Aqueous-phase autoxidation in the atmosphere: fate and formation of organic peroxides

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Abstract

Autoxidation is a widely recognized mechanism known to initiate the degradation of food and lipids and modify organic matter in the atmosphere. Given the low NOX concentration in aqueous media (e.g., cloud water and fog droplets), autoxidation can become vital to facilitate the formation of highly oxygenated molecules such as organic peroxides (ROOH and ROOR). Here, we have identified aqueous-phase autoxidation-initiated hydroperoxides in varying organic precursors, including a laboratory model compound and monoterpene oxidation products. Our results show that autoxidation-initiated ROOHs are suppressed at enhanced precursor and oxidant concentrations. Furthermore, we observed an exponential increase in the yield of ROOHs when UV light with longer wavelengths was used in the experiment, comparing UVA, UVB, and UVC. Water-soluble organic compounds represent a significant fraction of ambient cloud water component (up to 500 μM). Thus, aqueous-phase autoxidation can become
an important oxidation pathway for water-soluble species and as such facilitate the formation of ROOHs, thereby adding to the climate and health burden of atmospheric particulate matter.

Keywords
Autoxidation, Organic peroxides, Peroxy radicals, OH radicals, Mechanism, Wavelength, Photooxidation, Cloud water chemistry, Aqueous-phase.

Synopsis
Gas-phase autoxidation-initiated organic peroxide formation is known, but research on aqueous-phase autoxidation is scarce. This study presents autoxidation-initiated hydroperoxides in aqueous-phase with implications to cloud and fog water.

1 Introduction
Autoxidation is widely known for causing spoilage in food and wine, degrading petroleum and aviation fuels during storage and low-temperature combustion.\textsuperscript{1–6} Only recently, atmospheric autoxidation has been revealed to facilitate oxygenation during the rapid transformation of organic compounds.\textsuperscript{7,8} A critical aspect of autoxidation is a consecutive oxidative process via the formation of reactive intermediates - peroxy radicals (RO\textsubscript{2}) - and propagation by H-migration.\textsuperscript{6,9} The successive addition of O atoms during autoxidation is responsible for the formation of highly oxygenated molecules (HOMs) that contain multiple hydroperoxy functional groups.\textsuperscript{10,11} Such low volatile organic compounds make significant contributions to the formation and evolution of secondary organic aerosol (SOA).\textsuperscript{11,12}

Conventionally, autoxidation is considered to occur primarily in pristine environments, especially with low NO\textsubscript{X}.\textsuperscript{11,13} Under high NO\textsubscript{X} concentration, NO tends to compete with
intramolecular H-shifts induced by peroxy radicals (RO₂), constraining autooxidation.\textsuperscript{13,14} However, since the implementation of strict regulations of NO\textsubscript{X} emissions, unimolecular isomerization in autooxidation can compete with other bimolecular reactions, gaining traction in urban environments.\textsuperscript{15,16} While gas-phase autooxidation processes have been well studied;\textsuperscript{13,17} currently, there is no systematic investigation on aqueous-phase autooxidation processes occurring in the atmosphere. Cloud water and fog droplets serve as media with low NO\textsubscript{X} concentrations that are essential for this mechanism.\textsuperscript{18,19} Cloud droplets are photochemically active because they receive a considerable amount of sunlight, in particular, UV radiation that serves as the driver of tropospheric photochemistry.\textsuperscript{20} Potential autooxidation in cloud water may be responsible for rapid photochemical processing of water-soluble species and lead to the production of reactive intermediate species such as organic peroxides.\textsuperscript{21}

Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and organic peroxides (ROOH, ROOR) are reservoirs of HO\textsubscript{x} and RO\textsubscript{x} radicals and a class of reactive oxygen species (ROS), which can induce respiratory illnesses.\textsuperscript{22,23} Aqueous-phase photochemistry may give rise to ROOH intermediates that contribute to the burden of atmospheric ROS.\textsuperscript{24} Despite numerous investigations in aqueous-phase OH radical initiated oxidation of varying water-soluble organic precursors,\textsuperscript{25–29} there is no known laboratory study that links the formation of oxygenated products such as peroxides and autooxidation. It is attributable to the lack of observations for ROOH intermediates, which are regarded as crucial evidence for autooxidation.\textsuperscript{30} Molecular identification of organic peroxides can be challenging due to: (i) lack of selective analytical technique to allow targeted analysis,\textsuperscript{31} (ii) lability due to weak O-O bond and\textsuperscript{24,32} (iii) incorporation of unrealistic experimental conditions including UV light and oxidant/precursor concentrations during fundamental laboratory investigations.\textsuperscript{33–36} In particular, unambiguous identification of organic peroxides using direct mass spectrometric (MS) measurements can be difficult due to the inability of MS to provide functional group information and successive fragmentations of molecules in the ion molecular region.\textsuperscript{37,38} As such, chemically derivatized methods can be useful for the successful characterization of select functional groups.\textsuperscript{38–40} Based on the work
of Zhao et al, a combination of MS with the chemical assay of iodometry has proven to be advantageous for the selective identification of organic peroxides in a complex matrix.41

The aim of this study is to: (i) elucidate the aqueous-phase autoxidation mechanism initiated by the OH radical, (ii) examine the dependency of autoxidation-initiated hydroperoxides (ROOHs) under experimental conditions such as varying oxidant and precursor concentrations, and (iii) demonstrate the effects of interaction between ROOHs and the wavelength of irradiated light. We hypothesize that the use of short-wavelength UV light, as well as exceeding levels of oxidant and precursor used in laboratory experiments, can suppress autoxidation-initiated ROOHs.

2 Experimental

2.1 Materials

The following chemicals were purchased from Sigma Aldrich: 7-octenoic acid (7-OE, 99%), 1-octanoic acid (1-OA, 99%), acetic acid (AA, 99%), formic acid (FA, 99%), molecular iodine (I₂, crystallized, 99%), hydrogen peroxide (H₂O₂, 30 % w/w), cis-pinonic acid (CPA, 99%), pimelic acid (PMA, 99%) and azelaic acid (AZA, 99 %). Potassium iodide (KI, 99%) was bought from Fisher Scientific to carry out iodometry experiments. All chemicals were used without purification. H₂O₂ stock solutions were prepared fresh on a weekly basis. Other chemicals included: ultra pure water (18.0 MΩ cm, Millipore) and acetonitrile (ACN, HPLC grade). A previously synthesized sample of pinic acid (PNA) was used as is in this study. Details on the synthesis procedure are outlined elsewhere.42 Limononic acid (LMA) synthesis details are provided in Section S1.

2.2 Target Compounds

To demonstrate the prevalence of aqueous-phase autoxidation, we experimented with four organic acids (OAs) (structures shown in Figure 1). OAs are ubiquitous in the atmosphere
and cloud water.\textsuperscript{43,44} Practically, OAs can be readily detected with the negative mode of electrospray ionization mass spectrometry ((-)ESI-MS) and soft ionization (ESI) made detection of labile oxygenated compounds feasible.\textsuperscript{41,42,45,46} 7-OE was further chosen as the model compounds for two reasons: (i) the carbon chain length of 7-OE enables its separation from ROOH products on a C18 column, and (ii) the terminal C=C serves as the predominant reaction site with the OH radical, making the reaction mechanism predictable.\textsuperscript{3} For these reasons, 7-OE is used in this work to gauge the yield of ROOHs under various reaction conditions. 1-OA was chosen as a comparison to 7-OE, given the absence of the terminal C=C bond. PNA and LMA were chosen to illustrate the atmospheric relevance of autoxidation because they are major oxidation products from the ozonolysis of $\alpha$-pinene and limonene, respectively.\textsuperscript{26,27}

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Structures of model organic acids (OAs) employed to study autoxidation products.}
\end{figure}
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2.3 Photochemical Reaction

