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Alkylperoxy Radical Photochemistry in Organic Aerosol Formation Processes

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Supporting Information

ABSTRACT: Recent studies have shown that 254 nm light can be used to generate organic aerosol from iodoalkane/air mixtures via photodissociation of the C–I bond and subsequent oxidation of the alkyl radical. We examine organic aerosol formed from the 1-iodooctane photolysis at this wavelength using high-performance liquid chromatography (HPLC) with derivatization to selectively probe carbonyl- and hydroxyl-containing molecules. Tandem mass spectrometry reveals that the product distributions are much more complex than a traditional low-NO_x peroxy—peroxy oxidation mechanism from a single parent isomer would justify. We propose that this difference is due to peroxy radical photochemistry, leading to two major channels: direct peroxy radical isomerization via internal H-abstraction and reverse dissociation to form alkyl radical and O₂. The complexity of the product spectrum is derived from both scrambling of the radical site in the alkyl radical and the additional oxidation of otherwise stable peroxy radicals as a result of



the isomerization. A branching ratio for these channels is estimated using a canonical representation of the internal energy distribution. Lifetime estimates using extrapolated ethyl peroxy absorption cross sections and the actinic flux near 310 nm show that peroxy radical photochemistry may play a role in defining the composition of atmospheric secondary organic aerosol formed in pristine (low-NO_x) environments.

INTRODUCTION

The use of photolytic initiation for generating secondary organic aerosol (SOA) is well-established and is key to discerning oxidation processes that lead to gas-to-particle condensation. Smog chambers simulate near-atmospheric conditions and time scales and are typically initiated with fluorescent ultraviolet blacklights or Xe arc lamps with wavelengths longer than 290 nm.¹⁻⁵ Flow-tube studies probe particle formation processes under conditions that are no longer similar to those in the atmosphere but offer significant other advantages, including the ability to initiate oxidation from a single isomer.^{6,7} In addition, high concentrations of OH radical can be generated within such flow reactors to oxidize an input reactant rapidly and extensively, as is done in systems such as the Toronto Photo-Oxidation Tube⁸ (TPOT) and the Potential Aerosol Mass⁹ (PAM) reactor. These systems utilize much shorter wavelengths of light, typically Hg-I emission at 254 nm. However, the use of these shorter wavelengths can have a significant effect on the downstream chemistry, specifically in peroxy radical photochemistry, that has not been previously discussed in organic aerosol particle formation.

In this work, we examine aerosol generated from the 254 nm photodissociation of 1-iodooctane under conditions similar to those described recently by Kessler et al.⁶ Photolysis of the iodoalkane in air at 1 bar pressure and concentrations from $1-100 \,\mu$ mol mol⁻¹ leads to the spontaneous formation of particles

in the absence of an external seed particle. We apply a recently developed high-performance liquid chromatography (HPLC) derivatization methodology to the condensed-phase products of this aerosol to examine the functional group distributions of the product mixture.⁷ These distributions show a much more complex product spectrum than expected for traditional NO_x-free radical propagation involving only peroxy self-reactions.

We propose that 254 nm photochemistry of the peroxy radicals has two major effects on the condensed-phase product composition. Energy from the absorption of a 254 nm UV photon by a peroxy radical is rapidly redistributed among all of the molecule's vibrational modes.^{10,11} This additional energy permits direct isomerization and decomposition reactions to occur rapidly, leading to a bevy of products that are otherwise unseen at typical atmospheric temperatures and pressures. Similar observations have been made for near-infrared peroxy radical photochemistry;¹² however, the present wavelength will impart much more energy into the system and may be particularly relevant in experimental apparatus that use ultraviolet light for photochemical initiation. The newly available isomerization channels in particular propagate the overall oxidation cycle, leading to greater levels of oxygen

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Figure 1. Schematic of flow reactor and sampling equipment.

substitution than predicted by typical atmospheric oxidation models. A second effect is derived from the large amount of internal energy available after dissociation or isomerization occurs. Prior to collisional quenching, the available internal energies of these photoproducts are well above the isomerization barriers for H-atom migration. As a result, the radical sites will be scrambled throughout the molecule after cooling.

To study the effect of enhanced oxidation as a result of isomerization, a kinetics model attempting to capture the complexity of the distribution was constructed to examine the oxidation enhancement by the new photochemical pathways. Due to the extremely large number of possible products, the system was modeled by tracking the temporal order of functional group additions to the parent isomer. In addition to exploring the effects of the photon energy on the product spectrum, we consider the unimolecular peroxy radical photochemistry of both the parent peroxy radical and decomposition products and speculate on possible atmospheric implications that have not to our knowledge been considered in the literature.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Experiments were conducted using a laminar flow cell into which a mixture of dry air and 1-iodooctane ($C_8H_{17}I$) is introduced.^{*a*} Irradiation of the sample with light at 254 nm results exclusively in the $n \rightarrow \sigma^*$ photodissociation of the C–I bond to form the octyl radical, ${}^{\bullet}C_8H_{17}$ and primarily ${}^{\bullet}I({}^{2}P_{1/2})$.¹³ In the presence of oxygen, the primary octyl peroxy radical is formed and serves as the precursor to organic aerosol (OA) formation.

