abstraction of the C-H alpha to the -OOH group by an -OO via five- to eight-membered TS is defined as the standard isomerization, while intramolecular H-atom abstraction by an -O-O via five- to eight-membered TS from a C-H not alpha to the -OOH is the EA. The competition between standard isomerization and EA is determined by the TS ring size and the carbon type being abstracted (32). A few of these postulated reaction intermediates and their plausible structures have been recently identified in the low-temperature oxidation of selected VOC compounds, including n-butane (24, 33), n-pentane (37), 2-methylhexane (17), and dimethyl ether (26). The EA pathway leads to a radical P(OOOH), which can undergo cyclization to produce OH radical and a species of formula C_{n}H_{2n}O_{x+3}, albeit with one O heterocycle and one -OOH functional group.

**Third oxygen addition.** The abundance of isomers for highly oxygenated intermediates and the numerous possible structures and conformers have historically made it difficult to follow the autooxidation mechanism, even for two sequential oxygen additions (17, 26). However, this study makes it possible to follow these reactions for a third sequential O₂ addition in which O₂ adds to the radical site of P(OOOH) [e.g., C_{n}H_{2n+2}O(OOH)₂] and produces an OOP(OOH)₂ radical [e.g., OOC_{n}H_{2n+2}(OOOH)₃]. The unambiguous results from the oxygen isotope labeling and the H/D exchange experiments indicate (for 15 representatives of prototypical VOC classes) that reaction sequences occur similarly to those for the OOOOH radicals obtained after sequential addition of two O₂ molecules. The standard isomerization of OOP(OOH) and subsequent β-O-O scission forms C_{n}H_{2n}O_{x+5} (with one C=O and two -OOHs, C_{n}H_{2n+2}O₂O₂) and OH radical; the EA of OOP(OOH) leads to the T(OOOH)₂ radical [e.g., C_{n}H_{3}(OOOH)₂]. Further cyclization of T(OOOH)₂ also produces C_{n}H_{2n}O_{x+5} (with one O heterocycle and two -OOHs, C_{n}H_{2n+2}O₂O₂) and one OH radical. The reaction of P(OOOH)₂ with O₂, the concerted elimination of OOP(OOOH)₂ and the β-C-O scission of T(OOOH)₂ (not shown in Fig. 1) form C_{n}H_{2n}O_{x+5} (with one C=O and two -OOHs, C_{n}H_{2n+2}O₂O₂) and one HO₂ radical.

With the addition of three sequential oxygen molecules, additional reactions (denoted by dashed arrows in Fig. 1) may occur to form C_{n}H_{2n}O_{x+5} (with one C=O, C_{n}H_{2n+2}O₂O₂, C_{n}H_{2n+2}O₂O₂O₂, and one HO₂ radical. Note that the measured C_{n}H_{2n+2}O₂O₂ signal in this work may contain a contribution from secondary reactions, e.g., keto alcohols, from the bimolecular reactions of keto-alkoxy radicals (37). Brieﬂy, this reaction scheme explains the formation of the autooxidation intermediates: The highly oxygenated intermediates C_{n}H_{2n}O_{x+5} (n = 3–5) contain one or two hydroperoxy (OOH) groups and other functional groups include carboxyl (C=O), cyclic ether (O heterocycle), and alkene (C=C). The C_{n}H_{2n}O_{x+5} addition with one or two -OOHs, C_{n}H_{2n+2}O₂O₂ intermediates may be derived from subsequent reactions of C_{n}H_{2n+2}O₂O₂ (e.g., C_{n}H_{2n+2}O₂O₂) such as OH-radical-assisted water elimination (16, 35) and/or secondary reactions of C_{n}H_{2n}O_{x+5} (e.g., C_{n}H_{2n+2}O₂O₂). Their formation and relative ratios are not expected to signiﬁcantly alter the overall radical pool. It could be assumed that T(OOOH) undergoes further O₂ addition and subsequent intramolecular H shift to form intermediates with even higher oxygen content, especially for functional groups with longer carbon chains, appropriate functional groups, and in oxidation processes with adequate concentration of O₂ and appropriate temperature. Thus, the sequential addition of oxygen, as deﬁned here, may not end after the third step.

