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Yields of hydrogen peroxide from the reaction of hydroxyl radical with organic compounds in solution and ice

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Abstract

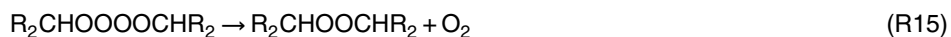
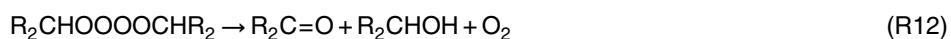
Hydrogen peroxide (HOOH) is a significant oxidant in atmospheric condensed phases (e.g., cloud and fog drops, aqueous particles, and snow) that photolyzes to form hydroxyl radical ($\cdot\text{OH}$). $\cdot\text{OH}$ can react with organics in aqueous phases to form organic peroxy radicals and ultimately reform HOOH, but the efficiency of this process in atmospheric aqueous phases, as well as snow and ice, is not well understood. We investigate HOOH formation from $\cdot\text{OH}$ radical attack of 10 environmentally relevant organic compounds: formaldehyde, formate, glycine, phenylalanine, benzoic acid, octanol, octanal, octanoic acid, octanedioic acid, and 2-butoxyethanol. Liquid and ice samples with and without nitrate (as an $\cdot\text{OH}$ source) were illuminated using simulated solar light, and HOOH formation rates were measured as a function of pH and temperature. For most compounds, the formation rate of HOOH without nitrate were the same as the background formation rate in blank water (i.e., illumination of the organic species does not produce HOOH directly), while formation rates with nitrate were greater than the water control (i.e., reactions of OH with the organic species forms HOOH). Yields of HOOH, defined as the rate of HOOH production divided by the rate of $\cdot\text{OH}$ production, ranged from essentially zero (glycine) to 0.24 (octanal), with an average of 0.12 ± 0.05 (95% CI). HOOH production rates and yields were higher at lower pH values. There was no temperature dependence of the HOOH yield for formaldehyde or octanedioic acid between -5 to 20°C and ice samples had approximately the same HOOH yield as the aqueous solutions. In contrast, HOOH yields in formate solutions were higher at 5 and 10°C compared to -5 and 20°C . Yields of HOOH in ice for solutions containing nitrate and either phenylalanine, benzoate, octanal, or octanoic acid were indistinguishable from zero. Our HOOH yields were approximately half that found in previous studies conducted using γ -radiolysis, but this difference might be due to the much lower (and more environmentally relevant) $\cdot\text{OH}$ formation rates in our experiments.

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The two peroxy radicals can then combine to form an intermediate tetroxide,



which can undergo four possible decompositions:



The kinetics and product yields from the aqueous reactions of *OH with a range of organic compounds have been previously studied using gamma (γ) radiation and pulse radiolysis (Christensen and Gustafsson, 1972; Nese et al., 1995; Pan et al., 1993a, b; Piesiak et al., 1984; Schuchmann and von Sonntag, 1977, 1979, 1982, 1983, 1984, 1988; Schuchmann et al., 1985, 1990, 1995; Ulanski et al., 1996; Zegota et al., 1984; Stemmler and von Gunten, 2000). HOOH yields in these experiments (defined as rate of HOOH production divided by the rate of *OH production) ranged from 0.02 to 0.57, with an average yield of 0.38. However, radiolysis of aqueous solutions also results in primary formation of HOOH and HO_2^*/O_2^- , so HOOH yields from reaction of *OH with organic will be lower than these values. Unimolecular elimination of HO_2^* radicals from α -hydroxyperoxy radicals (i.e., Reaction R6) represents a significant pathway for HOOH production in many of these experiments. However, the results also suggest that bimolecular reactions (e.g., Reaction R11 followed by Reactions R12–R16) can compete with unimolecular elimination (Schuchmann and von Sonntag, 1984) and that superoxide can cross-terminate with other peroxy radicals (Pan et al., 1993b). Work by Stemmler and von Gunten (2000) using the reaction of *OH with 2-butoxyethanol found a yield of HO_2^* of 0.25 and a yield of HOOH through pathways other than HO_2^* of 0.17, further showing that substantial HOOH can be produced via mechanisms other

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than the HO_2^*/O_2^- disproportionation reaction (R8 or R9). The yield of HOOH from the *OH -mediated oxidation of aqueous organic compounds probably varies considerably, depending on the production rate of *OH , concentrations of *OH and organic compounds, and other environmental conditions (Stemmler and von Gunten, 2000). But this yield is an important parameter since most aqueous *OH reacts with organic compounds and since HOOH is an important component of the oxidative capacity of cloud water droplets.

