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Accretion product formation in the self-reaction of ethene-derived hydroxy peroxy radicals†

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In this study we revisit one of the simplest RO₂ + RO₂ reactions: the self-reaction of the ethene-derived hydroxy peroxy radical formed via sequential addition of ‘OH and O₂ to ethene. Previous studies of this reaction suggested that the branching to ‘accretion products’, compounds containing the carbon backbone of both reactants, was minimal. Here, CF₃O − GC-CIMS is used to quantify the yields of ethylene glycol, glycolaldehyde, a hydroxy hydroperoxide produced from RO₂ + HO₂, and a C₆O₄H₁₀ accretion product. These experiments were performed in an environmental chamber at 993 hPa and 294 K. We provide evidence that the accretion product is likely dihydroxy diethyl peroxy (HOC₂H₄OOC₂H₄OH =ROOR) and forms in the gas-phase with a branching fraction of 23 ± 5%. We suggest a new channel in the RO₂ + RO₂ chemistry leading directly to the formation of HO₂ (together with glycolaldehyde and an alkoxy radical). Finally, by varying the ratio of the formation rate of RO₂ and HO₂ in our chamber, we constrain the ratio of the rate coefficient for the reaction of RO₂ + RO₂ to that of RO₂ + HO₂ and find that this ratio is 0.22 ± 0.07, consistent with previous flash photolysis studies.

Environmental significance

Peroxy radicals formed via oxidation of hydrocarbons in the troposphere play a central role in the radical cycling of the atmosphere. These compounds participate in reactions that terminate radical chemistry and in reactions that propagate the radical chemistry. Quantifying the relative importance of such reactions is important for understanding the impact of hydrocarbon emissions on tropospheric chemistry, including the chemistry that degrades air quality. In this work, we quantify the formation of a C₄ accretion product from the self-reaction of ethene-derived hydroxy peroxy radicals. In contrast to previous studies, the radical terminating reaction producing the accretion product is significant. The formation of such accretion products offers a more efficient pathway for peroxy radicals to form secondary organic aerosol.

1 Introduction

Non-methane hydrocarbons are emitted to the atmosphere by both anthropogenic and biogenic processes at a rate of approximately 1.5 gigatons per year, making their chemistry an essential driver of tropospheric composition. In the atmosphere, these compounds are oxidized by reaction with ‘OH, NO₃, Cl’, or O₃, often followed by addition of O₂ to form organic peroxy radicals (RO₂). RO₂ undergo a myriad of bimolecular and unimolecular reactions, including reactions that lead to radical termination or radical propagation. Some RO₂ reactions lead to the formation of highly oxidized organic molecules (HOMs) and subsequent particle formation and/or growth. To predict the effects of peroxy radical reactions on tropospheric chemistry, accurate measurements of the rates and products of their uni- and bimolecular reactions are required.

The diverse RO₂ reaction pathways yield products with differing effects on atmospheric chemistry and air quality. In environments with elevated NO+, RO₂ react to form alkyl radicals (RO') (Reaction (1a)) and alkyl nitrates (RONO₂) (Reaction (1b)). Reaction (1a) generally propagates the radical chemistry leading to the formation of ozone (Reaction (2)):

RO₂ + NO → RO' + NO₂

(1a)

RONO₂

(1b)

NO₂ + O₃

(2)

In low NOx environments, RO₂ undergo unimolecular or bimolecular reactions with HO₂ or other RO₂. For β-
hydroxperoxy radicals, reaction with HO\(_2\) leads to the formation of hydroperoxides (ROOH) (Reaction (3a)) or other products such as RO' (Reaction (3b)) or a carbonyl, which in the case of the title reaction will be an aldehyde (R-\(\text{H}1\)=O) (Reaction (3c));

\[
\text{RO}_2^+ + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2
\]

\[
\rightarrow \text{RO}' + \cdot\text{OH} + \text{O}_2
\]

\[
\rightarrow \text{R-\(\text{H}1\)=O} + \text{HO}_2 + \cdot\text{OH}
\] (3a)

(3b)

(3c)

The RO\(_2\) self- and cross-reactions include both radical propagating channels ([(4a), (4b)]) and radical terminating channels ([(4c), (4d)]). Reactions (4a), (4c), and (4d) have been observed or proposed previously, while Reaction (4b) is proposed here to explain the excess yield of R-\(\text{H}1\)=O relative to that of ROH, even in the absence of O\(_2\):

\[
\text{RO}_2^+ + \text{RO}_2 \rightarrow \text{RO}' + \text{RO}' + \text{O}_2
\]

\[
\rightarrow \text{RO}' + \text{R-\(\text{H}1\)=O} + \text{O}_2
\]

\[
\rightarrow \text{ROH} + \text{R-\(\text{H}1\)=O} + \text{O}_2
\]

\[
\rightarrow \text{ROOR} + \text{O}_2
\]

(4a)

(4b)

(4c)

(4d)

The rates and products of Reaction (1) in simple peroxy radical systems have been studied in detail and are generally well known, while those of Reaction (3) are more uncertain. Reaction (3a) is the dominant channel for most simple organic peroxy radical reactions. In more substituted RO\(_2\), other channels, such as Reaction (3b) and (3c), become non-negligible.

The dynamics of Reaction (4) are complex as these pathways require significant electronic rearrangement and/or hydrogen shifts. The proposed mechanism of Reaction (4d) requires an intersystem crossing (ISC) and was previously believed to be unimportant to the chemistry of the troposphere (see ESI Appendix A). Recent studies utilizing chemical ionization mass spectrometry (CIMS) techniques, however, have detected compounds with molecular weights matching the expected products of Reaction (4d), generating renewed interest in quantifying the formation of these peroxides (one of several compounds known as accretion products). In fact, several studies have found that for some RO\(_2\)'s, Reaction (4d) may proceed at rates approaching the collision rate, suggesting a drastic shift from previous assumptions. While this manuscript was under peer-review, Yue et al. reported that a peroxide is produced in the RO\(_2^+\) + RO\(_2\) chemistry following H-abstraction from ethane at approximately 10% yield, using VUV photoionization mass spectrometry at 266 Pa and 298 K.

Investigation of the production of peroxides via Reaction (4d) is of additional importance due to their potential to form secondary organic aerosol (SOA). Organic aerosols play an important role in climate forcing and have a negative impact on human health, but many routes leading to their formation are poorly quantified. Accretion products formed in Reaction (4d) are much higher in carbon and oxygen numbers than the reactants and therefore have much lower volatility, increasing the likelihood that they condense from the gas phase to the particle phase. In both laboratory and field experiments, compounds with masses assigned to such accretion products have been observed in the aerosol and in the gas phase confirming that their production can play an important role in the formation and growth of SOA. However, their identity and mechanism of formation remain unclear.