The experimental apparatus consisted of a Rayonet photoreactor (PR2P200) with 16 Hg lamps (five of which were exposed to the sample) and a 10 mL quartz vessel with a magnetic stirrer to allow constant mixing. A fan was used to minimize temperature rising during photooxidation. The quartz vial was used for the efficient generation of OH radicals from $\text{H}_2\text{O}_2$.\textsuperscript{42} The irradiation was performed with three different UV lights: UVC (254 nm), UVB (303 nm), and UVA (354 nm).\textsuperscript{47}

For aqueous-phase photooxidation, an aqueous solution containing one of the OA species and $\text{H}_2\text{O}_2$ was oxidized in the quartz vial for specific time periods. The experimental variables adopted during the photooxidation of OAs are listed in Table S1 (Section S2). The reaction progress was monitored by periodically sampling 840 $\mu$L of the solution from the photoreactor using polytetrafluoroethylene (PTFE) tubing. These aliquots were immediately treated by an iodometry protocol and analyzed by the sampling method described below. Quality control was maintained by performing each reaction condition in triplicate.

2.4 Sample Analysis

2.4.1 Iodometry Protocol

To allow selective identification of ROOHs, the photooxidized samples were treated via the iodometry method outlined in Zhao et al.\textsuperscript{41} Briefly, in the reaction vial, the concentration of $\text{I}^-$ was maintained in excess (60 mM) to allow reduction of peroxides into their corresponding alcohols within 1 hr.\textsuperscript{48} PMA and AZA were added as internal standards after photooxidation to account for instrumental variation and normalize the signal response of newly formed ROOHs. Photooxidized aliquots were processed as iodometry-control (ID-C) (without KI) and iodometry-treated (ID-T) (with KI). Specific reagent conditions for ID-C and ID-T are provided in Table S2. To allow comparative analysis, we made sure that the matrix in ID-C and ID-T was identical to solely reflect changes induced by iodometry and not by differences...
due to dilution or acidification.\textsuperscript{49} It is to be noted that there is hitherto rarely any evidence of the corresponding alcohol formed via the iodometric reduction of ROOH in the literature.\textsuperscript{50} In this work, alcohols formed following iodometry were monitored (Section 3.1), thereby providing an additional parameter in the detection of peroxide products.

Due to possible interferences, such as ionization suppression by iodide (I\textsuperscript{–})\textsuperscript{41} and non-OH losses,\textsuperscript{42} we performed additional control experiments. Our previous study showed that I\textsubscript{2} reacts with olefins,\textsuperscript{51} which indicates that peaks that react away during iodometry may not be all peroxides. As such an I\textsubscript{2} test is needed to confirm that the projected ROOHs do not react with I\textsubscript{2}. The conditions for these experiments are outlined in Table S2 and Table S3 (Section S3). From these experiments, we confirmed that ROOH products did not undergo side reactions with I\textsubscript{2}, internal standards showed no interference, and no product formation occurred between \textsubscript{2}O\textsubscript{2} and OA unless the light was shone on the mixture.

\subsection*{2.4.2 LC-MS Analysis}

Sample analysis was performed using the Agilent 1200 SL HPLC system with a Phenomenex Luna column (1.6 μm particle size, 100 Å, 50 × 2.1 mm, polar C18), equipped with Agilent 6220 accurate-mass TOF and (-)ESI mode. Due to limited column availability, Phenomenex Kinetex (2.6 μm particle size, 100 Å, 50 × 2.1 mm, polar C18) with a security guard cartridge was also employed to analyze photooxidized samples. Specific instrument parameters are described in Section S3.1. The ToF-MS used in this work could provide elemental compositions of detected compounds, which served as an additional method of identification. Elemental composition matches of potential product masses were acquired using the Agilent Mass Hunter software package (v.B04.00).

\subsection*{2.5 Investigation into Factors Affecting Autoxidation}

We probed into variables such as concentration, irradiation wavelength, and measurement time to understand the variability in autoxidation. We chose 7-OE as our model compound
to allow molecular specificity with respect to the addition of successive OOH groups, as OH radicals can predominantly attach themselves to the C=C. An overview of the conditions used in these experiments can be found in SI Table S1.