In addition to its role in aqueous reactions in the atmosphere, HOOH is also an important constituent in snow and ice. In long-term ice, HOOH has a half-life of approximately 5000 years in Greenland and 15 000 years in the Antarctic, and its presence in ice cores gives an indication of historical atmospheric oxidative capacity (Legrand and Mayewski, 1997; Hutterli et al., 2003). In the photic zone of the snowpack, HOOH photolyzes to *OH , which can oxidize compounds in the snow and form a variety of volatile species (e.g. HCHO and Br_2), which in turn can be emitted from the snow surface to the atmospheric boundary layer (Chu and Anastasio, 2005).

Laboratory experiments indicate that the photolytic lifetime of HOOH in polar snows during the summer should be on the order of weeks to a few months (Chu and Anastasio, 2005; Jacobi et al., 2006). Yet field measurements show that HOOH is present throughout the snowpack (Sigg and Neftel, 1991; Legrand and Mayewski, 1997), indicating its net lifetime in polar snow and ice must be long enough to survive burial by new snow until HOOH is beneath the photic zone. For example, at Summit, Greenland, where the photic zone for HOOH is approximately 30 cm (i.e., 2 times the e-folding depth (Galbavy et al., 2007)) and the snow accumulation rate is approximately 5 cm mo^{-1} , it would take approximately 5 mo to bury HOOH in surface snow to below the photic zone. This is much longer than the calculated 24-h-averaged lifetime of HOOH on the summer solstice of 140 h (Chu and Anastasio, 2005).

There are at least two possible explanations for the discrepancy between laboratory and natural HOOH lifetimes in snow and ice: (1) HOOH in natural snow has a longer photolytic lifetime than determined in laboratory ices, and (2) chemical reactions on

2.3 Illumination setup

Separate, but very similar, solar simulator illumination systems were used for aqueous and ice samples. Aqueous samples were stirred continuously, and maintained at the desired temperature with a recirculating water bath. The light source was a 1000 W high-pressure xenon-arc source, filtered to approximate sunlight using the method of Faust (1993). The illumination system held up to three cuvettes in series, with a PTFE block behind the last cuvette to reflect light back into the cuvettes. During an experiment, aliquots of illuminated solution were periodically removed to measure the HOOH concentration. Dark control samples were placed in quartz cuvettes, completely wrapped in foil, and kept in the illumination chamber away from the light path.

For ice samples, the simulated sunlight illumination system generally followed the method of Ram and Anastasio (2009). However, instead of diffusing the light with a PTFE sheet, a 3-mm thick quartz (GE 021) plate, roughly ground on both sides, was used. Beakers containing ice samples sat directly on a Peltier-cooled copper plate. A thermocouple probe was inserted into one control beaker filled with 0.5 ml of UV Milli-Q water for temperature monitoring and to maintain sample temperatures at -5°C . The plate measured $100\text{ cm} \times 100\text{ cm}$, allowing 49 beaker positions in a 7×7 grid; samples were placed clustered around the area of highest illumination at the center. Dark samples were placed towards the edges of the illumination area, and covered with foil to prevent light exposure. One polished quartz plate, covering the entire illumination area, was placed over all beakers to reduce air exchange. Dry air was blown across the top of this plate to prevent condensation. Cuvettes containing ice samples were placed on the same cooled plate used for beaker illuminations, with 2 rows of 7 cuvettes each. Dark samples were placed at the edges of the plate and covered with foil. The quartz cover plate and dry air were used as described above for beaker illuminations.