In this study, we revisit the self-reaction of the ethene-derived hydroperoxy radical, HOCH\(_2\)CH\(_2\)O\(_2\). Previous studies have suggested that the formation of accretion products in this reaction is minimal. In contrast, we find that the branching fraction, \(\alpha_{\text{4d}}\), is 23 ± 5%. Using H/D exchange experiments, GC techniques, and synthesized standards, we provide evidence that the accretion product is dihydroxy diethyl peroxydicarbonate (HOCH\(_2\)CH\(_2\)OOCH\(_2\)CH\(_2\)OH). We propose a new channel leading to direct HO\(_2\) production, Reaction (4b). Finally, we constrain the rate coefficient for Reaction (4) from the ratio of products produced in this reaction to ROOH produced via Reaction (3a).

2 Experimental

2.1 Experimental design

Our goal in this investigation is to quantify the branching fractions and constrain the rate coefficient for the self-reaction of HOCH\(_2\)CH\(_2\)O\(_2\) radicals formed following the sequential addition of OH and O\(_2\) to ethene:

\[
\text{C}_2\text{H}_4 + \cdot\text{OH} \rightarrow \text{HOCH}_2\text{CH}_2\text{O}_2
\]

(5)

In the presence of ethene, the production of 'OH via photolysis of \(\text{H}_2\text{O}_2\) in a 800 L FEP Teflon environmental chamber leads to the production of ethylene glycol (EG), glycolaldehyde (GA), dihydroxy diethyl peroxydicarbonate (ROOR), and a hydroxy hydroperoxide, HOCH\(_2\)CH\(_2\)OOH. All experiments were performed at 993 ± 10 hPa pressure and 294 ± 1 K.

'OH is produced via the photolysis of \(\text{H}_2\text{O}_2\), Eight Sankyo Denki G40T10 254 nm lamps illuminated for 2 min yield a mean photolysis frequency for Reaction (6) of \(3.0 \pm 0.5 \times 10^{-4}\) s\(^{-1}\):

\[
\text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{OH}
\]

(6)

To determine the fraction of ethene reacted, we measured the 'OH exposure ([OH] \times time) from the decay of 2,3-butane- diol during the oxidation period in several of our experiments. The primary product of this reaction, 2-hydroxy-3-butanol, is not made elsewhere in our reaction system. The rate coefficient for the reaction of 'OH with 2,3-butane-diol has been reported by Bethel et al. using the relative rate method to be \(2.4 ± 0.6 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Bethel et al. measured this rate coefficient relative to that of 'OH + n-octane, for which they assumed a value of \(8.67 ± 0.17 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Current recommendations suggest that the rate coefficient of 'OH with n-octane at 298 K is somewhat slower (\(8.11 ± 0.12\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) so we use \(2.25 ± 0.6 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for the 'OH + 2,3-butane-diol rate constant in this analysis. Approximately 500 ppbv of butanediol was injected...
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during these experiments. When 2,3-butanediol was not injected, we used a photochemical kinetic box model to determine the ‘OH exposure. For the experiments with added butanediol, the modeled and measured ‘OH exposure agree to within 30%. The total ‘OH exposure during our experiments was between 0.8 × 10^6–4.3 × 10^9 molecules cm^{-3}. To minimize secondary chemistry, the lights were turned off before 10% of the initial ethene had reacted, usually after 2 minutes. Specific experimental conditions for each experiment used in this analysis are given in Appendix B of the ESI (Table S1).†

The branching fractions for Reaction (4) are determined from the formation of the products. Note that in this study, we use the following definitions, where j is the total number of possible pathways of Reaction X, \( \alpha_{si} \) is the branching fraction of pathway i of Reaction X, and \( k_x \) is the rate constant of a Reaction X:

\[
\alpha_{si} = \frac{k_{si}}{k_x} \\
k_{si} = \alpha_{sj}k_x
\]

To quantify the ratio of the radical terminating branching channels, \( \frac{\alpha_{4d}}{\alpha_{4c}} \), we measured the yields of ethylene glycol (EG) and dihydroxy diethyl peroxide (ROOR). In the absence of secondary chemistry, the ratio of their concentration is equal to the ratio of their branching fractions. Secondary losses of the products by reaction with ‘OH is calculated to be minimal due to the small fraction of ethene oxidized during the experiment, and the main loss is photolysis. As described in the ESI (Appendix C),† we measured upper limits to the photolysis loss rates for EG, ROOH, glycolaldehyde (GA), and ROOR and find that these losses are also small (negligible for EG, less than 1% of GA, and less than 6% of ROOR and ROOH in a typical experiment). Additionally, we measured the wall loss rates for these compounds as a function of time and find that, over the time period of our experiments, these losses are negligible.

GA is produced in excess of EG in these experiments, consistent with significant additional sources beyond Reaction (4c). In 993 mbar of air, we attribute approximately half of the excess to the reaction of oxygen with the alkoxy radicals formed in Reaction (4a) and (4b):

\[
\text{HOCH}_2\text{CH}_2\text{O} + \text{O}_2 \rightarrow 2\text{CH}_2\text{O} + \text{HO}_2 \quad (7a) \\
\text{HOCH}_2\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HOCH}_2\text{CHO} + \text{HO}_2 \quad (7b)
\]

The fraction of the excess GA that results from Reaction (7b) is well-explained using results from Orlando et al.17 for experiments performed here under both much higher and lower [O_2] as discussed in Appendix C of the ESI.† Theoretically, direct hydrogen atom elimination from the initially produced hot alkoxy radical could also explain the excess glycolaldehyde production at low O_2, but it is expected that C–C bond scission will be much faster. Thus, we tentatively attribute the remaining excess GA to Reaction (4b).

To further constrain the branching fractions and kinetics of Reaction (4), we perform a series of experiments varying the ratio of the formation rates of HOCH_2CH_2O and HO_2. In the absence of external sources, HO_2 is produced directly in Reaction (4b) and indirectly via the subsequent chemistry of alkoxy radicals, e.g. decomposition (Reaction (7a)) or via their reaction with O_2 (Reaction (7b)). We increase the formation rate of HO_2 relative to RO_2 by adding CH_3OH to the chamber, which provides an external source of HO_2 independent of RO_2:

\[
'\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{HO}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (8)
\]

A small amount of additional RO_2 is also produced in our experiments in Reaction (9):

\[
'\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O} \quad (9)
\]

As our independent variable, we define \( F_{\text{external}} \), the ratio of the HO_2 produced externally to Reaction (4) via Reactions (8) and (9) to the amount of RO_2 produced via Reaction (5), where the \( k_8 \) are the relevant reaction rate coefficients:

\[
F_{\text{external}} = \frac{P_{\text{HO}_2,\text{external}}}{P_{\text{RO}_2}} = \frac{k_{\text{R8}[\text{CH}_2\text{OH}]} + k_{\text{R9}[\text{H}_2\text{O}_2]}}{k_{\text{R5}[\text{C}_2\text{H}_4]}} \quad (10)
\]