2.5.1 Wavelength

Given the fragility of the O-O bond,\textsuperscript{32,52} we examined the effects of wavelength of UV light used in irradiation. An aqueous solution of 7-OE and H\textsubscript{2}O\textsubscript{2} was oxidized under three wavelengths: UVC, UVB and UVA.\textsuperscript{47,53} The wavelength distribution spectrum and photon flux corresponding to each UV light are shown in Figure S3 (Section S4). Given that each UV type photolyzed H\textsubscript{2}O\textsubscript{2} with different efficiency, specific adjustments were made for the experimental protocols. For UVC, a switch experiment was conducted, in which we initially irradiated an aqueous solution of 7-OE at UVB to form peroxide products after which the solution was exposed to UVC. The concept was to acquire the degradation of ROOHs upon exposure to UVC. For UVA, we ramped the concentration of H\textsubscript{2}O\textsubscript{2} to 150 mM such that the consumption rate of 7-OE would be equivalent to that under UVB. To observe the differences solely induced by the light exposed to the aqueous solution, comparisons were drawn between the yield of ROOHs. Since we do not have standard chemicals for ROOHs, we used the peak areas of ROOHs as proxies for their concentrations in this work. The calculations pertaining to the estimation of yield are described in Section S6.1.

2.5.2 Concentration

We investigated the dependency of autoxidation-initiated products on the concentration of precursor and oxidant by performing two sets of photooxidation experiments. In the first set, we maintained a constant concentration of 7-OE, while H\textsubscript{2}O\textsubscript{2} was varied to achieve three different steady-state OH concentrations ([OH]\textsubscript{SS}). [OH]\textsubscript{SS} was experimentally determined by observing the pseudo-first-order decay of 7-OE. Given that the second-order rate coefficient of 7-OE has never been reported in the literature, a relative rate kinetic investigation was
first conducted to determine it. Details on the kinetic investigation are described in Section S6.2. For the second set of experiments, H$_2$O$_2$ was kept constant while the concentration of 7-OE was varied. Photooxidation exposure time was changed such that the consumption of 7-OE was relatively similar across varying H$_2$O$_2$ and 7-OE concentrations. The yield of ROOHs is estimated under these varying conditions. These observations are discussed in detail in Section 3.3.

3 Results & Discussion

3.1 Aqueous-Phase Autoxidation

The presence of ROOHs is key to identifying aqueous-phase autoxidation. As such, we performed detailed analyses on the peroxide functional group arising from the photooxidation of each target compound. Figure 2 shows LC/(-)ESI-MS extracted ion chromatograms (EIC) corresponding to certain mass-to-charge (m/z) ratios of ROOHs originating from 7-OE, 1-OA, and PNA. The assessed ROOHs are represented in their deprotonated form ([M-H]$^-$) due to the carboxylic acid functional group on each OA.$^{41,54}$ Figures 2 (A) and 2 (B) represent first- and second-generation ROOHs of 7-OE observed at m/z 191 (III, Scheme S1) and m/z 223 (IV, Scheme S1) respectively. Figure 2 (C) highlights the EIC of second-generation peroxide from 1-OA at m/z 207 ($C_9H_{16}O_6$). Figure 2 (D) is demonstrating the EIC of newly found ROOH from PNA, constituting 2-OOH groups at m/z 249 ($C_9H_{14}O_8$). Many of these products have a very small signal intensity and identifying them as ROOH is challenging. However, performing each reaction condition in triplicates offers confidence. Each EIC in Figure 2 is a comparison between ID-C and ID-T chromatograms obtained by averaging triplicate measurements. We have normalized the ion signal intensity with our internal standard (AZA). Currently, we have only shown one of the triplicate measurements for PNA and 1-OA to represent optimum chromatographic separation. An average chromatogram is shown in Figure S5 (Section S7.1). As an exception, we decreased I$^-$ concentration by 10
times for the current investigation into PNA due to the overloading of salt concentration.