Apparatus. The flow reactor used in these experiments is shown schematically in Figure 1 and consists of a quartz tube, 183 cm in length with an outer diameter of 15.2 cm and an inner diameter of 14.0 cm. The inlet of the flow cell passes through a stainless steel flange where a mixture of sample and air is introduced perpendicularly to the cell flow via a spray nozzle. 1-Iodooctane is introduced by bubbling argon through a liquid sample held at 291.2 \pm 0.1 K, which typically provides $2-12 \ \mu \text{mol mol}^{-1}$ concentrations in the reactor. All inlet flows are controlled by mass flow controllers (MKS π MFC, Andover, Maine). The quartz flow cell is surrounded by a bank of 12 nonozone producing "germicidal" fluorescent light bulbs (General Electric 29499 G32T10), nominally producing 14 W of 253.6 nm light each. The light shroud produces significant heat, and the cell operates at 315 ± 2 K under these conditions. Uncertainties throughout this manuscripts are 1σ , unless otherwise noted.

The output flange contains numerous radially oriented ports, which are sent to a single vent and collectively identified as the waste vent in the figure. The bulk of the output passes through a larger central port and is sampled through a 12.7 mm stainless steel tube; the flow rate through this central outlet relative to the flow rate through the waste vent is controlled by a vacuum pump and typically set to 80-90% of the total inlet flow, as measured by a bubble flow calibrator (Sensidyne Gilibrator-2 Standard and High Flow Cells, St. Petersburg, FL) corrected to room temperature and pressure. The flow rate in the system was set at 8.5 L min⁻¹ (standard conditions, 273.15 K, 1.013 bar) for a residence time of 3.0 ± 0.1 min. The output aerosol sampling flow is split with $3.3 \pm 0.4\%$ of the total flow going to a particle size spectrometer (TSI, Shoreview, MN; 3080L scanning mobility particle sizer and 3775 n-butanol condensation particle counter), and the remainder is simultaneously collected on a quartz microfiber filter (47 mm, Munktell, Falun, Sweden). Measurement of the size distribution and collection of the aerosols onto the filter occur continuously throughout the duration of the experiment.

OA particles formed spontaneously under these conditions, and condensed-phase mass yields of up to 3% were obtained. A plot of the mass yield variation with sample mass is provided as Supporting Information. Typical experiments in this work were done at the lower concentration range, $2-3 \mu mol mol^{-1}$. These concentrations yielded approximately log-normal particle distributions down to 15 nm with a mode 34.6 ± 1.3 nm and a geometric standard deviation of 1.78. A second distribution at smaller sizes (mode <15 nm) appears to be present, but because the analysis in this work is primarily mass-based, no further attempt to characterize the small particles was made.

Analysis. Filter samples were typically collected for 2.0 \pm 0.2 h and extracted via sonication with 2.000 \pm 0.014 mL dry ACN for 1 h. The extracts were filtered with a PTFE filter (Restek, Bellefonte, PA) and analyzed. A derivatization procedure⁷ was used to differentiate the oxygen-containing moieties on the collected products: 4-(dimethylamino)benzoyl chloride (DMABC) for alcohols (OH moiety), 2-picolylamine (2-PA) for carboxylic acids (COOH), and 5-(dimethylamino)naphthalene-1-sulfonyl hydrazine (DnsHz) for nonacid carbonyls (CO). The procedure provides a means to selectively observe components containing the functional groups of interest using both ultraviolet-visible spectroscopy (UV-vis) and electrospray ionization mass spectrometry (ESI-MS). These reagents all include an aromatic component to enhance UV absorption response, and a basic nitrogen moiety to enhance positive ionization of the products in the electrospray ionizer. In this system, the UV absorption response of each of the singly derivatized samples are expected to be similar to the free reagent,⁷ permitting relative concentration measurements. The use of tandem MS analysis allows specific mass



Figure 2. Normalized HPLC–UV/vis spectra for hydroxyl (DMABC, upper plot) and carbonyl (DnsHz, lower plot) derivatizations. Annotations are of the form (m, n) indicating the labeled peak has a mass of an eight-carbon backbone with *m* OH and *n* CO, $C_8H_{18-2n}O_{m+n}$.

distributions to be observed through multiple reaction monitoring (MRM) of fragments of the bound derivatization moiety ($[M + H]^+ \rightarrow 170$ for DnsHz and $[M + H]^+ \rightarrow 148$ for DMABC). Throughout this work, the DnsHz derivatization will be identified as a "carbonyl" derivatization and DMABC as a "hydroxyl" derivatizations. No carboxylic acid was observed with the 2-PA derivatization.

Each of the derivatized solutions was analyzed by highperformance liquid chromatography (HPLC) coupled to an ultraviolet–visible absorption spectrometer (Dionex, Germering, Germany, Ultimate 3000RS) and an an Agilent 6410 electrospray ionization triple-quadrupole tandem mass spectrometer in series. The derivatized samples were separated using a reversed-phase linear gradient elution with organic concentrations ranging from 20–90% (v/v) acetonitrile over 8 min and held at 90% for 2 min. The aqueous mobile phase was a 0.1% (v/v) formic acid solution. Separation was performed on a Restek (Bellefonte, PA) Pinnacle II C-18 column (3 μ m particle size, 2.1 × 50 mm) at a flow rate of 800 μ L min⁻¹.

Chemicals. 1-Iodooctane (98%, stabilized with copper, Sigma-Aldrich) was used as the gas-phase precursor without further purification. The chemicals used for derivatization of the samples and standards include triphenylphosphine (TPP) (>98.5%), 2,2'-dipyridyl disulfide (DPDS) (>99.0%), 2-picolylamine (PA) (99%), dansyl hydrazine (DnsHz) (98%), and 4-(dimethylamino)benzoyl chloride (DMABC) (97%), pyridine (99.0%), and trifluoroacetic acid (TFA) (99%). All derivatization agents were purchased from Sigma-Aldrich and used without further purification. When necessary for derivatization, acetonitrile and pyridine were dried over 3 Å molecular sieves (Aldrich) Acetonitrile (Aldrich CHROMASOLV, HPLC-grade >99.9%) was used as the derivatization medium, a solvent in the standard and sample preparation, and as a mobile phase for HPLC analysis. Water (18 M Ω , generated with Water Pro PS filtration system, Labconco, Kansas City, MO) containing 0.1% (mass) formic acid (Sigma-Aldrich) was employed for HPLC analysis.

