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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 hydroperoxalkyperoxy 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 unravel a generalized reaction mechanism involving the autooxidation of peroxy radicals with at least three stages of sequential O2 addition. We elucidate important underlying kinetics and structural characteristics 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.

Author contributions: Z.W., N.H., P.D., and S.M.S. designed research; Z.W., D.M.P.-V., B.C., K.M., S.Y.M., H.W., S.S., M.A.R., N.H., P.D., and S.M.S. performed research; Z.W. analyzed data; and Z.W., D.M.P.-V., B.C., K.K.-H., N.H., P.D., S.R.L., and S.M.S. wrote the paper.

The authors declare no conflict of interest.

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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. Crouse et al. (23) also showed that functionalized species with carboxyl, 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/engine 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., C₅H₁₂O) in the SVUV-PI-MBMS and APCI-OTMS experiments. Autooxidation products, with the general molecular formula CₓHᵧ − 2O₂ + n (n = 0–5) and CₓHᵧ − 3O₂ + 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 peroxo 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-dimethylloctane 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 − 3O₂ + 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 bi-molecular 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., CₓHᵧO₂ + CₓHᵧO₂) is on the order of 10¹⁴ 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 10⁻⁵ s⁻¹ at 298 K (23). However, the intramolecular H-atom abstraction is strongly temperature dependent and its rate is on the order of 10⁻¹⁰ 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 ¹⁶O₂ and then ¹⁸O₂ as the oxidizers in autooxidation of 2,7 dimethylloctane and cyclohexane. Fig. 2A for 2,7 dimethylloctane (C₁₃H₂₅O₂) shows that replacing ¹⁶O₂ by ¹⁸O₂ increases the mass-to-charge ratio, m/z, of highly oxygenated intermediates CₓHᵧOₙ, CₓHᵧO₁₈, CₓHᵧO₁₆, CₓHᵧO₁₄, and CₓHᵧO₁₂ by 6, 8, 8, and 10, respectively. Similarly, species 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

Fig. 1. Generalized autooxidation mechanism of organic compounds (i.e., CₓHᵧO₂), involving formation of intermediates with molecular formula of CₓHᵧ − 2O₂ + n (n = 0–5, labeled in blue and boxed). The structures of probable intermediates for autooxidation of R with a radical site at the primary carbon of 2,7-dimethylloctane are presented. Pathways to CₓHᵧ − 3O₂ and CₓHᵧ − 2O₂ highly oxygenated intermediates are highlighted with bold arrows. The extensive autooxidation and third sequential oxygen addition reaction pathways are denoted by red arrows. Intramolecular H-atom abstraction of the C-H alpha to the -OOH group by an -OOH is a standard isomerization; intramolecular H-atom abstraction from a C-H not alpha to the -OOH group by an -OOH is an extensive autooxidation.

Fig. 2.
peaks of C_{10}H_{20}O_{3}, C_{10}H_{18}O_{4}, C_{10}H_{20}O_{4}, and C_{10}H_{20}O_{5} (accuracy < 5 ppm, Fig. 2F) for 2,7-dimethyltetcane and analogous highly oxygenated intermediates for cyclohexane (SI Appendix, Fig. S9).

Similar oxygenated hydrocarbon species have been detected from the atmospheric ozonolysis and autoxidation 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_{20}O_{5} from 2,7-dimethyltetcane 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 autoxidation (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-dimethyltetcane, as well as ethanol, propenal, acetone, tetrahydrofuran, methyl peroxide, and hydrogen peroxide (SI Appendix, section 1.7 and Fig. S11). Products resulting from the autoxidation of 2,7-dimethyltetcane 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-dimethyltetcane autoxidation 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_{20}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_{20}O_{5}, and appearance of C_{10}H_{19}DDO_{3}, C_{10}H_{18}DDO_{3}, and C_{10}H_{19}DDO_{3}, and C_{10}H_{18}DDO_{3}. We note that a weak signal near m/z 190 is the isotopic peak of C_{10}H_{19}DDO_{3}. Further evidence is provided in Fig. 3 D–F, which shows the photoionization efficiency spectra of C_{10}H_{19}DDO_{3}, C_{10}H_{18}DDO_{3}, and C_{10}H_{19}DDO_{3}, and the corresponding deuterated compounds, C_{10}H_{19}DDO_{3}, C_{10}H_{18}DDO_{3}, C_{10}H_{19}DDO_{3}, and C_{10}H_{18}DDO_{3}. 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 autoxidation mechanisms would suggest that bimolecular reactions of peroxy radicals, as well as bimolecular reactions of alkyl 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_{18}O_{4} contains one –OOH group, and C_{10}H_{20}O_{5} 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_{19}DDO_{3} (a smaller peak than that of C_{10}H_{19}DDO_{3} 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_{19}O_{4}^{+} (SI Appendix, Fig. S10.4) are plausible fragments of the primary ion C_{10}H_{20}O_{3}^{+}, after elimination of –OOH and through dissociation of the O–OH bond in the hydroperoxy group, respectively. Similarly, C_{10}H_{18}O_{5}^{+} and C_{10}H_{19}O_{3}^{+} (SI Appendix, Fig. S10 B and D) are likely the