When no methanol is added to the chamber and \( k_{\text{R8}[\text{H}_2\text{O}_2]} \ll k_{\text{R5}[\text{C}_2\text{H}_4]} \), \( F_{\text{external}} \) approaches zero and HO_2 is produced only as a result of Reaction (4). In this ‘high RO_2’ limit, significantly more RO_2 is produced in the chamber than HO_2, and, according to our box model simulations, more than 90% of the HO_2 reacts with RO_2 to produce ROOR (the products of Reaction (3)) will be discussed further in a later section). As such, the production of ROOR provides a probe of the branching to the radical propagating channels in Reaction (4). To quantify this, we define the dependent variable \( Q \):

\[
Q = \frac{[\text{ROOR}]}{[\text{HOCH}_2\text{CH}_2\text{OH}]} + [\text{ROOR}] \quad (11)
\]

In the limit where \( F_{\text{external}} \rightarrow 0 \), \( Q \) is a measure of the ratio of the branching fractions of the radical propagating channels to the radical terminating channels:

\[
Q_{\text{high RO}_2 \text{limit}} = \frac{2(\alpha_{\text{R4a}} + \alpha_{\text{R4b}})}{\alpha_{\text{R4c}} + \alpha_{\text{R4d}}} \quad (12)
\]

where the factor of 2 in the numerator arises because Reactions (4a) and (4b), including the subsequent reactions of the alkoxy radicals, each produce two HO_2. Therefore, the \( y \)-intercept of \( Q \) as a function of \( F_{\text{external}} \) provides a constraint on the ratio of the radical propagating and radical terminating channels of Reaction (4).

To further constrain the kinetics of Reaction (4), we explore the ‘high HO_2’ limit, where \( F_{\text{external}} \gg 1 \). In this limit, nearly all the ‘OH produced from the photolysis of H_2O_2 reacts via Reactions (8) and (9) to produce HO_2. Because the formation rate of HO_2 greatly exceeds that of RO_2, the HO_2 self-reaction is its main loss.
the chamber to form product ions. CF$_3$O $^\text{+}$ from the ion source. Reagent ions then react with analytes from in the high HO$_2$ limit (direct sampling mode). The CF$_3$O $^\text{+}$ in the absence of methanol addition is produced by passing dilute CF$_3$OOCF$_3$ gas in N$_2$ through a polycarbonate-coated glass critical oriifice into a fluorocopolymer-coated glass flow tube maintained at a pressure of 35 mbar, where it is diluted with N$_2$ and mixes with the flow from the ion source. Reagent ions then react with analytes from the chamber to form product ions. CF$_3$O $^\text{+}$ reacts with many multifunctional organic compounds at the ion–molecule collision rate to yield cluster ions at the mass of the reagent ion (85) plus the mass of the analyte. For example, ethylene glycol, with a molecular weight of 62, is detected at m/z 147. These ion clusters enter the mass spectrometer through a pinhole and a conical hexapole ion guide. In addition to forming clusters, hydroperoxides produce a small fraction (a few %) of characteristic fragmentation ions at m/z 63 and m/z 81, enabling identification of such analytes. For some analytes (e.g. H$_2$O$_2$) the cluster ions are not well bound, such that not all collisions result in a stabilized ion cluster. For these analytes, the resulting sensitivities are therefore lower than estimated based on the ion–molecule collision rate. The HRTof-CIMS collected ion signals ranging between m/z 19 and m/z 396 at a mass resolving power of approximately 3000 (m/Δm).

The GC consists of a 1 meter fused silica column (Restek RTX-1701) cooled via evaporation and expansion of liquid CO$_2$ and warmed with resistive heating elements connected to a Watlow temperature controller. The sample is diluted by a flow of dry N$_2$ before being cryotrapped on the head of the column at a temperature of $-40 \, ^\circ\text{C}$ or below for between 5 and 10 minutes. The specific trapping temperature, time, and dilution for each experiment are chosen to optimize the amount of analyte collected while minimizing the water trapped. When trapping is complete, 5 scm N$_2$ flows through the column while the temperature of the GC steadily increases at a predetermined ramp rate chosen to best separate analytes of interest in the minimum amount of time. The elution stream from the GC oven is combined with a 200 scm flow of nitrogen and routed to the mass spectrometer flow tube. Specific conditions for the experiments discussed in this paper are given in Appendix F of the ESI (Table S8).†

2.3 Reagent preparation

H$_2$O$_2$ (30% by mass, Macron Fine Chemicals) was pipetted into a three-way glass vial and weighed for accurate mass determination. Dry air was then passed through the vial into the experiment chamber at 20 SLM until all the reagent was evaporated, as verified by reweighing the vial after injection. 2,3-Butanediol (98%, Sigma-Aldrich) was added to the chamber in a similar manner.

Ethene ($\approx99.5\%$, Sigma-Aldrich) and methanol ($\approx99.9\%$, Sigma-Aldrich) samples were prepared in 500 mL glass bulbs using manometry. The bulb was attached to a vacuum/N$_2$ system and reagent source, and the desired concentration of ethene and methanol was obtained via serial dilution measured with pressure sensors (MKS 1000 and 10 torr Baratron pressure transducers). Concentrations were also determined using FTIR measurements by fitting spectra to absorption cross sections from the PNNL IR Database.† The manometry and IR determinations agreed to better than 10%.

2.4 CIMS calibration

Quantification of the various RO$_2$ reaction products requires knowledge of their sensitivity in the CIMS instrument. The Caltech CIMS implementation uses a transverse ionization approach where the CF$_3$O $^\text{+}$ reagent ions travel across the 35 mb gas mixture flow in approximately 5 ms before entering the
mass filter. The short reaction time of the reagent ions with the analytes yields a sensitivity for each compound that is proportional to: the ion–molecule collision rate with the analyte, the fraction of such collisions that result in ion products, the transmission efficiency of such ions, and whether there is fragmentation, all modulated by the number of \( CF_3O^- \) produced in the polonium source. As the fraction of reagent ions, here primarily \( CF_3O^- \) and its clusters with \( H_2O \) and \( H_2O_2 \) (observed at \( m/z \) 85, 103, and 119, respectively), that react with the analytes is small, we first normalize the signals at the cluster mass (e.g. the counts at \( m/z \) 163 for the hydroxyhydroperoxide) by the sum of signal for the reagent ions. Because the number of reagent ions is very high, to remain in a linear counting regime, we use the reagent ion signal for the sum of the minor isotope logue at \( m/z + 1 \) (e.g. 86 for \( CF_3O^- \)). So, the sensitivities listed in Table 1 below are normalized by the sum of \( m/z \) 86 + \( m/z \) 104 + \( m/z \) 120. These normalized signals are proportional to concentration of each analyte ionized in the flow.