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2.4 Actinometry

2-nitrobenzaldehyde (2NB) was used as a chemical actinometer to measure the photon flux in each illumination system on each experimental day, following the method of Ram and Anastasio (2009). As described recently (Galbavy et al., 2010), 2NB is a robust actinometer whose rate constant for photodecay is independent of phase (liquid or ice), temperature, and illumination wavelength. For aqueous samples, the rate constant for 2NB photodegradation ($j(2\text{NB})$) was measured daily for each of the cuvette positions. For ice samples, daily measurement of every illumination position was impractical, so a correction factor method was used (Ram and Anastasio, 2009). $j(2\text{NB})$ values at every beaker or cuvette position were measured several times over the course of this study and a correction factor ($F_{2\text{NB},x}$) was determined for each beaker position (x) relative to the position of maximum intensity (the reference position, "ref"):

$$F_{2\text{NB},x} = \frac{j(2\text{NB})_x}{j(2\text{NB})_{\text{ref}}} \quad (1)$$

Values of $F_{2\text{NB},x}$ ranged from 0.71 to 1, i.e., corrections were relatively minor. The $j(2\text{NB})$ value at the reference position was measured on each experiment day. During ice illumination, one sample was removed at each illumination time point and analyzed for HOOH. The amount of HOOH produced in each ice sample at a given position was corrected for differences in photon flux using

$$[\text{HOOH}]_{\text{corrected}} = [\text{HOOH}]_0 + \frac{[\text{HOOH}]_x - [\text{HOOH}]_0}{F_{2\text{NB},x}}, \quad (2)$$

where $[\text{HOOH}]_0$ is the HOOH concentration at time zero and $[\text{HOOH}]_x$ is the measured concentration in the sample at position x (at some time t).

Typical $j(2\text{NB})$ values for our simulated sunlight illuminations were 0.019 s^{-1} for aqueous solutions and 0.017 s^{-1} for ice samples. These are similar to ambient values; for example, $j(2\text{NB})$ was calculated as 0.018 s^{-1} at the snow surface at Summit, Greenland on midday on 5 August 2005 (Galbavy et al., 2010) and measured as

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Using the value of $(j(\text{NO}_3 \rightarrow \text{OH})/j(2\text{NB}))_{\text{ref}}$, we calculated the $j(2\text{NB})$ normalized rate of production of OH in a given illuminated solution with nitrate using

$$R(\text{OH})/j(2\text{NB}) = [\text{NO}_3^-] \times \left(\frac{j(\text{NO}_3^- \rightarrow \text{OH})}{j(2\text{NB})} \right)_{\text{ref}} \quad (5)$$

where $j(2\text{NB})$ is the value measured on that day, and $[\text{NO}_3^-]$ is the nitrate concentration (0.50 mM).

3 Results and discussion

3.1 Model organic compounds

A tremendous variety of anthropogenic and biogenic organic species have been detected in snow and ice, although research efforts to date have identified only a small fraction of those (Grannas et al., 2006, 2004; Legrand and Deangelis, 1995; Satsumabayashi et al., 2001; Laniewski et al., 1998; Desideri et al., 1994; Fries et al., 2008; Hutterli et al., 2004; Grollert and Puxbaum, 2000). For this study, we selected ten model organic compounds (Table 1) to span a wide range of organic functional groups that have either been found, or could reasonably be expected to exist, in snow and atmospheric water drops. Of the compounds we chose, formaldehyde and formate are two of the most abundant organic compounds in natural snow and ice, as well as in atmospheric aqueous phases (Barrie et al., 1992; Hutterli et al., 2004; Dibb and Arsenault, 2002; Perrier et al., 2002; Finlayson-Pitts and Pitts, 2000). Amino acids are represented by glycine and phenylalanine, which have been found in atmospheric aerosols and fog waters (Zhang and Anastasio, 2003, 2001), and undoubtedly exist in snow. In addition to phenylalanine, we studied one other aromatic compound – benzoic acid – which has been found in snow (Satsumabayashi et al., 2001). Four of our model compounds contain an 8-carbon chain, but with different terminal functional groups:

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octanol, octanal, octanoic acid, and octanedioic acid (also known as suberic acid). Finally, we also included 2-butoxyethanol, a widely used, highly soluble, glycol ether that has been studied previously for HOOH yield (Stemmler and von Gunten, 2000).