Similar to other studies, ion signals that dropped to more than 90% in triplicated experiments were categorized as ROOHs.\textsuperscript{41,55} Figure 2 (B) further demonstrates the selectivity of iodometry. Here, we observe multiple chromatographically separated peaks in the ID-C sample, amongst which only the peak at retention time (Rt) of 1.6 min was reduced to >90%. The peaks in ID-T samples are noise after smoothing and do not represent EIC at specific m/z. In contrast, the peak at Rt of 3 min in Figure 2 (B) for the ID-C sample remained unchanged in comparison to the ID-T sample.

Apart from the reduction of signal response, alcohol formation is another indication of peroxy functionality on a compound.\textsuperscript{56,57} Although I$^{-}$ is known to reduce ROOH to corresponding alcohols,\textsuperscript{41,55} previous studies have not demonstrated the formation of such alcohols.\textsuperscript{41,49,55} In the current study, we have observed that m/z corresponding to alcohols from peroxide precursor showed an enhanced signal response when comparisons were drawn between ID-C and ID-T samples. For instance, the reduction of the first-generation peroxide of 7-OE (m/z 191) would yield an alcohol at m/z 175 due to the loss of one O atom. Thus, the overlaid normalized signal response of m/z 175 in the inset window of Figure 2 (A) showed an increased signal response when compared with the ID-C sample. This observation was unanimously observed for each ROOH product in experimented OAs, as monitored in the insets of Figure 2 (B), 2 (C), and 2 (D). It is understood that the formation of alcohols and other side products would be expected (e.g., Scheme S1, Russell mechanism) during the photooxidation of select OAs.\textsuperscript{58,59} Therefore, it is understandable that the peaks corresponding to alcohols were present before the iodometry treatment.
Figure 2: Extracted Ion Chromatogram (EIC) of key ROOHs from different OA precursors. Signals, in the format of [M-H]-, for each sample have been normalized with respect to the internal standard. The inset represents the formation of corresponding alcohol after iodometry treatment. (A) First-generation ROOH of 7-OE at m/z 191 (C₈H₁₆O₅); (B) Second-generation ROOH of 7-OE at m/z 223 (C₈H₁₆O₇); (C) ROOH from 1-OA at m/z 207 (C₈H₁₆O₆); (D) ROOH from PNA is found at m/z 249 (C₉H₁₄O₈).

We assessed the environmental relevance of aqueous-phase autoxidation by studying peroxide formation in PNA and LMA, which are major oxidation products from the ozonolysis of terpenes.²⁶,²⁷,³³,⁶⁰–⁶⁴ A recent study by Vejdani Amorim et al,³³ explored aqueous-phase oxidation of PNA and highlighted the formation of first-generation peroxide products, but there was no evidence of the formation of second-generation oxygenated species. However, this could be due to different chemical conditions.³³ Based on the detailed oxidation mechanism of PNA³³ and general dependency of RO₂ radical-driven H-shifts on precursor structures,⁶⁵,⁶⁶ we found that the oxygenated products from PNA were similar to that of 1-OA (Scheme S2). In contrast, LMA only exhibited the formation of a first-generation peroxide at m/z 233 (C₁₀H₁₈O₆) as shown in Figure S6 (Section S7.2). We propose that despite a similar allylic
position of $\pi$-electrons in 7-OE and LMA, intramolecular H-shifts in LMA were kinetically and sterically infeasible.\textsuperscript{67,68} Our current observations on LMA are consistent with the work of Witkowski et al.\textsuperscript{28} A more detailed discussion on the mechanism for expected product formation is provided in Section S5. While aqueous-phase photochemical production of peroxides is known,\textsuperscript{21} there is a lack of evidence to link autoxidation with this process. For the first time, we measured the ubiquitousness of aqueous-phase autoxidation by successfully identifying autoxidation-generated ROOHs from a number of precursors. In the next section, we investigated the factors affecting autoxidation as an indicator to gauge the prevalence of autoxidation in ambient cloud water.