Gases used in this work include dry air from a Parker-Balston Purge Gas Generator (Model 75-62) passed through a TSI, Inc. Filtered Air Supply System (Model 3074B) and argon (Roberts Oxygen Co., Rockville, MD, ultra high purity, 99.999%)

Computational Methods. Chemical kinetics modeling calculations were performed using Cantera 2.0.1.¹⁴ Lawrence Livermore National Laboratories SUNDIALS 2.4.0 suite^{15,16} was used as an integrator via the Cantera interface.

Quantum chemistry calculations were performed using Gaussian03¹⁷ on a 64-bit AMD cluster with the G3MP2B3 method.^{18,19} Energies and frequencies were used directly in the internal energy calculations without additional scaling or correction.

RESULTS

HPLC/UV-vis chromatograms of the derivatized products extracted from the filter samples are shown in Figure 2 for the products of carbonyl (via DnsHz) and hydroxyl (via DMABC) derivatizations. The chromatograms are complex, each having multiple dominant peaks, numerous small satellite peaks, and a broad unresolved component that is particularly evident in the carbonyl derivatizations. The figure annotations represent

assignments of the peaks to masses corresponding to different numbers of hydroxyl (n_{OH}) and carbonyl $(n_{C=O})$ moieties in the form $(n_{OH}, n_{C=O})$. The satellite peaks in both spectra show a large range of masses, up to and including four oxygenated substituents in both spectra and masses corresponding to five substituents in the unresolved regions of the carbonyl (DnsHz) derivatization. Major contributors to the unresolved mixture in the DnsHz sample included numerous (0, 2), (1, 1), and (1, 2)species. The 2-PA derivatization for carboxylic acids revealed no significant products.

The observed octanal and octanol concentrations in the condensed-phase samples are anomalously large on the basis of their vapor pressures, which is much higher than the total amount of parent iodide input into the flow cell. These large concentrations are due, at least in part, to sticking on the filter by gas-phase products, which was confirmed by flowing octanal through a filter and analyzing it identically to a particulate filter sample. It is also possible that particles are seeded by more highly oxidized species, and the singly oxidized compounds dissolve in those particles as azeotropes. Whether these initial species undergo homogeneous nucleation or nucleate on another species, such as I[•] or I⁻ is unclear. A water extract of a filter sample did not yield a large m/z - 127 peak, and the fate of the iodine was not considered further in this study.

Derivatization of the product extract with DMABC (hydroxyl) yielded significant signals corresponding to the mass of octanal to which the derivatization reagent is not sensitive.⁷ Furthermore, peaks with the hydroxyketone mass were observed at very long retention times (7.6 min). As shown in Figure 2, we have tentatively assigned these peaks, and peaks in the DnsHz consistent with this interpretation, to systems with OH groups and a double bond, which provides the same mass as a single CO group. These are indicated in the figure as double bonds (=). A probable mechanism for forming these species is provided below.

Ion chromatograms are shown in Figure 3 for the hydroxyland carbonyl-derivatized samples with transitions m/z 292 \rightarrow



Figure 3. Normalized MRM chromatograms for derivatized hydroxyketones from filter extracts. Numerous isomers are observed, although the major peak is expected to be 4-hydroxyoctanal.

144 and m/z 392 \rightarrow 170, respectively, corresponding to hydroxyketones (1, 1). In this case, the spectra are both dominated by a single hydroxyketone isomer but show a remarkable number of additional isomers. On the basis of the expected mechanism and additional channels discussed below, we tentatively assign this peak to 4-hydroxyoctanal.⁶ We propose that many of the additional peaks originate from photolytic processes. MS-MS chromatograms are shown in Figure 4 for the carbonyl derivatization of trisubstituted compounds, which are abundant and varied in retention time.



Figure 4. MS–MS chromatograms ($W \rightarrow 170$) corresponding to triply substituted products derivatized with DnsHz. Similar spectra are found when DMABC is used as a derivatization reagent.

Similar signals corresponding to most combinations of $(n_{OH}, n_{C=O})$ (nonacid) for up to four total substitutions were observed in significant concentration from both both carbonyl and hydroxy derivatizations.

DISCUSSION

Compositional Complexity. One of the anticipated advantages of photolyzing a single iodide isomer to generate OA is simplicity in the condensed-phase product spectrum due to the small number of reaction pathways in the oxidation mechanism. A typical mechanism^{5,6} for the oxidation of an alkyl radical under these conditions is shown in Figure 5. After



Figure 5. Mechanism showing showing major propagation channels for oxidation in NO_x free environments. The arrow from the [•]QOH species refers to the fact that the newly hydroxylated radical undergoes the same oxygen addition continuing propagation scheme, regardless of the presence of the added OH.