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

![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_{20}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_{20}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_{20}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.](image)
products of the primary ions C_{10}H_{13}O_5^- and C_{10}H_{15}O_3^- after elimination of -OOH.

Autoxidation Mechanism Involving Sequential Oxygen Addition. Similar distributions of autoxidation 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-PI-MBMS experiment. This information on autoxidation 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_{x}H_{y}O_{z} [i.e., reactions involved in the formation of autoxidation intermediates with the general formula C_{x}H_{y} - O_{z} + n (n = 0–5)]. Fig. 1 illustrates a generalized reaction mechanism and the pertinent processes for 2,7-dimethyloctane oxidation.

**First and second oxygen addition.** The reaction sequence starts with H-atom abstraction from the parent organic molecule (i.e., C_{10}H_{13}O_4, C_{10}H_{12}O_3) to produce a radical R (C_{10}H_{10} - O_{2}, C_{10}H_{12}O_2). Italized 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 autoxidation of R with the radical site at the primary carbon.

Intramolecular H-atom abstraction of ROO, OOQOOH, and OO(POOH)₃ 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_{10}H_{10} - O_{3} + n (n = 3–5), C_{10}H_{12}O_2, C_{10}H_{14}O_2, and C_{10}H_{16}O_3]. The first O₂ addition to the radical R produces an alkylperoxy radical (ROO, C_{10}H_{12}O_2(OO)) that may isomerize to a hydroperoxyalkyl radical (36) (OOO, C_{10}H_{14}O_2(OOH)). A second O₂ addition to OOO yields a hydroperoxalkyloxy radical (OOOOOH, OOC_{10}H_{14}O_2(OOH)). Intramolecular H-atom abstraction of the C-H alpha to the -OOH group in OOOOOOH, with subsequent β-O-O scission, forms highly oxygenated intermediates C_{10}H_{10} - O_{4} + y (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 -OOO via five- to eight-membered TS is defined as the standard isomerization, while intramolecular H-atom abstraction by an -OOO via five- to eight-membered-ring 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). An EA pathway leads to a radical P(OOOH)₂, which can undergo cyclization to produce OH radical and a species of formula C_{10}H_{10} - O_{4} + 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 autoxidation mechanism, even for two sequential oxygen addition reactions (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)₂ [e.g., C_{10}H_{12}O_2(OOH)₂] and produces an OOP(OOH)₂ radical [e.g., OOC_{10}H_{14}O_2(OOH)]. 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 OOOOOOH radicals obtained after sequential addition of two O₂ molecules. The standard isomerization of OOP(OOH)₂ and subsequent β-O-O scission forms C_{10}H_{10} - O_{5} + 5 (with one C=O and two -OOHs, C_{10}H_{14}O_3(O) and OH radical; the EA of OOP(OOH)₂ leads to the T(OOOH)₃ radical [e.g., C_{10}H_{13}(OOH)₃]). Further cyclization of T(OOOH)₃ also produces C_{10}H_{10} - O_{6} + 5 (with one O heterocycle and two -OOHs, C_{10}H_{14}O_3(O) and one OH radical. The reaction of P(OOH)₂ with O₂, the concerted elimination of OOP(OOH)₂, and the β-C-O scission of T(OOOH)₃ (not shown in Fig. 1) form C_{10}H_{10} - O_{5} + 4 (with one C=O and two -OOHs, C_{10}H_{14}O_3(O) and one HO₂ radical.

Fig. 1 shows the structure of the probable intermediates from the autoxidation of R with the radical site at the primary carbon. H-atom abstraction by an

**TS is defined as the standard isomerization, while intramolecular H-atom abstraction of the C radical (ROO, C_{10}H_{12}O_2) that may isomerize to a hydroperoxyalkyl radical (36) (OOO, C_{10}H_{14}O_2(OOH)). A second O₂ addition to OOO yields a hydroperoxalkyloxy radical (OOOOOH, OOC_{10}H_{14}O_2(OOH)). Intramolecular H-atom abstraction of the C-H alpha to the -OOH group in OOOOOOH, with subsequent β-O-O scission, forms highly oxygenated intermediates C_{10}H_{10} - O_{4} + y (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 -OOO via five- to eight-membered TS is defined as the standard isomerization, while intramolecular H-atom abstraction by an -OOO via five- to eight-membered-ring 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). An EA pathway leads to a radical P(OOOH)₂, which can undergo cyclization to produce OH radical and a species of formula C_{10}H_{10} - O_{4} + 3, albeit with one O heterocycle and one -OOH functional group.