To determine the sensitivity of the CIMS to ethylene glycol, we used two methods to produce gas phase standards. In the first, ethylene glycol (Sigma-Aldrich) was evaporated into a 200 L Teflon bag, which was then attached to an FTIR and a flow dilution system in series with our GC-CIMS. The concentration of EG in the Teflon bag was quantified using the FTIR and cross sections from the PNPL IR Database as air from the 200 L bag flowed through a 19 cm pyrex FTIR cell with CaF2 windows at a rate of 484 sccm. The uncertainty in the FTIR cross sections is estimated to be \( \pm 7\% \). Following the FTIR cell, a subsample (34 sccm) was diluted into a 2 SLM nitrogen flow yielding EG concentrations of approximately 1 ppmv which was directed into the CIMS instrument. In the second method, we prepared a known concentration of EG by flowing 20 sccm of air over a diffusion vial maintained at 30 °C. The diffusion vial containing EG was regularly weighed. The mass loss rate of EG over time, and the flow rate in the CIMS flow tube were used to calculate the mixing ratio of EG in the flow tube. The sensitivity calculated using these two methods agrees within 8%. The sensitivity using the diffusion vial method was repeated often and the average is listed in Table 1.

To estimate the sensitivity for the other \( RO_2 \) reaction products, we calculate their ion–molecule collision rate relative to that of EG. \( CF_3O^- \) binds strongly to most multifunctional organic compounds24 and as such, the fraction of each product ionized depends linearly on the ion–molecule collision rate. For some analytes, such as \( H_2O_2 \), the ion–molecule complex binding energy is small, and not all collisions lead to stabilized product ions. This dissociation is diagnosed by evaluating the sensitivity as a function of temperature and water vapor. For weakly bound clusters, the sensitivity decreases as a function of temperature and generally has a complex behavior as a function of water—sometimes increasing at low concentrations as the water chaperone increases cluster formation, before decreasing at high water concentrations due to ligand switching.19,21 For the product clusters described in this work, we find that the sensitivity is largely insensitive to temperature and both water and \( H_2O_2 \), consistent with high stability for the ion clusters. Even for well bound clusters, the efficiency of formation of \( CF_3O^- \) clusters following collision can be less than unity if they fragment into smaller ions. The data obtained with the GC enables us to quantify this fragmentation for each analyte, and we observe very little such fragmentation for the species reported here. The hydroxyhydroperoxide \( (m/z \) 163) produces a very small signal at \( m/z \) 145 (\( <2\% \)) and \( m/z \) 63 + 81 (2–3\%). (The latter two ions are diagnostic of organic hydroperoxides.22–24) Given the size and stability of the ion products and the lack of significant fragmentation, we expect that for all the \( RO_2 \) reaction products, the sensitivity of each for its \( CF_3O^- \) cluster will scale with the ion–molecule collision rate to within \( \pm 20\% \).

To calculate the ion–molecule collision rate, we use the method of Su et al.25 together with calculated dipole moments and polarizabilities using quantum calculations.26 The calculated ion–molecule collision rates, relative to that for ethylene glycol are listed in Table 1.

### 2.5 Peroxide synthesis

Previous studies of the formation of accretion products have observed compounds at the mass of the peroxides (ROOR) using CIMS techniques,1,8,16 but the identity of these products has not been typically confirmed. Studies by Kenseth et al.27 have, for example, shown that accretion products produced in the ozonolysis of pinenes are not peroxides and do not form in the gas phase. Here, a method for the synthesis of a standard for the \( C_4 \) dihydroxy peroxide for comparison to our oxidation products is outlined.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Measured sensitivity(^a) (cts pptv(^{-1}))</th>
<th>Calc. ( CF_3O^- )-molecule collision rate(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>( 2.5 \pm 0.2 \times 10^{-4} )</td>
<td>1</td>
</tr>
<tr>
<td>( H_2O_2 )</td>
<td>( 1.65 \pm 0.06 \times 10^{-4} )</td>
<td>0.94</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>( 2.8 \pm 1.6 \times 10^{-4} )</td>
<td>1.02</td>
</tr>
<tr>
<td>2-Hydroxy-3-butanol</td>
<td>( 2.7 \pm 0.2 \times 10^{-4} )</td>
<td>1.08</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>( 1.05 )</td>
<td>1.08</td>
</tr>
<tr>
<td>HOCH(_2)CH(_2)OOC(_2)CH(_2)OH</td>
<td>( 1.05 )</td>
<td>1.08</td>
</tr>
</tbody>
</table>

\(^a\) Signals are normalized to the signal of the \(^{13}\)C isotope of the reagent ion (\( m/z \) 86 + \( m/z \) 104 + \( m/z \) 120). \(^b\) Relative to ethylene glycol. \(^c\) The ratio of sensitivity to ethylene glycol is lower than the ratio of the ion–molecule collision rate coefficients due to incomplete stabilization of collisions.\(^19\)
2.5.1 General information

2.5.1.1 Caution. Although no explosions were experienced in this work, organic peroxides are potentially hazardous compounds and must be handled with great care: avoid direct exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition-metal ions. A safety shield should be used for all operations involving H₂O₂.

Unless otherwise stated, reactions were performed in flame-dried glassware under ambient conditions using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reagents were purchased from commercial sources and used as received. Reaction temperatures were controlled by an IKAmag temperature regulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (250 μm) and visualized by UV fluorescence quenching, potassium permanganate staining, or p-anisaldehyde staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. Preparative HPLC was performed using an Agilent 1200 HPLC system equipped with an ACE C18 column (5 μm, 21.2 mm × 250 mm). ¹H and ¹³C NMR spectra were recorded on a Varian Inova 500 (500 and 125 MHz, respectively) spectrometer and are reported in terms of chemical shift relative to CHCl₃ (δ 7.26 and 77.16 ppm, respectively). Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant, integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were obtained from thin films deposited on NaCl plates using a PerkinElmer Spectrum BXII spectrometer and are reported in wavenumbers (cm⁻¹). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 10 mm path-length cell. All of the spectral data can be found in the ESI† (Appendix F of the ESI).

2.5.2 Alkyl peroxides 1–3. Compounds were prepared according to a modified literature procedure (Fig. 1).²⁸ To a flame dried 25 mL round bottom flask was added ethereal H₂O₂ (ref. 29) (1 M solution, 10 mL, 10 mmol, 1.0 equiv.). This solution was brought to 0 °C, and ethylene oxide was bubbled into the solution for 30 s. PMA (phosphomolybdic acid, 182 mg, 0.1 mmol, 0.01 equiv.) was added and the reaction mixture was stirred at 0 °C for 20 min. After 20 min, H₂O₂ remained by TLC analysis (100% ethyl acetate, visualized with p-anisaldehyde). Ethylene oxide was again bubbled into the solution for 30 s, and an additional 500 mg (0.27 mmol, 0.027 equiv.) of PMA was added. The reaction mixture was stirred for another 1 h at 0 °C, at which point TLC indicated consumption of H₂O₂. The reaction mixture was pushed through a short silica plug and concentrated. Analysis of the crude clear residue using GC-CIMS showed the presence of a compound with m/z = 163, eluting at 31 °C, and two compounds with m/z = 207, eluting at 52 °C and 64 °C, respectively (Fig. 2). All chromatograms were run under the same conditions as those described in the Appendix F of the ESI for the oxidation experiments, with at least 5 minutes of trapping time at −45 °C.