photodissociation of the C–I bond in the input 1-iodoalkane, the resulting alkyl radical reacts rapidly with O₂ to form a 1alkylperoxy radical. Under low-NO_x conditions, the peroxy radicals are relatively stable, and oxidation would be propagated only by the slow $R_iO_2^{\bullet} + R_jO_2^{\bullet} \rightarrow R_iO^{\bullet} + R_jO^{\bullet} + O_2$ reactions (right side of Figure 5, where $R_iO_2^{\bullet}$ and $R_jO_2^{\bullet}$ are taken as combinations of all peroxy radicals in the system). The peroxyperoxy reactions lead to alkoxy radicals, RO^{\bullet} , which undergo isomerization at room temperature, $RO^{\bullet} \rightarrow {}^{\bullet}QOH$. The ${}^{\bullet}QOH$ then reacts again with O₂ to form a hydroxyalkylperoxy radical, ${}^{\bullet}QOH + O_2 \rightarrow {}^{\bullet}OO-QOH$, which forms a hydroxyaldehyde after a second peroxy-peroxy reaction. The presence of substitution can have a significant impact on the reactivity as well, such as in the formation of stable hydroxyketone from hydroxyalkoxy radicals. However, the observed product spectrum is drastically more complex than such a simple mechanism would imply, as evidenced by the range of clearly resolved products and large unresolved mixture signal.

Kinetics Model. To evaluate the mechanism's ability to predict the observed products, a chemical kinetics model was utilized that attempts to capture all of the important reactions in the oxidation model.²⁰⁻²³ A complete model including the repeated oxidation steps required to obtain a tetrasubstituted product is computationally intractable to solve for an eight carbon system. To capture the diversity of possible products in a computationally feasible way, we have elected to track temporal order in which hydroxyl (OH), carbonyl(C=O), and hydroperoxide (OOH) functional groups are added as the oxidation takes place. These "products" could, in principle, be individually modeled to yield an overall set of true products, but tracking the order of functional group addition acts as a good proxy for the variability in product formation channels. The list of species to be modeled is generated by combining the eightcarbon stem $[C_8H_x]$ with the functional groups [C=O, OH,and OOH] sampled up to four times with replacement in all possible permutations.

The overall kinetics model is constructed by including a set of generative reactions shown as reactions 1-9 in Table 1 for

 Table 1. Template for Reactions Relevant to the Formation of Photolytically Initiated Organic Aerosol^a

	reaction	rate constant, (cm^3) molecule ⁻¹ s ⁻¹)	ref
1	$R_iH + OH \rightarrow R_i^{\bullet} + H_2O$	1.0×10^{-11}	20
2	$\mathbf{R}_{i}^{\bullet} + \mathbf{O}_{2} \rightarrow \mathbf{R}_{i}\mathbf{O}_{2}^{\bullet}$	2.0×10^{-12}	
3	$R_i O^{\bullet} \rightarrow Q_i O H$	1.0 k_{isom}	24
4	$R_i O^{\bullet} \rightarrow small=O + small^{\bullet}$	7.2×10^{3}	24
5	$R_i O^{\bullet} + O_2 \rightarrow R_i = O + HO_2$	8×10^{-15}	24
6	$R_i O_2^{\bullet} + HO_2^{\bullet} \rightarrow R_i OOH + O_2$	1.5×10^{-11}	21,22
7	$R_i O_2^{\bullet} + R_j O_2^{\bullet} \rightarrow R_i = O + R_j OH + O_2$	$0.34k_{peroxy}$	23
8	$R_i O_2^{\bullet} + R_j O_2^{\bullet} \rightarrow R_j = O + R_i OH + O_2$	$0.34k_{peroxy}$	23
9	$R_i O_2^{\bullet} + R_i O_2^{\bullet} \rightarrow R_i O^{\bullet} + R_j O^{\bullet} + O_2$	$0.66k_{peroxy}$	23
10	$\mathbf{R}_i \mathbf{O}_2^{\bullet} \to \mathbf{R}_i^{\bullet} + \mathbf{O}_2$	$2.68\kappa_{hy}(1 -$	
		x_{isom})	
11	$R_i O_2^{\bullet} \rightarrow {}^{\bullet} Q_i OOH$	$2.68\kappa_{h\nu}x_{\rm isom}$	
12	$R_iOOH \rightarrow R_iO^{\bullet} + OH$	$0.021\kappa_{h u}$	

"For the present 1-iodooctane system, R_i and R_j are C_8H_x substituted up to four times with =O, —OH, and —OOH in all possible substituent permutations that represent the temporal order in which the individual moieties were added. "small•" is also used as R_i and is a place holder for all small products formed from decomposition. $\kappa_{h\nu}$ is the first-order rate constant for iodooctane dissociation and is scaled by the ratio of absorption coefficients as shown.

every species on the list by substituting them for R_i . New stable species are formed via termination, shown by reactions 5–8, which lead to greater levels of substitution for each species. The R_j in reactions 7–9 are substituted by all of the species in the model for each R_i representing all of the cross peroxy–peroxy radical reactions. The unstable species are tracked as shown by combining the stem from the list of R_i with an unstable functional group (e.g., a peroxy radical is tracked as the stem name combined with O_2).

Rather than dealing with all decomposition products explicitly, a "small" stem was also included in the set of modeled species to generically capture all of the RO[•] decomposition products (reaction 4 in Table 1). These products are not considered in developing the product spectrum under the assumption that their vapor pressure will be large relative to their concentrations and will not be captured on the filter. This assumption is not good for the highly oxidized smaller radicals, but because these studies are mass- and functional-group specific, interference from the highly variable small radical products is expected to be minimal. However, the "small-O₂•" concentration (i.e., the load of small peroxy radicals in the system) is key in accurately assessing the peroxy–peroxy radical conversion rates.