3.2 Typical experiment – illumination of formaldehyde

Figure 1 shows kinetic results for a typical aqueous experiment, conducted here with formaldehyde. Formaldehyde in aqueous solution undergoes hydration and is primarily present as the gem-diol form, $\text{CH}_2(\text{OH})_2$; the ratio of $\text{CH}_2(\text{OH})_2$ to HCHO in water at room temperature is 2000:1 (Bell et al., 1956). The squares and dotted line show the production of HOOH by formaldehyde when illuminated (in the absence of nitrate), while the circles and solid line show production of HOOH in the presence of nitrate during illumination. Adding nitrate (as a photochemical source of OH) to the formaldehyde solution causes the rate of HOOH production to approximately double. To calculate the net HOOH production rates and HOOH yields for each model compound (discussed below), we subtract the production of HOOH in the absence of nitrate from the production in the presence of nitrate to account for any HOOH produced by direct reaction of the model compound (Sect. 2.6).

3.3 HOOH production rates in solution at pH 5

Figure 2 shows a comparison of HOOH production rates, normalized by $j(2\text{NB})$, with and without nitrate for nine model organic compounds and UV Milli-Q at pH 5 and 5°C . Without nitrate (open circles), all but one (formate) of the model organic compounds have HOOH production rates that are indistinguishable from that of UV Milli-Q water at a 95% confidence interval, so HOOH production rates for these solutions are probably attributable to background material in the water, and not to photoreaction of the model compound. In contrast, HOOH does appear to be produced from formate reaction without nitrate: the 95% lower confidence limit (LCL) for HOOH production from formate without nitrate ($0.80 \text{ nM s}^{-1}/s^{-1}$), is slightly higher than the 95% upper confidence limit (UCL) for HOOH production by UV Milli-Q water ($0.64 \text{ nM s}^{-1}/s^{-1}$).

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The solid circles in Fig. 2 show the $j(2\text{NB})$ -normalized HOOH production rates for solutions with nitrate. Production rates of HOOH in UV Milli-Q water with and without nitrate are not statistically different (95% confidence interval). Glycine also shows similar production rates with and without nitrate, indicating that $\bullet\text{OH}$ reaction with glycine does not form appreciable amounts of HOOH. While the rate constant for reaction of OH with glycine is modest ($k = 8.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), the reaction products include alkyl, carboxy, and aminyl radicals, which should be capable of reacting with molecular oxygen to form organic peroxy radicals (Stefanic et al., 2001). So the lack of HOOH production by glycine remains unexplained. The other model compounds, however, do have statistically significant (95% confidence) HOOH production rates in the presence of nitrate, indicating HOOH is produced following $\bullet\text{OH}$ attack on the compound. $j(2\text{NB})$ -normalized production rates without nitrate ranged from $0.19 \text{ nM s}^{-1}/\text{s}^{-1}$ (octanol) to $0.91 \text{ nM s}^{-1}/\text{s}^{-1}$ (formate), with an average of $0.49 \pm 0.20 \text{ nM s}^{-1}/\text{s}^{-1}$ (95% confidence). With nitrate, HOOH production rates were $0.49 \text{ nM s}^{-1}/\text{s}^{-1}$ (glycine) to $2.8 \text{ nM s}^{-1}/\text{s}^{-1}$ (octanal), with an average of $1.6 \pm 0.55 \text{ nM s}^{-1}/\text{s}^{-1}$ (95% confidence). The average ratio of the HOOH production rate with nitrate to that without nitrate was 4.6, and ranged between 1.2 (glycine) to 10.8 (2-butoxyethanol).

Figure 3 shows the HOOH yields from OH reaction with the model compounds at pH 5 (5°C); as described in Sect. 2.6, our yield describes the number of molecules of HOOH formed for every reaction of $\bullet\text{OH}$ with organic compound. As could be expected, compounds with higher rates of production of HOOH (Fig. 2) generally have higher yields. HOOH yields for the model organic compounds at pH 5 (5°C) range from essentially zero (glycine) to 0.24 (octanal), with an average of 0.12 ± 0.05 (95% confidence interval) and a median of 0.11. Error bars in Fig. 3 show the net indeterminate error for each value expressed as ± 1 SE; therefore, the error bars represent the likely range of true values for each measurement, and are larger than just precision measurements based on repeated experimental measurements of each value. The average relative standard error for the HOOH yield for our compounds (excluding glycine) was 34%.