The clear residue was purified via preparatory TLC (5% methanol/ethyl acetate, visualized with p-anisaldehyde). All major bands were collected and were subjected to GC-CIMS analysis. Only two compounds were observed via GC-CIMS analysis: one major compound at m/z 163 and one major compound at m/z 207 (Fig. 2). The chromatograms of both of these compounds contain daughter ions characteristic of −OOH functional groups (m/z 63 and m/z 81).

The two isolated products were identified to be hydroxyhydroperoxide 1 (20.0 mg, 3% yield, colorless oil) and ether 2 (5.4 mg, less than 1% yield, colorless oil). We believe that peroxide 3 forms under the reaction conditions, as a second peak at m/z = 207 is observed in the crude reaction mixture, but is not stable to isolation. Additionally, compound 3 elutes at the same temperature as the putative accretion product in our oxidation experiments.

3 Results and discussion

3.1 The identity of the accretion product

Although several recent studies have reported formation of accretion products in oxidation experiments of organic compounds,¹⁴,¹⁰ the identity of these compounds remains generally unclear. For example, Kenseeth et al.²⁷ have recently shown that accretion products formed in the ozonolysis of α- and β-pinene arise not directly in the gas phase but rather from heterogeneous reactions of alcohols and (likely) peroxides.
produced via O₃ and 'OH chemistry, respectively. Here, in this simplest of systems, we show that the accretion product is likely an organic peroxide, HOCH₂CH₂OCH₂CH₂OH. As shown in Fig. 3, across all our experiments from those with minimal HO₂ chemistry to those dominated by such reactions, the yield of the accretion product closely tracks the yield of ethylene glycol, a unique gas-phase product of the self-reaction of HOCH₂CH₂OO’, suggesting that it is also produced in the gas phase via this self-reaction.

Shown in the first panel of Fig. 2 are gas chromatograms of the products formed in our ‘high RO₂’ experiments. Due to its high vapor pressure, glycolaldehyde is not efficiently trapped on the column. All the other products – ethylene glycol, the hydroperoxide, and the accretion product – are efficiently collected, separated, and detected at their CF₃O⁻ cluster m/z. The average GC transmission efficiencies of all of these species is between 90–100%.

Three plausible molecules with the formula C₄O₄H₁₀ can be postulated to form in the gas-phase chemistry of HOCH₂CH₂OCH₂CH₂OH, and in the condensed-phase synthesis, characterizing the starting materials: a hydroperoxyhydroxyether, a dihydroxyperoxide, and a triol ether. The last compound can be distinguished from the first two by the number of readily exchangeable hydrogens. To rule out the triol ether, we added D₂O to the GC effluent and, as shown in panel b of Fig. 2, ethylene glycol and the C₂ hydroxyhydroperoxide shift up 2 m/z, consistent with two exchangeable hydrogens. Likewise, the accretion product shifts up 2 m/z. No +3 m/z isotopologues are observed. As such we eliminate consideration of the triol as a plausible structure for the accretion product.

Also shown in Fig. 2 (panels c and d) is the chromatograph of the synthetic products from the liquid phase condensation of the hydroperoxide (as described above). Two compounds at the m/z of the accretion product (m/z 207, mw 122) are observed in the crude mixture, while only one C₄O₄H₁₀ compound is stable to prep TLC separation. The isolated compound eluting at approximately 65 °C is identified as the hydroperoxy hydroxy ether, HOCH₂CH₂OCH₂CH₂OOH, based on the ¹H and ¹³C NMR spectra [see ESI†] and on the observed fragmentation of m/z 207 to m/z 63 and m/z 81 in CF₃O⁻ CIMS, fragments characteristic of hydroperoxides. The first peak, the peroxide, elutes at the same temperature as the accretion product formed in the gas-phase experiments. Therefore, we conclude by elimination that the accretion product formed in the gas-phase ethene oxidation experiments is likely the dihydroxyperoxide (ROOR).

3.2 Product branching fractions

To calculate the branching fractions of the self-reaction, we quantify the closed-shell end products of these reactions (with the exception of formaldehyde, which does not cluster with CF₃O⁻). Reaction (4) directly produces three products: ethylene glycol, glycolaldehyde, and the accretion product (ROOR).

Shown in Fig. 3 are the concentrations of ROOR and glycolaldehyde as a function of the concentration of ethylene glycol. The points are colored by the value of F_external. The observed yield of ROOR relative to EG is 0.56 ± 0.02. In 21% O₃ at 993 hPa, the yield of GA relative to EG is 1.50 ± 0.03. The ratio of the ROOR to EG is independent of F_external. The ratio of GA to EG increases at the highest F_external as a result of secondary chemistry of the ROOH, and therefore we do not include these points in the above fit (see ESI Appendix C†).

Absent secondary chemistry, the ratio of the product yields equals the ratio of their production. To accurately determine the ratio of their production, however, secondary losses must be considered. Here, this potentially includes the photolysis of the peroxide product (ROOR), the hydroperoxide (ROOH), and glycolaldehyde. We measured the upper limit of the photolysis rate of these compounds in our chamber as follows: after synthesizing them in the gas phase via an ethene oxidation experiment in the high RO₂ limit, we evacuated the chamber through a coil of Teflon tubing submerged in an ethanol/liquid nitrogen bath maintained at approximately −30 °C, trapping the low volatility products while allowing the remaining ethene and high volatility products to be pumped away. We then flushed out the chamber with clean air and returned the contents of the trap to the Teflon chamber by flowing dry air back through the trap at room temperature (294 K). Finally, we added 50 ppmv methanol to convert any ‘OH produced by subsequent photochemistry to HO₂, thereby isolating the loss due to photolysis. We then turned on the UV lights and measured the loss rates of the relevant compounds (Table 2). During a typical 2 min photolysis experiment, we calculated that 1% of the GA is photolyzed and at most 6% of the ROOR was lost. Photolysis of the hydroxyhydroperoxide (ROOH) results in a maximum loss of a few percent. However, these measured photolysis rates are an upper limit to the loss via photolysis, as there may be additional secondary losses during these photolysis experiments – we expect that the true photolysis rates of ROOR and ROOH are likely closer to that of hydrogen peroxide. Therefore, in our subsequent analysis, we assume that over the 120 s time period of our experiments, the average photolysis frequency for the ROOR and ROOH is 3.0 × 10⁻⁴ s⁻¹. If instead we use the upper
limit to the photolysis frequencies, the estimated branching ratios to ROOR and ROOH increase by approximately a factor of 1.05. We observe no significant photolysis of ethylene glycol over the experiment timescales. In addition to secondary losses, GA is also formed via the reaction of $'OH$ with ROOH and EG and via photolysis of ROOH and subsequent reaction of O$_2$ with the generated RO'. This chemistry is only significant when ROOH is much larger than GA (e.g. at high $P_{\text{external}}$ (see ESI Appendix C†)).