### 3.2 Wavelength Exposure

The fate of numerous water-soluble organic compounds in tropospheric cloud water can be photochemically controlled by oxidants such as HO$_x$ radicals.\textsuperscript{20} However, the production of such oxidants can be dependent on both the intensity and the type of incoming UV radiation.\textsuperscript{20,69} To elucidate the magnitude of autoxidation, we made a relative comparison in the amount of ROOHs formed by acquiring an empirical yield ($\gamma$) (eq-S2). Due to a lack of appropriate standards, we are currently unable to quantify the ROOHs and thus, assume that the peak area is proportional to the concentration of ROOHs as a preliminary way to estimate the $\gamma$ of ROOHs. A more detailed discussion on the estimation of $\gamma$ is provided in Section S6.1. Figure 3 displays experimentally determined $\gamma$ of m/z 223 as a function of varying wavelengths. The inset window shows the absorption spectra corresponding to the lamps used in our photo reactor. The intensity of each lamp was kept constant as demonstrated by photon flux in Figure S3 (Section S4). The peroxide product at m/z 223 was non-quantifiable after exposure to UVC due to complete degradation during photooxidation. This degradation was corroborated via a switch experiment from UVB to UVC as shown in Figure S7.1 (Section S8.1). These observations highlight that UVC can compromise the stability of ROOHs, despite its efficient production of OH radicals.\textsuperscript{69,70} Photolysis of
ROOH species by UVC gives rise to another OH radical and alkoxy radicals (RO),\textsuperscript{71} which will subsequently decompose to form small OAs (C\textsubscript{2}-C\textsubscript{4}). The method used in the current study could not retain these small and polar compounds. In contrast to UVC, the peroxide production under UVB was relatively easier to estimate as noticed by an increase in the $\gamma$ for m/z 223. Additionally, we also explored the effects of longer wavelengths on the formation of expected ROOHs. Due to the lower efficiency of OH radical generation at UVA,\textsuperscript{24,25,72,73} we scaled photooxidation time and the concentration of H\textsubscript{2}O\textsubscript{2} to match the consumption of 7-OE across UVB and UVA (Table S4). Exposure to UVA showed a greater increase in the $\gamma$ of m/z 223. This trend was similarly observed for the first-generation peroxide product at m/z 191 as shown in Figure S7.2 (Section S8.1). There have been several studies which have explored aqueous-phase photooxidation of OAs,\textsuperscript{25,72,74} a few of which have focused on the formation of organic peroxides.\textsuperscript{74–76} UVC is often employed in laboratory-conducted aqueous-phase investigations on photochemical oxidation of OAs,\textsuperscript{30,70,76} but some studies have utilized UVA and UVB to achieve the same purpose.\textsuperscript{25,77} Our observations highlight that despite achieving steady-state concentration of OH radicals under varying irradiated wavelengths, the degradation of ROOHs is exacerbated under exposure to UVC than UVB and UVA. Our findings demonstrate that the transformation of water-soluble organics could be crucially dependent on illuminated light utilized in cloud water simulators, especially for fundamental laboratory investigations.
Figure 3: Estimated yield ($\gamma$) of second-generation autoxidation product of 7-OE at m/z 223 as a function of varying wavelengths: UVC, UVB and UVA. The inset represents the absorption spectra for each wavelength. Error bars represent 1σ for triplicate measurements.