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Examining the HOOH yields in Fig. 3 indicates that the number of carbons on the organic compound does not predict yield, as single-carbon compounds (formaldehyde and formate) have yields in the same range as the 8-carbon compounds. Indeed, HOOH yields for most of the compounds fall within a relatively small range, regardless of compound size or class. For three of the 8-carbon compounds (octanal, octanoic acid, and octanedioic acid) increasing the degree of oxidation decreases the HOOH yield, but this does not hold true for octanol, which is the least oxidized and has a low yield. Both phenylalanine and benzoic acid contain aromatic rings, but this does not appear to influence HOOH production, as their HOOH yields are not noticeably different than those of the other model compounds. Glycine, the simplest amino acid, is the only compound without any appreciable production of HOOH following reaction with $\bullet\text{OH}$.

3.4 pH dependence of HOOH production rates and yields in solution

Figures 4a and 4b show the pH dependence of the $j(2\text{NB})$ -normalized rates of HOOH production with and without nitrate, respectively. Results for UV Milli-Q are shown with blue diamonds; error bars (given only for UV Milli-Q) are the 95% confidence interval around each measurement. With nitrate (Fig. 4a), most model compounds show HOOH production rates significantly greater than UV Milli-Q water: at pH 2, all model compounds show production statistically greater than UV Milli-Q, while at pH 5 and 7, respectively, all but one (glycine) and two (formaldehyde and benzoic acid) compounds do so. As shown in Fig. 4a, all compounds show a pH dependence with nitrate, with increased HOOH production at lower pH values. Octanal has the highest production rate at pH 2, approximately 2.5 times as high as the lowest producer, glycine. Octanal also has the highest production rate at pH 7, approximately three times higher than most other model compounds. For all model organics tested, the average $j(2\text{NB})$ -normalized production rate of HOOH ($\pm 95\%$ confidence limit) was 3.1 ± 0.33 , 1.7 ± 0.26 , and $1.3 \pm 0.36 \text{ nM s}^{-1}/\text{s}^{-1}$ at pH 2, 5, and 7, respectively.

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In the absence of nitrate, illumination of most model compounds gives HOOH production rates that are indistinguishable from UV Milli-Q water (Fig. 4b). At pH 2, formate and octanal have production greater than UV Milli-Q water at the 95% confidence level; at pH 5, only formate does. At higher pH values, model compounds generally show HOOH production rates similar to UV Milli-Q water, indicating that direct photoreactions of the compounds to produce HOOH become insignificant at higher pH values.

Figure 5 shows the yields for the model compounds at pH values ranging from 2.0 to 8.5. Similar to the HOOH production in the presence of nitrate (Fig. 4a), the HOOH yields also depend on pH, with higher yields at lower pH. Octanal shows the largest yield of any of the model compounds, with a maximum of 0.35 at pH 2.0. Glycine, with a yield nearly zero at pH 5, has a yield (0.17) much closer to other compounds at pH 2. Two of the model compounds (formaldehyde and octanal) will have the same molecular form at all pH values tested. Glycine and phenylalanine contain amino nitrogens, but these will be protonated (i.e., as RNH_3^+) at all pH values we tested. Based on their pKa values (Table 1), six of the model organic compounds (glycine, phenylalanine, benzoic acid, octanoic acid, octanedioic acid, and formate) all should be present with neutral, protonated carboxylic acid groups (i.e., RCOOH) at pH 2 and with the group deprotonated (i.e., RCOO^-) above pH 6. The pKa for the carboxylic acid of glycine is 2.4 (Voet et al., 2006), thus at pH 2, 40% of the carboxylic acid group is deprotonated, while it is essentially completely deprotonated at pH 5. While this protonation state of the carboxylic acid group might be related to the pH dependence of the HOOH yield of glycine, phenylalanine has a similar pKa value of 2.2 (Voet et al., 2006), but it shows significant HOOH production at pH 5. Despite the differences in acid-base speciation and sensitivity, all of the model organic compounds have pH-dependent yields of HOOH.