Accounting for the photolysis losses and glycolaldehyde production, we find that the ratio of the production of ROOR and GA to ethylene glycol are $0.57 \pm 0.10$ and $1.55 \pm 0.20$, respectively, where the uncertainty is derived primarily from the uncertainty in the relative calibration of the CIMS for these compounds. In the first-generation chemistry of this reaction system, Reaction (4) is a unique source of the accretion product and EG, so the ratio of their production is equal to the ratio of the branching in Reaction (4) $\frac{a_{4d}}{a_{4c}}$. GA, however, is also produced in the subsequent reactions of the alkoxy radical and O$_2$ (Reaction (7b)) and, speculatively, via a radical propagating reaction, Reaction (4b). There may be additional GA formed via Reaction (3). The formation of GA in these experiments is discussed further below.

### 3.3 Glycolaldehyde formation

As shown in Fig. 3, the yield of glycolaldehyde is consistently higher than the yield of ethylene glycol across our experiments. This is true even when oxygen is reduced to 1% of the total volume to minimize the extent of Reaction (7b) (see ESI Appendix C†). This observation is consistent with prior studies of GA formation in the ethene oxidation system. In the FTIR study of the title reaction by Barnes et al., the analysis of their data yields $40\%$ higher than EG at low oxygen mixing ratios (5 hPa). At 180 hPa and 200 hPa [O$_2$], similar to the concentrations in our study, GA yields were 70% and 95% larger, respectively.

There is no previous estimate for $a_{3c}$ or $a_{3b}$, both of which would yield glycolaldehyde from the Reaction of RO$_2$ with HO$_2$. Shown in Fig. S5† is the ratio of modeled and measured GA to ethylene glycol as a function of the ratio of HO$_2$ to RO$_2$ steady state concentration (as simulated by the box model). Using this comparison of the box model with the data, we find that a branching fraction to the formation of GA of more than 1% from the RO$_2$ + HO$_2$ reaction is incompatible with the observations over a wide range of RO$_2$ fate. This in turn suggests that $a_{3c} + 5 \times a_{3b}$ is less than 0.01, where the factor of 5 accounts for our determination that in 1 atmosphere of air at 294 K, approximately 20% of alkoxy radicals react via Reaction (7b). In our subsequent analysis we assume both $a_{3c}$ and $a_{3b}$ are zero, producing no GA in our experiments, and attribute excess GA with low partial pressures of O$_2$ to Reaction (4b). We quantify the importance of this reaction pathway by assigning all GA produced in excess of EG in our low [O$_2$] experiments to this reaction channel. It is also a theoretical possibility that this excess GA is formed by the loss of a hydrogen atom from alkoxy radicals with excess energy—however, we do not expect such a reaction to be competitive with C-C bond scission or Reaction (4b). From our experiments, we determine that the branching to pathway (4b) is 26% of the branching to Reaction (4c) $\left(\frac{a_{4b}}{a_{4c}} = 0.26 \pm 0.05\right)$. The large uncertainty in this result reflects the fact that this ratio is determined by the difference between the yield of GA and ethylene glycol at 0% O$_2$ and, as such, is highly sensitive to error in our knowledge of the relative sensitivity of the CIMS to these compounds.

Finally, the extent of Reaction (7b) to the formation of glycolaldehyde is quantified by comparing the relative concentrations of GA and ethylene glycol at varying O$_2$ partial pressures. Fig. S4† shows $\frac{[\text{HOCH}_2\text{CHO}]}{[\text{HOCH}_2\text{CH}_2\text{OH}]}$ as a function of [O$_2$], which we determine from $\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}}$ as described in ESI Appendix C.† This figure also shows this ratio as determined from the data of Barnes et al. and Orlando et al. Direct comparison of these data is complicated by the difference in total pressure between our experiments and those of Orlando et al. and Barnes et al., which may change the relative branching to decomposition and reaction with O$_2$. Additionally, the alkoxy radicals in the experiments of Orlando et al. were generated by the reaction of RO$_2$ with NO$^*$. In this system, a temperature-dependent fraction of the alkoxy radicals have excess energy, and undergo prompt decomposition, whereas the rest of the alkoxy radicals are thermalized and can then either undergo decomposition or reaction with O$_2$. The fraction of thermalized alkoxy radicals generated in Reaction (4) may differ from that generated by the reaction between RO$_2$ and NO$^*$. The analysis of our data, as presented in ESI Appendix C,† indicates that approximately 20% of the alkoxy radicals in our system react with O$_2$, whereas 29% of the alkoxy radicals in the system studied by Orlando et al. react with O$_2$ at 298 K. While this
difference is well within the uncertainty of our quantification of EG and GA, it may reflect either the difference in pressure or a difference in the fraction of thermalized radicals in our system. The comparison between our data to the data of Orlando et al. and Barnes et al. is discussed further in ESI Appendix C.† In our subsequent analysis, we use a value of 20% for branching to Reaction (7b) in air.

3.4 Radical propagation vs. chain termination in Reaction (4)

As described above, in the limit where \( F_{\text{external}} \to 0 \), \( Q \) (eqn (11)) is a measure of the ratio of the radical propagating channels to the radical terminating channels of Reaction (4). In the limit where all \( \text{HO}_2 \) is produced internally to Reaction (4), >90% of the \( \text{HO}_2 \) reacts with \( \text{HOCH}_2\text{CH}_2\text{OOH} \), and there are no secondary losses,

\[
Q_{\text{high RO}_2 \text{ limit}} = \frac{2(\alpha_{R4d} + \alpha_{R4b})}{\alpha_{R4c} + \alpha_{R4d}} \quad (17)
\]

Shown in Fig. 4 is \( Q \) plotted as a function of \( F_{\text{external}} \). The \( y \)-intercept, \( (F_{\text{external}} = 0) \), is 1.07 suggesting that about half of the \( \text{RO}^+ \), reacting via \( R4 \), yields \( \text{HO}_2 \). The solid line shown in Fig. 4 is our box model results optimized to fit these data. The model includes external production of \( \text{HO}_2 \), estimates for the loss of \( \text{HO}_2 \) via its self reaction, and photolysis losses of both ROOH and the accretion product. The optimized model suggests that the ratio of the radical recycling channels \( (\alpha_{R4a} + \alpha_{R4b}) \) to the radical terminating channels \( (\alpha_{R4c} + \alpha_{R4d}) \) is 0.54 ± 0.11. Independent of the subsequent fate of the alkox radical, under our reaction conditions two \( \text{HO}_2 \) are produced in each of the chain propagating channels. The uncertainty in this ratio represents error in the relative sensitivity of the CIMS to ROOH vs. ethylene glycol and ROOR (±25%) and uncertainty in their photolysis frequencies (±28%). As an additional check on the quantification of ROOH, the box model suggests that in the ‘high \( \text{HO}_2 \)’ limit, the formation of ROOH should be within a few percent of the reacted ethene. After accounting for the small photolysis losses, we find that the ratio of ROOH to ethene reacted is on average 90% for the high \( \text{HO}_2 \) experiments (see Fig. S12†).