The compounds given initial concentrations in the model are identical to those introduced into the cell, namely iodooctane and air. The photolysis of iodooctane,

 $C_8H_{17}I + h\nu \rightarrow C_8H_{17}^{\bullet} + I^{\bullet}$

is the initiation reaction and is included in the model as a firstorder decay of C₈H₁₇I to form a bare "C₈H₁₇" stem and I atoms with a rate constant calculated from the absorption cross section of iodopropane²⁵ (assumed to be identical to iodooctane) at 253.6 nm, 1.36×10^{-18} cm², and input photon flux. The input power used in the flux calculation was determined by measuring the decay of ozone in the cell using a UV absorption ozone analyzer (Teledyne, San Diego, CA) in the presence of the light and using a simple kinetics model (provided as Supporting Information) to determine the input power to be $8 \pm 1\%$ of the rated bulb power. The rate constants k_{isom} and k_{peroxy} are for the alkoxy isomerization and the total peroxy-peroxy reactions, respectively. Three different values for the peroxy-peroxy radical reaction rate constants were used in the model, as suggested by Ziemann and Atkinson for different reaction types.⁵ For the self-reaction of $1-C_8H_{17}O_2$, a typical primary + primary radical recombination rate of $k_{pp} = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used. A secondarysecondary reaction rate constant of $k_{ss} = 5.0 \times 10^{-15}$ cm³ molecule⁻¹s⁻¹ was used for the reaction of any two substituted peroxy radical species, and the geometric mean of these rate constants $k_{\rm ps} = (k_{\rm pp}k_{\rm ss})^{1/2} = 3.5 \times 10^{-14} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ was used for the reaction of 1-C8H17O2 with any substituted radical species. Additionally, the alkoxy radical chemistry is highly simplified in this model (reaction 3 only). However, the lack of peroxy-peroxy reactions and relatively slow photolysis of hydroperoxides leads to a total alkoxy radical concentration less than 0.1 nmol mol⁻¹ relative to the amount of reacted parent iodide, and the addition of more complex alkoxy radical chemistry is not justified here. Overall, this method leads to a model containing 904 species and 23 148 total reactions, the majority of which are RO2 • recombination reactions. This system was modeled as a simple constant-pressure reactor with 140s time in light. An additional 15 s in the dark sampling tube was modeled by zeroing all reaction rates involving photolysis light; in this case only the iodooctane photolysis was stopped in this dark region.

Figure 6 shows functional group distributions for the outputs as open circles by considering the fractional amounts of hydroxyl, carbonyl, and hydroperoxide groups at different levels of overall substitution. Included in this figure are all species with concentrations that varied more than 1 μ mol mol⁻¹ (ppm) of the initial parent concentration. In the present model (without any photochemistry other than the iodide photolysis) the variation in functional groups is small and dominated by OH substitutions. The OH preference is the result of the simple propagation mechanism shown in Figure 5 that strongly



Figure 6. Functional group distributions from generative model in Table 1 including peroxy photochemistry (solid circles) and without peroxy photochemistry ($\kappa_{h\nu} = 0$ in the table, open circles). The three vertically-oriented ternary plots show molar concentrations of products with with $n_{\rm OH}$ hydroxyl, $n_{\rm OOH}$ hydroperoxyl, and $n_{\rm CO}$ carbonyl moieties within products containing two, three, and four oxygen-containing substituents. Each plot is shown at the same scale, and circles are normalized for each plot.

favors RO[•] isomerization as the means of adding additional oxygenated substituents. The large number of observed peaks in the spectra shown in Figures 3 and 4 is not consistent with the relatively simple distribution expected from this system. The large number of different isomers with three or more substituents observed in Figure 2, particularly in the unresolved mixture found in the DnsHz derivatizations, cannot be described by the mechanism in Table 1. The fate of the hydroperoxides formed in this system is an open question; in highly acidic environments, decomposition and rearrangement can occur, leading to carbonyls and smaller alcohols.²⁶ The electrophilic nature of the -OOH leads to several possibilities in the presence of carbonyls or alkene moieties.²⁷ However, primary hydroperoxides are stable toward HPLC analysis,²⁸ and we have elected to explicitly show the -OOH moieties within the model with the view that other products may form particularly at higher levels of oxygen substitution. We do not believe that the uncertainty in the fate of the hydroperoxide will significantly impact the conclusion that the distribution of products at low oxygen substitutions is much more complex than the model in Table 1 would indicate.

These reactions occur in an environment bathed in 254 nm light, and photochemistry can play a key role in producing this compositional complexity.

Photochemistry of Octyl Peroxy Radicals. We believe that the complexity of the product spectrum is due to the photochemistry of the octyl peroxy radicals at 254 nm, which, to our knowledge, has not been studied previously. Much of the remainder of this discussion will be devoted to examining the likelihood of this hypothesis and discussing possible implications of it. To anticipate the behavior of these longer-chain species, we utilize work on smaller linear radicals where available to estimate necessary parameters, including absorption cross sections, quantum yields, and relevant reactions.

The absorption spectrum of alkylperoxy radicals has been well-studied for small radicals with ethyl peroxy having an absorption at 254 nm of 3.8×10^{-18} cm² cross section,²⁵ which we adopt for the octyl peroxy radicals. Much less work has been done on the ultraviolet photochemistry of these systems. Hartmann et al. studied gas-phase methyl peroxy radical CH₃O₂[•] photolysis at 248 nm and found it to be primarily predissociative on the ground electronic state via reactions A–C in Table 2.²⁹ Although this does not rule out excited state chemistry, in this discussion, we have assumed that the system undergoes reactions only on the ground state.