The HOOH yield for octanal remains noticeably higher than the yields for the other model organic compounds at all pH values tested. With the exceptions of octanal and of glycine at pH 5, all other compounds have similar yields at a given pH, and show a similar decrease in HOOH yield as pH increases. The high yield of octanal resists

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ready explanation, but might be related to the aldehyde group. For example, while the other 8-carbon compounds show lower yields, there is no other compound that is predominantly an aldehyde in solution since formaldehyde in solution is present mainly in the gem-diol form, $\text{CH}_2(\text{OH})_2$. In contrast, the aldehyde group in octanal does not hydrate to a significant degree (Zhao et al., 2005).

It is unclear to us why the HOOH yields depend on pH. Reaction (R8) above, the disproportionation of the hydroperoxyl/superoxide radicals to form HOOH, is pH dependent, with a maximum reaction rate at pH 4.8 (Bielski et al., 1985). However, if this reaction were the rate-limiting step, HOOH production should be higher at pH 5 and lower at pH 2, which is the opposite of the pattern seen in our data (Fig. 4a).

Stemmler and von Gunten (2000) found that bimolecular decay reactions of peroxy radicals (corresponding to our Reactions R12–R14) were not pH dependent, and that the HOOH yield was not different between pH 3 and pH 6. These results suggest our pH-dependent yields are not caused by pH dependence in the reactions of the tetroxide intermediates. Another possibility is that the fates of HO_2^\bullet and $^\bullet\text{O}_2^-$ might be different. For example, Lelieveld and Crutzen (1991) found a tripling of aqueous HOOH concentrations in a modeled cloud with a pH change from 6 to 4, because while ozone is not a sink for HO_2^\bullet (at pH 4), it is a sink for superoxide (at pH 6):



This reaction would deplete superoxide and thereby reduce HOOH production via hydroperoxyl/superoxide disproportionation (Reactions R8 and R9) at higher pH values. Ozone formed from the minor channel of nitrate photolysis (Warneck and Wurzinger, 1988) in our solutions might be responsible for such superoxide depletion. Even though the RO_2^\bullet recombination reactions do not require $^\bullet\text{O}_2^-$ to make HOOH (Reaction R13), a loss of $^\bullet\text{O}_2^-$ in our solutions would decrease the production of HOOH via $\text{HO}_2^\bullet/^\bullet\text{O}_2^-$ disproportionation (Reactions R8 and R9).

Another possible reason for the observed pH dependence in our HOOH production rates and yields is metal contamination, e.g., from the sulfuric acid that we used to

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adjust pH. While we used high quality (Optima grade) H_2SO_4 , it certainly contains some metals and iron and copper are redox-active metals that can enhance HOOH production (Deguillaume et al., 2004). However, one argument against this hypothesis is that the pH 2 solutions contained approximately 1000 times more H_2SO_4 than the pH 5 solutions, while the HOOH yields increased only by approximately a factor of 2.

3.5 Temperature dependence of HOOH yields

The work described above was all for aqueous solutions at 5°C . As shown in Fig. 6a through c, we also examined HOOH yields in solution at higher temperatures and in ice at -5°C . Neither formaldehyde (at pH 2 or 5) nor octanedioic acid showed a temperature dependence. In contrast, HOOH yields from the reaction of OH with formate (Fig. 6b) did vary with temperature, with very similar results for both the pH 2 and 5 samples. Oddly, the HOOH yields were greatest at the intermediate temperatures (0.10 to 0.13 at 5 and 10°C) and lowest at both ends of the temperature range (approximately 0.03 at both -5 and 20°C). For all three organic compounds in Fig. 6, the HOOH yields for ice samples (-5°C) were not markedly different than values in solution: the average HOOH yield on ice was 0.12 at pH 2 and 0.050 at pH 5.

In contrast, we saw a different behavior for the four other model organic compounds we tested in ice at -5°C : phenylalanine (pH 4.0), sodium benzoate (pH 5.0), octanal (pH 5.6), and octanoic acid (pH 2.9 and pH 5.0). For these compounds in the presence of nitrate, there was no apparent production of HOOH on ice, although each formed HOOH in solution. Thus, in contrast to the results obtained with formaldehyde, formate, and octanedioic acid, it appears that reaction of $\cdot\text{OH}$ with phenylalanine, benzoate, octanal, or octanoic acid does not produce HOOH in/on ice.