**Extended Peroxy Radical Autoxidation.** An interesting aspect of the proposed reaction mechanism is the EA of OOOOOOH and subsequent third O₂ addition pathways. To provide further insights into this reaction type, Fig. 4 presents the relative ratios of C_{10}H_{10} - O_{3} to C_{10}H_{10} - O_{1} from autoxidation 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_{10}H_{10} - O_{2} and C_{10}H_{10} - O_{3} 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 OOOOOOH and third O₂ addition reaction and the propensity to produce higher oxygenated species (i.e., C_{10}H_{10} - O_{2}). Note that the cyclization of P(OOOH)₂ also forms C_{10}H_{10} - O₃, but simulations have proven that C_{10}H_{10} - O₃ is primarily formed via the standard isomerization of OOOOOOH (17, 38). Fig. 4 shows that C_{10}H_{10} - O₃'s yield depends on the molecular structure of the VOC. For example, n-heptane has the lowest yield, 2-methylhexane and 2,5-dimethylhexane have an intermediate yield, and cycloheptane has the highest yield among the C₅ and C₆ alkanes. An analogous tendency to form C_{10}H_{10} - O₃ is observed for the C₆ alkanes in the order of n-decane < 2-methylmethylene < 2,7-dimethyloctane < n-butylcyclohexane, indicating that hydrocarbons with a tertiary C-H site and ring structures favor the formation of C_{10}H_{10} - O₃ 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 OOOOOOH radicals can be produced from the autoxidation process. Several typical α,γ-OOOOOHs, from normal alkane, 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 pery 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 $\alpha_\gamma$-OOOOOH radical $\alpha$, $\beta$, and $\gamma$ in Fig. 5 is feasible. An EA of OOQOOH radical by $\alpha$-OOH group is impossible without altering the cyclic ring structure. Table S4). The structure of the axial–axial conformer hinders the formation of $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_3$ (keto-hydroperoxide) because the standard isomerization process by intramolecular H abstraction of the equatorial-C–H alpha to the OOH group is impossible without altering the cyclic chair structure.

Cycloalkanes containing alkyl side chains further promote the production of $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_3$ intermediates, as in the case of $n$-butylcyclohexane. Fig. 5F shows one exemplary $\alpha_\gamma$-OOOOOH radical in $n$-butylcyclohexane autooxidation, where the –OOH and –OO are both at the axial position and the $n$-butyl is at the equatorial position. The –OO group can abstract the axial C–H of carbon site five in the ring, or abstract the C–H of carbon site seven in the side chain via six-membered-ring TS. The free rotation of the side chain significantly reduces the energy barrier from 26.4 kcal/mol (41) to 21 kcal/mol (42), which then accelerates the EA process in $n$-butylcyclohexane.

Summary and Conclusions

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 O$_2$ 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/O$_2$/N$_2$ mixtures at 600 K, with an ~20% reduction at 1 bar and 60% reduction at 50 bar (SI Appendix, Fig. S17 and Table S4).

O–OH bond dissociation in hydroperoxy groups of highly oxygenated intermediates plays an important role in radical chain branching that drives ignition processes in combustion engines. The $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_3$ intermediates produced via the third sequential O$_2$ 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

Fig. 4. Relative ratios of $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_3$ to $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_2$ in eight hydrocarbon autooxidation reactions (A–H), indicating the likelihood of extensive autooxidation of OOOOOH and third O$_2$ addition reaction, which affect the propensity to produce higher oxidized intermediates (i.e., $\mathrm{C}_n\mathrm{H}_m\ldots\mathrm{O}_3$). Data for 2-methylhexane and 2,5-dimethylhexane autooxidation from Wang et al. (16, 17).

Fig. 5. Structural analysis of $\alpha_\gamma$-OOOOOH intramolecular H abstraction. Blue underlined numbers denote activation energy, unit is kcal/mol; red italicized numbers denote entropy change, unit is cal/mol/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.
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, which is relevant to the oxidative stability of lubricants and other industrial fluids. The formation of atmospheric SOA under low NO2 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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