Table 2. Alkylperoxy Radical 248 nm Photolysis Channels

	reaction	$R = CH_3 branching ratio29$	
Α	$ROO \rightarrow R^{\bullet} + O_2$	0.74	reverse addition
В	$ROO \rightarrow RO^{\bullet} + O(^{3}P)$	0.20	radical loss
С	$ROO \rightarrow R=O + OH$	0.06	four-centered elimination
D	$ROO \rightarrow QOOH$	N/A	isomerization

More extensive work in condensed-phase systems has been done in liquefied gas matrices $^{30-32}$ and grafted to surfaces 33 with similar bond scissions observed, although the details of the photochemistry remain unclear. Channels A-C may also be important in octyl peroxy radical (i.e., $R = C_8 H_x O_y$) photochemistry, but as discussed in detail below, the large amount of energy contained in the absorbed photon will sufficiently partition into vibrational energy to permit isomerization via H-atom migration (channel D) to occur readily, a channel that is well-established in alkane combustion.³⁴ The absorbed photon provides 472 kJ mol⁻¹ of energy, well above all isomerization barriers for hydrogen shifts in alkyl radicals.³⁵⁻³⁸ Under these conditions, repeated isomerizations and rapid scrambling of the radical location along the carbon chain³⁹ will be expected until the system is collisionally quenched.

In Table 2 reaction A reverses the initial oxygen addition, but the resulting radical will have a large amount of excess energy. In methyl peroxy dissociation, no unimolecular reactions in the hot methyl radical are possible, and the system is collisionally quenched to act as a straight reverse reaction. However, a longer chain system can undergo isomerization by H-atom migration along the chain. Such reactions can occur numerous times and the long-chain alkyl radicals formed by reaction A will have scrambled isomeric distributions. The resulting set of scrambled radicals will rapidly react with O_{22} and the oxidation process will continue repeatedly. It has been noted³³ that $O_2(^1\Delta)$ may result on grafted surfaces, and in this case, the 94.3 kJ mol⁻¹ singlet oxygen internal energy⁴⁰ will result in substantially less activation of the alkyl radical.

The second reaction (B) in Table 2 converts the peroxy radical into highly photoactivated alkoxy radicals. Typically, decomposition of an octoxy (RO) radical under atmospheric conditions is quite slow relative to isomerization or termination via H-abstraction.²⁴ However, "prompt" decomposition can occur from vibrationally excited alkoxy radicals, such as from chemical activation from the $RO_2^{\bullet} + NO \rightarrow RO^{*\bullet} + NO_2$ reaction.^{5,41} Photoactivation from absorption of a 254 nm photon followed by loss of an oxygen atom will yield much greater alkoxy vibrational excitation than in these chemical activation reactions. Reaction C is a four-center elimination channel and would be a source of direct aldehyde (octanal in the first step) and OH with no obvious isomerization pathways. Ultimately, however, neither of these channels is important in octyl peroxy radical photochemistry due to the energetically more favorable H-atom migration channels. As noted below a five-center concerted elimination reaction common in combustion⁴² is also significant, leading to an alkene and a hydroperoxyl radical, rather than the carbonyl/hydroxyl radical combination in reaction C.

For longer-chain radical species, isomerization of the peroxy radical produces a series of hydroperoxyalkyl radicals (collectively 'QOOH), as shown in reaction D in Table 2. The isomerization is not observed in most cases at room temperature, although the isomerization of peroxyaldehydes at room temperature has been observed via abstraction of the aldehydic H-atom to eliminate CO and OH, RCH(OO[•])- $CHO \rightarrow RCH(O) + CO + {}^{\bullet}OH$ with more recent experimental and computational evidence for room-temperature isomerization of other oxygenated peroxy radicals.^{43,44} These channels are also possible in this system, but in the absence of substantial OH oxidation, which is not borne out by the modeling results (cf. reaction 1), the initial peroxy radical isomerizations cannot occur via these mechanisms. For the octyl radical oxidation under the present conditions, isomerization due to photoexcitation seems to initiate and propagate the complex system. Further work is certainly necessary to establish the extent of photochemical isomerization versus spontanous isomerization of the highly oxidized species in defining the product spectrum complexity.

The photochemistry propagates oxidation by driving the initial RO2° species to add additional oxygen via the °QOOH + $O_2 \rightarrow ^{\bullet}OO-QOOH$ reactions. The total impact of these photochemical reactions on the final product spectrum can be evaluated by adding Reactions A, C, and, D to the generative model in Table 1 (as reactions 10-12). In these reactions, x_{isom} is the branching ratio of the photoactivated peroxy radical isomerization (i.e., the branching of reaction D in Table 2) and $\kappa_{h\nu}$ is the first-order rate constant for iodooctane photodissociation, which is scaled by the ratios of relevant absorption coefficients for each reaction. These reactions include those in Table 2 in addition to specific alkoxy and peroxy radical isomerizations that are discussed below. The addition of these photolysis channels has a significant influence on the modeled product spectrum, as shown by comparing the open circles, which represent $\kappa_{h\nu} = 0$, to the closed circles (full photochemistry) in Figure 6. The extent of substitution has increased substantially and is more strongly biased toward -OOH. Due to the strong overlap of the chromatographic peaks and

uncertainty in derivatization of highly substituted compounds, a quantitative comparison of the model results and experimental data is impossible. However, the extreme complexity of the photolysis model is consistent with the complexity and extensive oxidation observed in the experimental data.

Peroxy and Alkoxy Radical Isomerization. A mechanism describing the fate of the photoactivated peroxy radicals is shown in Figure 7. The upper half of the figure shows the



Figure 7. Mechanism for peroxy radicals in the photoreactor. The bold **Q** indicates a complex, highly scrambled isomeric distribution.

typical peroxy–peroxy propagation and termination pathways.⁵ The lower portion shows the photoactivated species with branching to products as in Table 2, including the octyl peroxy isomerization reaction that is not important under typical atmospheric conditions. In this way, oxidation processes commonly observed in combustion play a significant role in determining the OA product spectrum.