3.3 Effects of Concentration

Studies on gas-phase autoxidation have demonstrated that the lifetime of RO$_2$ radicals is a determinant factor for autoxidation.\textsuperscript{13} RO$_2$ has multiple reaction pathways,\textsuperscript{78} and the lifetime of RO$_2$ radicals is intricately affected by the concentration of reacting partners.\textsuperscript{79} Thus, in this section, we have investigated the impact of reactant and oxidant concentrations on the $\gamma$ of ROOHs. Figure 4 illustrates the intercomparison between $\gamma$ of first- and second-generation autoxidation ROOHs found at m/z 191 and m/z 223 respectively under varying oxidant and precursor concentrations. [OH]$_{ss}$ is estimated using the relative rate method as explained in Section S6.2. Our current investigations were conducted with relevant steady-state cloud water OH concentrations to observe product formation.\textsuperscript{80,81} Figures 4 (A) and 4 (B) are representative of estimated yields for m/z 191 and m/z 223 as a function of increasing [OH]$_{ss}$ while 7-OE is kept constant. The estimated [OH]$_{ss}$ corresponding to each H$_2$O$_2$ concentration
is reported in Table S5. The $\gamma$ of m/z 191 was estimated at $\sim$50-65% consumption of 7-OE while that of m/z 223 was estimated at $>$90% consumption. The reasoning behind this difference was based on the fact that $\gamma$ is time-dependent, as shown in Figure S8 (Section S8.2). Therefore, in order to demonstrate the observations for the effects of RO$_2$ chemistry, we chose the period of OE consumption which would give a relatively consistent yield for each peroxide. Note that despite our careful attempts, it was difficult to acquire yield for m/z 223 under a lower 7-OE consumption range (20-50%). This is because there is not enough first-generation RO$_2$ radical (P1-Scheme S1) to successfully form the expected second-generation product. We observed a declining trend in the $\gamma$ of m/z 191 and m/z 223 with increasing [OH]$_{SS}$. This trend can be understood on the basis of reaction pathways demonstrated in Scheme 1. Under relatively lower [OH]$_{SS}$, we observed higher yields of m/z 191 and m/z 223. Such a trend could be due to the favoured formation of expected products under pathway 1c. However, as [OH]$_{SS}$ increases, termination by pathway 1c becomes less favourable due to the potentially interfering chemistry of HO$_2$ radicals as evident by pathways 1a and 1b.$^{46,75}$

Figures 4 (C) and 4 (D) illustrate the $\gamma$ corresponding to m/z 191 and m/z 223 as a function of 7-OE concentration while H$_2$O$_2$ was maintained at a constant concentration. Similar to the measurements for increasing [OH]$_{SS}$, the $\gamma$ of m/z 191 was estimated when 7-OE was partially consumed while that of m/z 223 was estimated under excessive consumption. The intercomparison between m/z 191 and m/z 223 showed a non-linear increase for $\gamma$ of m/z 191, while $\gamma$ of m/z 223 continuously declined with increasing 7-OE concentrations. Note, we also observed a steady decline in [OH]$_{SS}$ as 7-OE concentration was increased from 179 $\mu$M to 1000 $\mu$M. These values are reported in Table S5 (Section S6.1). The lifetime of RO$_2$ radicals can be very difficult to gauge due to undergoing multiple reaction pathways.$^{58,82}$ Despite the complexity associated with RO$_2$ radicals,$^{79,82,83}$ we believe that the decreasing trend in the $\gamma$ of m/z 223 (Figure 4 (C)) can be attributed to pathway 1d in Scheme 1. It is our understanding that at enhanced precursor concentrations, the RO$_2$ radicals can form unstable oxygenated intermediates (e.g., tetroxides),$^{58,82}$ which are highly likely to decompose.
to alcohols and carbonyls. While additional decomposition products such as ROOR can be expected, it would be possible at even higher precursor concentrations (>10 mM), which are currently beyond the scope of this study. Some of these decomposition products have been observed as mentioned in Section 3.1.

Figure 4: Estimated γ for first- and second-generation autoxidation-initiated ROOHs, presented as a function of varying [OH]SS and precursor (7-OE) concentration. γ is shown as a function of increasing [OH]SS for (A) m/z 191 and (B) m/z 223. γ of m/z 191 and m/z 223 is demonstrated as a function of increasing 7-OE concentration in (C) and (D) respectively. Error bars represent 1σ from triplicate measurements.
Scheme 1: Major peroxo radical chemistry occurring during photooxidation experiments.
Based on the above observations, we hypothesize that the $\gamma$ of autoxidation-initiated ROOHs can be suppressed by increasing oxidant and precursor concentrations. Previous studies have shown that the total concentration of water-soluble organics in the ambient cloud water can vary between 67-500 $\mu$M (assuming a 3-5 C number range). While our experimented concentration falls within this range, many of the laboratory-led aqueous-phase investigations have typically experimented with high concentrations of organic precursors and oxidants. These conditions can inadvertently suppress the formation of key autoxidation intermediates (e.g., ROOH). Based on the total concentration of water-soluble organics reported in the literature, it is our understanding that RO$_2$ radical chemistry will likely play an important role in facilitating the formation of autoxidation-initiated products. As such the prevalence of autoxidation should be carefully investigated in modelled representations of RO$_2$ radicals in both remote biogenic and urban environments.