**Extensive Peroxy Radical Autooxidation.** An interesting aspect of the proposed reaction mechanism is the EA of OOOOH and subsequent third O₂ addition pathways. To provide further insights into this reaction type, Fig. 4 presents the relative ratios of C_{n}H_{2n}O_{x+5} to C_{n}H_{2n}O_{x+1} from autooxidation of n-heptane, 2-methylhexane (17), 2,5-dimethylhexane (16), cycloheptane, n-decane, 2-methylnonane, 2,7-dimethyloctane, and n-butylcyclohexane (SI Appendix, section 1.9 and Fig. S12). C_{n}H_{2n+2}O₂O₂ and C_{n}H_{2n+3}O₂ are representative products from the third and second O₂ addition, respectively, as highlighted in Fig. 1. The ratio of these two intermediates indicates the likelihood of the EA isomerization of OOOOH and third O₂ addition reaction and the propensity to produce higher oxygenated species (i.e., C_{n}H_{2n}O₂O₂). Note that the cyclization of P(OOOH)₂ also forms C_{n}H_{2n}O₂O₂, but simulations have proven that C_{n}H_{2n}O₂O₂ is primarily formed via the standard isomerization of OOOOH (17, 38). Fig. 4 shows that C_{n}H_{2n}O₂O₂’s yield depends on the molecular structure of the VOC. For example, n-heptane has the lowest yield, 2-methylhexane and 2,5-dimethyloctane have an intermediate yield, and cycloheptane has the highest yield among the C₈ and C₉ alkanes. An analogous trend to form C_{n}H_{2n}O₂O₂ is observed for the C₁₀ alkanes in the order of n-decane < 2-methylnonane < 2,7-dimethyloctane < n-butylcyclohexane, indicating that hydrocarbons with a tertiary C=H site and ring structures favor the formation of C_{n}H_{2n}O₂O₂ highly oxygenated intermediates. The tertiary C=H site and ring structures that favor the EA process permit intramolecular H-abstraction reactions to proceed via a six-membered-ring TS, since they are the most favorable pathways (15). Numerous OOOOH radicals can be produced from the autooxidation process. Several typical α,γ-OOQOHs, from normal alkanes, branched alkane, and cycloalkane, have been chosen for discussion here. α is the position of the -OO group while γ is the position of the -OOH group. The activation energies and entropy changes for intramolecular
H-abstraction reactions in Fig. 5 A-C have been computed from quantum calculations. Details of the kinetic analysis with temperature are shown in SI Appendix, section 2.1 and Fig. S13. The peroxy radicals investigated in this work have a high degree of torsional anharmonicity, which can lead to discrepancies in partition function calculations (39, 40). Further study on the standard isomerization and EA of the peroxy radicals using more accurate treatment of the thermodynamic and kinetics calculations is needed.

The kinetic analysis reveals that EA of α,γ-OOQOOH radical A, B, and C in Fig. 5 is feasible. An EA of OOQOOH radical by abstracting a tertiary C–H is preferred over an EA by abstracting A, B, and C in Fig. 5, indicating the likelihood of extensive autooxidation of OOQOOH and third O2 addition reaction, which affect the propensity to produce heavier highly oxygenated intermediates (i.e., C5H5–OO). Data for 2-methylhexane and 2,5-dimethylhexane autooxidation from Wang et al. (16, 17).

Fig. 4. Relative ratios of C5H5–OO to C5H5–O2 in eight hydrocarbon autooxidation reactions (A–H), indicating the likelihood of extensive autooxidation of OOQOOH and third O2 addition, which affect the propensity to produce heavier highly oxygenated intermediates (i.e., C5H5–OO). Data for 2-methylhexane and 2,5-dimethylhexane autooxidation from Wang et al. (16, 17).

In summary, highly oxygenated intermediates with one to two hydroperoxy groups were detected during the autooxidation of 15 organic compounds at combustion-relevant temperatures, and a peroxy radical reaction mechanism with three stages of sequential O2 addition was confirmed. A combination of experimental techniques was used to determine the structures and functional groups of these elusive intermediate species. Experimental observations for different VOC structures, combined with a kinetics analysis, highlighted the role of EA isomerization reactions in forming highly oxygenated intermediates. Including these reaction pathways in chemical kinetic simulations was shown to decrease the ignition delay time predictions of n-heptane/O2/N2 mixtures at 600 K, with an ~20% reduction at 1 bar and 60% reduction at 50 bar (SI Appendix, Fig. S17 and Table S4).

Fig. 5. Structural analysis of α,γ-OOQOOH intramolecular H abstraction. Blue underlined numbers denote activation energy, unit is kcal/mol; red italicized numbers denote entropy change, unit is calmol/K. Activation energies and entropy change of intramolecular H-abstraction reactions in A–C and activation energy in F were computed as described in SI Appendix, section 2. The activation energy and entropy change for the extensive autooxidation pathway in D is not shown since a competing standard isomerization pathway does not exist. Activation energies of 26.4 and 21 kcal/mol in F estimated from quantum-chemistry calculations of Xing et al. (41) and Ning et al. (42), respectively.

Summary and Conclusions

In summary, highly oxygenated intermediates plays an important role in radical chain branching that drives ignition processes in combustion engines. The C5H5–O2 intermediates produced via the third sequential O2 addition scheme are additional radical chain-branching intermediates (16) which may extend ignition limits under certain conditions (43). The absence of these additional radical chain
branching pathways in simulations may explain the underprediction of ignition delay times of long chain alkanes at high pressures (44). It is possible that intermediates with even higher oxygen content may be produced under low-temperature and high-pressure combustion conditions. This autoxidation mechanism also has implications for the formation of cool flames in alkane fuel droplets under microgravity conditions (45). This chemistry is important in liquid hydrocarbon degradation in the temperature range of 400–500 K (7), which is relevant to the oxidative stability of lubricants and other industrial fluids. The formation of atmospheric SOA under low NOx concentrations (10) is also driven by similar chemical processes. The experimental results presented here for molecules with oxygen-containing functional groups (e.g., carbonyl and hydroxy) are in agreement with prior theoretical work on mechanisms for creating and aging the organic content of atmospheric particulate matter (23). Further advances in understanding autoxidation processes can be achieved by bridging experimental and theoretical methods used by atmospheric and combustion scientists.

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