The presence of the isomerization pathway and the concerted elimination channel make it unreasonable to assume that the relative branching ratios for the methyl peroxy radical decomposition are similar in octyl peroxy. Calculation of such a branching using an microcanonical rate/master equation is complex for this system due to the presence of two barrierless dissociation channels. Although numerous simulation methods exist for such systems,⁴⁵ the challenge of choosing appropriate transition state locations on assumed potential energy surfaces and the overestimate of the rate constant inherent in variational rate theories¹¹ make such a calculation beyond the scope of this work.

However, due to the large size of the octyl peroxy radical (75 vibrational modes), the energy distributions of the product molecules at high excess energies can be closely approximated⁴⁶ by treating the microcanonical energy distribution as a Boltzmann distribution at an effective temperature, T^* , which lies well above the reactant temperature.¹¹ The effective temperature may be obtained from a prior distribution by iteratively finding T^* to obtain the input excess energy imparted by the photon:⁴⁷

$$E_{h\nu} - E_{\rm b} = kT^* + \frac{r}{2}kT^* + \sum_{p \in \text{products}} \sum_{i=1}^{N} \frac{\varepsilon_{p,i}}{\exp(\varepsilon_{p,i}/kT^*)}$$

where $E_{h\nu}$ is the energy of the absorbed photon, E_b is the bond energy (or reaction energy in the case of isomerization), T^* is the effective temperature, r is the number of product rotational degrees of freedom (3 for the loss of an atom or unimolecular reaction, 5 for the loss of a diatomic), and $\varepsilon_{p,i}$ are the vibrational modes of the individual products. We have utilized unscaled frequencies from G3MP2B3 quantum chemistry calculations

Table 3. Estimates of	f Branching I	Ratio for RO ₂	• → Produ	cts Channels a	after Abso	rption of	254 nm Photo	on"
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products	$a (s^{-1})^b$	n^b	E/R (K) ^b	$k (s^{-1})$	half-life (ns)	ϕ
$R^{\bullet} + O_2$	2.04×10^{22}	-2.58	18120	5.12×10^{8}	1.35	0.62
$C = C + HO_2$	6.29×10^{7}	1.38	14540	6.09×10^{7}	11.4	0.074
C=O + OH	3.28×10^{4}	2.57	18320	1.34×10^{7}	51.8	0.016
QOOH 4 ^c	3.03×10^{6}	1.65	14240	2.58×10^{7}	26.8	0.031
QOOH 5 ^c	4.26×10^{6}	1.37	9008	1.77×10^{8}	3.91	0.22
QOOH 6 ^c	1.76×10^{6}	1.20	8504	3.01×10^{7}	23.0	0.037
QOOH 7 ^c	2.67×10^{5}	1.12	7901	3.88×10^{6}	179	0.0047

^aThese estimates assume the parent temperature remains at 1444 K throughout, so channels with half-lives greater than ~ 10 ns are somewhat overestimated. ^bReference 42. ^cCarbon number of radical site relative to OOH.

for the octyl-1-peroxy, 1-octoxy, and 1-octyl radicals and O2. The effective temperatures of the underlined polyatomic products were found to be $T^*(RO_2^{\bullet} \rightarrow {}^{\bullet}QOOH) = 1444(8)$ K, $T^*(\mathrm{RO}_2^{\bullet} \to \underline{RO} + \mathrm{O}^{\bullet}) = (887 \pm 5) \text{ K and } \overline{T^*(\mathrm{RO}_2^{\bullet} \to \underline{R}^{\bullet} + \mathrm{O}^{\bullet})}$ O_2 = (1182 ± 11) K. For these calculations, the *n*-butyl bond energies of Simmie et al. were used, 262 ± 2 and 145 ± 5 kJ mol⁻¹ for the O-O and C-O bonds,⁴⁸ respectively, and the reported uncertainties in the temperatures are derived solely from these literature bond energy uncertainties. The isomerization reaction energy was calculated by G3MP2B3 to be -26kJ mol⁻¹ for abstraction from the third-carbon (a six-centered cyclic H-atom transfer), which is the most favorable channel, with an assigned uncertainty of 4 kJ mol⁻¹. For the dissociation reactions, the energy partitioning into translation, rotation, and vibration for the RO + O system was calculated to be (f_t, f_r, f_v) = $(0.035 \pm 0.001, 0.053 \pm 0.001, 0.912 \pm 0.001)$ respectively. The R + O₂ system shows similar partitioning $(f_v, f_v, f_v) =$ $(0.030 \pm 0.001, 0.045 \pm 0.001, 0.915 \pm 0.001); f_v$ in this case refers only to the alkyl radical.