4 Atmospheric Implications

For the first time, our study has systematically investigated aqueous-phase autoxidation, which can significantly contribute to the formation of organic peroxides in atmospheric cloud water. Our findings demonstrate that autoxidation-initiated ROOHs are observed in the aqueous-phase photooxidation of four OAs employed in our study. Structural suitability, concentration, and irradiation wavelength play an important role in propagating the formation of observed ROOHs. While our study focused on a specific class of organic compounds, i.e., OA, we believe that autoxidation is applicable to a wide spectrum of water-soluble organic compounds present in cloud water. The occurrence of autoxidation in the aqueous phase facilitates the formation of low-volatility organic compounds and HOMs such as peroxides, which are a class of ROS and significantly contribute towards the formation of SOA, thereby adding to the climate and health burden of atmospheric particulate matter. Further, ROOH species serve as reservoirs of radicals; as such, their formation
via autoxidation has significant implications for the HOx cycle and atmospheric oxidative capacity.

Based on our observations, we postulate that many of the previous laboratory studies may have overlooked the importance of aqueous-phase autoxidation because commonly used experimental conditions impeded the formation of key ROOH intermediates. Ambient sunlight reaching the ground level contains no UVC, while the photon flux increases exponentially from 290 nm (UVB) to 400 nm (UVA) and visible light. Our observations show that the yield of ROOHs also followed an exponential increase as UV light with longer wavelengths (UVB and UVA) was used. UVC, which is irrelevant to the ambient sunlight yet has been used in laboratory studies, has completely photolyzed ROOHs. Our observation also suggests that increasing concentrations of reactants, including both the OH radical and the precursor organic compound, likely suppress autoxidation. However, the underlying chemistry is nonlinear and could not be explicitly explained with our approach.

The OH radical concentration in ambient cloud water is in the range of 10^{-12}-10^{-14} M. On the other hand, the concentration of water-soluble organics in ambient cloud water can range between 67-500 μM (or 200-2230 μmol C L^{-1}). In polluted environments, the concentration of water-soluble organic compounds in fog waters can be up to 800 μM (equivalent to 4000 μmol C L^{-1}). The concentrations experimented in our study falls within this range (179-1000 μM). On the other hand, laboratory experiments have typically employed OH radical and organic precursors at much greater concentrations, which may have impeded autoxidation.

Through a detailed mechanistic investigation, we found that the mechanism of aqueous-phase autoxidation is likely analogous to its gas-phase counterpart. Yet, there are a few reasons we believe that aqueous-phase autoxidation should be further investigated. First, the atmospheric aqueous-phase is home to a group of water-soluble compounds that may or may not be present in the gas phase. For instance, PNA and LMA, which we investigated in this work, represent a group of compounds arising from monoterpene oxidation.
group of compounds is predominantly in the aqueous phase when cloud water is present. Aqueous-phase autoxidation can likely offer an oxidation pathway for water-soluble species that are not subject to gas-phase autoxidation. Second, the lifetime of RO$_2$ radicals, which is a determinant factor for autoxidation, is highly dependent on the concentration of NO. Due to the low Henry’s law constant of NO$_X$, aqueous media (e.g., cloud and fog droplets) can serve as a unique medium with low NO$_X$ concentrations. It would be important to investigate whether the aqueous phase can offer a reaction medium for autoxidation in environments that would be traditionally considered too high in NO$_X$ concentrations. As demonstrated in this work, the lifetime of RO$_2$ radicals and the extent of autoxidation are intricately dependent on the reaction conditions and reactant concentrations. Our study suggests the need to further understand the relevance of autoxidation in the atmosphere through field studies and model simulations.
Notes
The authors declare no competing financial interest.

Supporting Information Available
Additional experimental details, including product synthesis, mechanism, kinetic investigation, yield calculations and product characterization.

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Cloud water

ROOH