3.5 The rate coefficient of Reaction (4)

As discussed earlier, when \( F_{\text{external}} \) is high, \( Q \) is proportional to \( \frac{1}{2k_{R13}} \times \frac{k_{R4}^2}{k_{R4}^2(\alpha_{R4c} + \alpha_{R4d})} \) To estimate \( k_4 \) and the branching fractions of Reaction (4), we perform a least-squares fit of \( Q \) from the box model to \( Q \) calculated from our CIMS data. The branching fraction \( (\alpha_{R4d}) \) to the formation of the accretion product and the self-reaction rate constant \( (k_4) \) are the only fitted parameters. Other unknown parameters are written in terms of these parameters using the relationships developed in the previous sections, as demonstrated below:

\[
\alpha_{R4c} = \alpha_{R4d} \frac{\alpha_{R4c}}{\alpha_{R4d}} = 1.72 \alpha_{R4d}
\]

\[
\alpha_{R4b} = \alpha_{R4c} \frac{\alpha_{R4b}}{\alpha_{R4c}} = 0.46 \alpha_{R4d}
\]

\[
\alpha_{R4d} = 1 - \alpha_{R4b} - \alpha_{R4c} - \alpha_{R4d} = 1 - 3.18 \alpha_{R4d}
\]

In addition to constraining \( \frac{k_4^2}{k_{R4}} \), we report the value of \( k_4 \) assuming the currently accepted value for \( k_{R13} \) (2.5 × 10\(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) when accounting for both the termolecular and bimolecular pathways – note that in our experiments, the enhancement due to water vapor and methanol is negligible\(^{10}\) and assuming a value of \( k_5 \) = 1.1 × 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).\(^{12}\) Additionally, we report the ratio of the radical propagating channels to the radical terminating channels and the fitted results for all of the branching fractions of the self-reaction pathways (Table 3). In summary, we find the following branching fractions for the self-reaction pathways:

\[
\text{RO}_2 + \text{RO}_2 \rightarrow \text{RO}^+ + \text{RO} + \text{O}_2 \quad \alpha_{R4c} = 0.27 \pm 0.10
\]

\[
\rightarrow \text{RO}^+ + \text{R}_{-\text{H}2}\text{O} + \text{HO}_2 \quad \alpha_{R4b} = 0.10 \pm 0.04
\]

\[
\rightarrow \text{ROH} + \text{R}_{-\text{H}2}\text{O} + \text{O}_2 \quad \alpha_{R4c} = 0.40 \pm 0.10
\]

\[
\rightarrow \text{ROOR} + \text{O}_2 \quad \alpha_{R4d} = 0.23 \pm 0.05
\]

3.6 Comparison with earlier studies

We find the measured branching fraction to formation of the accretion product, \( \alpha_{R4d} \) = 0.23 ± 0.05, is much larger than that observed by Barnes et al. who found the ROOR formation to contribute at most 1% of the total products. Barnes et al. performed their experiments in a quartz reaction chamber that included metal mirrors. To evaluate the stability of the peroxy accretion product on quartz (and steel), we performed an ethene oxidation experiment in the high \( \text{RO}_2 \) limit and, during direct sampling into the CIMS, replaced a portion of the Teflon
sampling line with a length of approximately 60 cm of quartz or metal tubing, which at our flow rate produced a residence time in the quartz/metal tube of <3 s. Despite this very short interaction time, we observed a more than a 50% loss of the accretion product (Fig. S3†). Such wall loss likely limited the ability of Barnes et al.13 to observe the ROOR. Additionally, a recent study published on the reactions of ethyl peroxy radicals11 found a branching ratio to the accretion product of 10 ± 5%, demonstrating that formation of the accretion product is significant even in small unsubstituted peroxy radical systems, lending further support to our results.

Our estimate of the ratio of radical propagation to radical termination (α_{ab} + α_{ad}/α_{ac} + α_{ad} = 0.54 ± 0.11) in Reaction (4) is lower than several recent studies.13,16,18 The study most similar to the work presented here is that of Barnes et al.,13 a product study conducted with FTIR, which reports equal contributions of radical propagating and radical terminating channels. In that work, the concentrations of ethylene glycol, glycolaldehyde, and formaldehyde are compared to determine that α_{ac} and α_{ad} are approximately equal (eqn (18)):

\[
\frac{\alpha_{ac}}{\alpha_{ad}} = \frac{[\text{HOCH}_2\text{CH}_2\text{OH}]}{\frac{1}{2}([\text{HOCH}_2\text{CHO}] - [\text{HOCH}_2\text{CH}_2\text{OH}]) + \frac{1}{4}[\text{HCHO}]}
\]

This expression assumes, however, that additional glycolaldehyde is only formed as a result of allyko radical chemistry

| Table 3 | Quantification of Important HOCH₂CH₂OO⁺ + HOCH₂CH₂OO⁺ reaction parameters and the sources of uncertainty. S_{compound} refers to the sensitivity of the relevant compound. \(T = 294\) K and \(P = 993\) mbar |
|---|---|---|---|
| Quantity | Constraint | Sources of uncertainty | Value |
| \(\frac{\alpha_{ac}}{\alpha_{bc}}\) | [ROOR] | \(S_{\text{ROOR}}\) (15%), fit Fig. 3 (3%), secondary chemistry (3%) | 0.57 ± 0.09 |
| \(\alpha_{bc}\) | [ROOH] | \(\frac{S_{\text{ROOH}}}{S_{\text{ROH}}}\) (15%), \(\frac{\alpha_{ab} + \alpha_{ac}}{\alpha_{ac}}\) (20%) | 0.20 ± 0.1 |
| \(\alpha_{bc}\) | [ROH] | \(\frac{S_{\text{ROH}}}{S_{\text{ROH}}}\) (15%) | 0.26 ± 0.5 / -0.26 |
| \(\alpha_{bc} + \alpha_{ac}\) | [ROOH] | \(\frac{S_{\text{ROOH}}}{S_{\text{ROH}} + S_{\text{ROOR}}}\) (15%) | 0.54 ± 0.11 |
| \(\alpha_{bc} + \alpha_{ad}\) | [ROOH] + [ROOR] | \(1 - \frac{\alpha_{ab} - \alpha_{ac} - \alpha_{ad}}{\alpha_{ac}}\) | 0.27 ± 0.10 |
| \(\alpha_{bc}\) | \(\alpha_{ac}\) | \(\frac{\alpha_{ab}}{\alpha_{bc}}\) (29%), \(\frac{\alpha_{ac}}{\alpha_{bc}}\) (25%), \(\frac{\alpha_{ad}}{\alpha_{bc}}\) (18%) | 0.40 ± 0.10 |
| \(\alpha_{bc}\) | \(\alpha_{ac}\) | \(\frac{\alpha_{ac}}{\alpha_{bc}}\) (15%) | 0.10 ± 0.04 / -0.10 |
| \(\alpha_{bc}\) | \(\alpha_{ac}\) | \(\frac{\alpha_{ad}}{\alpha_{bc}}\) (18%), \(\frac{\alpha_{ae}}{\alpha_{bc}}\) (10%) | 0.40 ± 0.10 |
| \(\alpha_{bc}\) | \(\alpha_{ac}\) | \(\frac{\alpha_{ad}}{\alpha_{bc}}\) (15%) | 0.23 ± 0.05 |
| \(k_1^2\) | \(k_{13}\) | \(\frac{k_1^2}{k_{13}k_{4}}\) (30%), \(k_3\) (30%), \(k_{53}\) (15%) | 2.4 ± 1.0 |