The use of a canonical Boltzmann temperature for the photoexcited species allows data relevant to combustion to be utilized in determining reactivity and possible product identities. As a means to estimate the branching ratios for the peroxy radical decomposition, we have utilized theoretical calculations of rate rules^{42,49} by Dean and co-workers describing high-temperature reactions of alkylperoxy radicals. Immediately after absorption of the photon by peroxy radical, the instantaneous rates can be calculated at the canonical Boltzmann temperature. At this temperature, the rate expression for the dissociation of RO2 was calculated by Villano et al.⁴² to be $k(s^{-1}) = 2.04 \times 10^{22} (T/K)^{-2.58}$ $\exp(-18120/(T/K))$ on the basis of typical room-temperature association rates and calculated equilibrium constants. At 1444 K, the half-life of the RO_2^{\bullet} with respect to dissociation is computed to be 1.35 ns, corresponding to ~10 bath gas collisions at the experimental temperature and pressure. We have therefore elected to estimate the branching on the bsais of the calculated Villano et al. rate expressions solely at the Boltzmann temperature. The branching estimates for the primary channels are shown in Table 3. Because these branching ratios are calculated by assuming the initial canonical Boltzmann temperature, the channels with lower rate constants are overestimated. As a result, we estimate the dissociation to isomerization to C5 ($RO_2^{\bullet} \rightarrow {}^{\bullet}QOOH^5$) ratio to be ~3:1 with a small contribution from the concerted elimination and no significant additional isomerization. In this case, the alkoxy channel is expected to be unimportant in the dissociation of this large molecule, due to the large O-O bond energy and extremely rapid dissociation and isomerization, as opposed to $CH_3O_2^{\bullet}$ where it represents an important channel.

The branching estimates provide a means to reverse the oxygen addition, produce alkanes, and undergo isomerization to a single hydroperoxyalkyl isomer, but these do not justify the exceptional complexity. However, on this time scale, the alkyl dissociation product (R^{\bullet}) will still have ~300 kJ of internal energy, and the hydroperoxyalkyl radical (•QOOH) will be chemically activated to an internal energy greater than the input photon energy. In both cases, there is sufficient energy to overcome the typical 120 kJ mol⁻¹ barriers³⁸ to 1,2 H-shifts as well as other isomerizations along the chain. In this case, scrambling of the radical site and β -bond scission reactions will produce numerous other isomers and smaller alkenes and alkyl radicals.^{35,37,42} In addition, Villano et al. note that several reactions of activated [•]QOOH, including isomeric scrambling, cyclic ether formation, and additional β -bond scissions can be important.⁴⁹ Experimental evidence for such photochemically induced scrambling in similar systems exists. Heazlewood et al. have noted that deuterated acetaldehyde undergoes drastic isotopic scrambling upon absorption of light with much longer wavelengths and providing lower excess internal energy than in the present work.⁵⁰ At elevated temperatures, such scrambling is a well-known effect.³⁹ After collisional quenching, the new radical site will be rapidly populated with O_{2} , and the oxidation will continue.

Heimann et al. has studied the gas-phase products of the 253.6 nm photodissociation of 1- and 3-iodopentane in air in a static bulb with a Hg arc lamp source.⁵¹ The 1-iodopentane photolysis products observed by them and the associated reaction mechanism are largely consistent with the well-known mechanism shown in Table 1 of this work. However, a large concentration of additional products were observed as a broad unidentified chromatogram and assumed by those authors to be a result of isomerization. Little evidence of decomposition was observed. We speculate that these additional products may be a result of the associated peroxy radical photochemical isomerization pathways discussed in this work.

Possible Atmospheric Implications. Although the wavelength in this study is not important to tropospheric chemistry, the absorption coefficients of ethyl peroxy radical at wavelengths >290 nm remain above 1×10^{-21} cm² for wavelengths up to 340 nm, based on a Gaussian extrapolation of the NASA Jet Propulsion Laboratory-recommended absorption spectrum.²⁵ The actinic flux at these wavelengths is significant throughout the troposphere.⁵² At the surface, the photochemical lifetime of ethyl peroxy radical is estimated to be 190 min based on the actinic flux and extrapolated absorption spectrum. In urban high-NO_x environments, such a channel can be neglected, because the RO₂[•] + NO \rightarrow RO[•] + NO₂ channel will dominate; however, clean rural environments provide much longer peroxy radical lifetimes. This calculated photochemical

lifetime is similar to that predicted by models of NO_x -free methylperoxy radical night-time lifetimes based on measurements at Mace Head, a remote site on the Atlantic coast of Ireland.⁵³ Peroxy radical concentrations are highly variable both diurnally and daily,^{54,55} and peroxy radical photochemistry may play a role in such environment, particularly if more highly substituted compounds are more active photochemically.

At 315 nm, the approximate wavelength at which the solar peroxy radical photolysis rate constant is at a maximum, the canonical Boltzmann temperature for 1-octylperoxy radical is still 1284 K, giving a computed dissociation lifetime of 4.8 ns with a 2:1 branching ratio of dissociation to H-atom migration. In addition, the channel will increase in importance with increasing altitude; at 20 km, the actinic flux in this wavelength region is generally 1.5–2 times higher, leading to an estimated lifetime of 98 min. Experiments probing the effects of longer-wavelength light on the aerosol product distribution are currently underway.

CONCLUSIONS

The use of 254 nm light to generate particles leads to a complex product spectrum inconsistent with the simple RO₂• selfreaction models typically used to describe atmospheric oxidation in low-NO_x environments. The UV photolysis of peroxy radicals is proposed as the means by which (1) the number of oxygenated groups on a molecule is markedly increased and (2) a more complex product spectrum is formed from vibrationally hot reaction products from peroxy radical isomerization and dissociation. Modeling the propagation reactions, the unimolecular reactions of the photoexcited parent, and the decomposition products has shown that both processes are important and capable of producing such compositional complexity. In addition, calculated rates of peroxy radical photochemical processes at atmospheric wavelengths show photochemical lifetimes similar to the lifetimes of peroxy radicals measured at pristine atmospheric sites.

ASSOCIATED CONTENT

Supporting Information

The mass yield as a function of organic material reacted and the chemical kinetics model used to determine the photon flux. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTE

^{*a*}Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation of or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment is necessarily the best available for the purpose.

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