| Table 4 | Comparison between kinetic parameters in this and prior studies. We omit from this table the study of Anastasi et al.14 as explained in detail in Murrells et al.15 Note that \(\alpha_{\text{radical}}\) is the fraction of the self-reaction that proceeds by radical propagating pathways. Uncertainties on values given in previous studies are the reported uncertainties |
|---|---|---|---|---|---|
| Study | \(\frac{k_{\text{obs}}}{\sigma_{250\text{nm}}}\) (10^6 cm⁻³ s⁻¹) | \(\alpha_{\text{radical}}\) | \(k_1\) (10⁻¹² cm³ molecule⁻¹ s⁻¹) | \(T\) (K) | \(k_{4,\text{recalc}}\) (10⁻¹² cm³ molecule⁻¹ s⁻¹) |
| This study | 0.37 ± 0.10 | 0.37 ± 0.10 | 2.4 ± 1.0 | 294 | 2.4 ± 1.0 |
| Jenkins et al.16 | 6.5 ± 0.4 | 0.18 ± 0.2 | 1.4 ± 0.2 | 298 | 2.3 ± 0.6 |
| Murrells et al.15 | 6.6 ± 1.1 | 0.36 ± 0.07 | 2.2 ± 0.5 | 296 | 2.3 ± 1.3 |
| Jenkins et al.15 | 7.1 ± 0.6 | 0.50e | 2.1 ± 0.5 | 298 | 2.5 ± 1.4 |
| Boyd et al.16 | 0.47 ± 0.04f | 2.4 ± 0.2f | 303 | 3.0 ± 0.2f |

\(\frac{k_{\text{obs}}}{\sigma_{250\text{nm}}}\) is the reported value in each study, where applicable, for the observed rate of decay of absorption at 250 nm divided by the cross section at 250 nm. \(k_{4,\text{recalc}}\) is the value of \(k_4\) recalculated given \(\alpha_{\text{radical}} = 0.37\) and at 294 K, and \(\sigma_{250\text{nm}} = 4.75 \times 10^{-18}\) cm² molecule⁻¹, as given in Lightfoot et al.16 The temperature dependence is taken from Boyd et al.16 The temperature dependence reported in Boyd et al.16 is that of Boyd et al.16. Calculated at 294 K using the temperature dependence reported in Boyd et al.16.
from Reaction (4a) and that no accretion product is formed. Barnes et al. did observe excess GA at low O₃ conditions similar to our findings, suggesting an additional source of GA beyond alkox chemistry. After accounting for this channel and the formation of ROOR, our optimized box model is fully consistent with the yields of ethylene glycol, GA, and formaldehyde reported by Barnes et al.

The rate coefficient for the title reaction (k₄) has been measured in several previous studies (Table 4). These have all been flash photolysis experiments where the decay of HOCH₂-C₂H₂O₂ has been monitored by UV spectroscopy. In addition to requiring knowledge of the UV cross sections of this radical, knowledge of the yield and formation timescale of HO₂ is also needed as the reaction of HO₂ with RO₂ contributes significantly to the observed decay rate of RO₂. While the ratio of the decay rate of the RO₂ to the assumed RO₂ cross sections have been similar in these experiments, the reported rate coefficients have varied due to differences in the inferred cross sections and HO₂ chemistry. Most of these studies determine the absolute rate from the observed decay rate of RO₂ by assuming a steady state of HO₂, whereby the following equation holds:

$$k_{4\text{obs}} = k_4(1 + \alpha_{\text{radical}}) = k_4(1 + \alpha_{4a} + \alpha_{4b})$$

(19)

where $\alpha_{\text{radical}}$ is the fraction of the self-reaction that proceeds via radical propagating channels. Therefore, the results of these studies are also sensitive to $\alpha_{\text{radical}}$. Similar to Boyd and Lesclaux,³⁶ using our box model we find that the inferred rate coefficient for Reaction (4) from these flash photolysis experiments is somewhat sensitive to assumed kinetics of the HO₂ chemistry and the details of how the absorption data are fitted (fitting window and signal-to-noise). Nevertheless, to place these different studies on a similar footing, we use the reported decay rate of the UV absorption at 250 nm and a common value for the UV cross section of the peroxy radical (assumed to be 4.75 $\times$ 10⁻¹⁸ cm² molecule⁻¹)³⁵ and use eqn (19) with the recycling fraction from this work. Finally, we adjust for the difference in the experimental temperature using the temperature dependence for Reaction (4) from Boyd and Lesclaux.³⁶ These are reported in the last column of Table 4.

The experiments reported here provide an entirely different constraint on the kinetics. Here, we quantify the relative reaction rate of the RO₂ with itself vs. with HO₂ under conditions where the ratio of the production rates of HO₂ to RO₂ is known, and obtain a value of $k_4$ (294 K) = 2.4 ± 1.0 $\times$ 10⁻¹² cm³ molecule⁻¹ s⁻¹. Despite the very different approaches and entirely different error sources, our inferred rate coefficient for Reaction (4) is remarkably similar to the kinetics measurements by flash photolysis.

4 Conclusions

Bimolecular peroxy radical reactions play an important role in the chemistry of the troposphere, and accurately measuring the rates of these reactions relative to other important RO₂ loss processes is central to determining their ultimate effect on air quality. In this study, we have shown that the accretion product formed in the reaction of the ethene-derived peroxy radical is likely a peroxide and is produced with a branching fraction of approximately 23%. We have further measured the ratio of radical propagating to radical terminating chemistry as well as the branching to glycolaldehyde, which is produced in both chain propagating and chain terminating channels. Finally, we have constrained the rate coefficient of the title reaction relative to the reaction rate coefficient of the peroxy radical with HO₂, and obtain a value consistent with those of previous flash photolysis studies. The branching fractions and kinetics along with their uncertainties (derived from comparison of our observations with a box model) are summarized in Table 3. Future studies will extend the methods discussed here to study the RO₂ + RO₂ chemistry in more diverse systems.

Conflicts of interest

There are no conflicts to declare.

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Notes and references