3.6 Comparison with previous work

As noted above, the reaction of $\cdot\text{OH}$ with organics has been previously studied in aqueous systems, although with several important methodological differences compared to

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our work. First, $\cdot\text{OH}$ in past studies was generated by radiolysis of water, while we used simulated sunlight photolysis of nitrate. One complicating factor in the pulse or γ -radiolysis of water used in previous studies is that they directly produce HO_2^\bullet and $\cdot\text{O}_2^-$. As shown in Reactions (R8) and (R9), these compounds can combine to produce HOOH, possibly confounding experimental results, although a few of the past studies discussed the relative magnitude of the possible error. Second, the rate of $\cdot\text{OH}$ production in radiolysis is typically much higher than our production rate, which might change product yields by affecting the steady-state concentrations of intermediates such as peroxy radicals. For example, the standard $\cdot\text{OH}$ production rate in the experiments of Stemmler and von Gunten (2000) was 245 nM s^{-1} ; in contrast, ours was 0.2 nM s^{-1} , which is comparable to the rates of OH production seen in ambient atmospheric aqueous drops (Anastasio and McGregor, 2001; Faust and Allen, 1993; Ervens et al., 2003).

Because previous authors typically did not correct measured HOOH yields for the direct radiolytic production of HO_2^\bullet , it is difficult to draw conclusions about the actual source of HOOH production in these experiments. Von Sonntag and Schuchmann (1997) summarize many of these studies, often giving HOOH yields adjusted for primary radiolytic HOOH production, both directly and via $\text{HO}_2^\bullet/\cdot\text{O}_2^-$. HOOH yields in this subset of experiments ranged from 0.02 to 0.42, with an average yield of approximately 0.22. In our work at pH 5 (5°C), we found a range of 0 to 0.24, with an average of 0.12 ± 0.05 (95% confidence interval). Given the differences in experimental methods, and the likely impact of $\cdot\text{OH}$ flux on HOOH yields described below, these results agree reasonably well.

One compound we studied, 2-butoxyethanol, was also studied previously using a γ -radiolysis method (Stemmler and von Gunten, 2000). Our HOOH yields from the reaction of $\cdot\text{OH}$ with 2-butoxyethanol (20°C) are 0.09 at pH 6 and 0.20 at pH 3. Stemmler and von Gunten found OH reaction with 2-butoxyethanol (pH 6, temperature unspecified) produced HOOH and HO_2^\bullet at yields of 0.17 and 0.25, respectively. Assuming all of the HO_2^\bullet disproportionated to form HOOH, the net yield of HOOH from the $\cdot\text{OH} + 2$ -butoxyethanol reaction would be 0.30. It is unclear why our value (0.09 at pH 6) is

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lower, but is likely because of differences in the flux of $\bullet\text{OH}$ in the two experiments: Stemmler and von Gunten ran an additional experiment with a lower $\bullet\text{OH}$ production of 37 nM s^{-1} (instead of their standard flux of 245 nM s^{-1}) and found a reduced overall yield of HOOH. Unfortunately, it is not possible to quantify the HOOH yield from OH reaction with 2-butoxyethanol in this second experiment because the authors did not determine the direct contribution of water radiolysis to HOOH for this condition. Nonetheless, it seems clear that lower $\bullet\text{OH}$ production rates lead to decreased yields of hydrogen peroxide; thus HOOH yields from our experiments are broadly consistent with results from previous studies.

4 Implications and conclusions

As atmospheric chemistry models such as CAPRAM (Ervens et al., 2003; Herrmann et al., 2005) continue to develop in sophistication and include additional reactions of $\bullet\text{OH}$ with organics, accurate assessment of reaction rates and product yields will be required to optimize model outputs. Comparing our range of HOOH yields to those from radiolytic studies suggests that past HOOH yields might be overestimated in previous work, and thus models that use these past results might be biased. In addition, our findings for some individual reactions indicate that HOOH yields can be less than expected from common assumptions. For example, atmospheric chemistry models often assume α -hydroxyperoxyl radicals will decompose with 100% efficiency to form an oxidized compound and a hydroperoxyl radical (see for example, the treatment of formaldehyde in Ervens et al., 2003). The resulting hydroperoxyl radical should readily form HOOH via R9, especially when the solution pH is near the pKa of $\text{HO}_2\bullet$. However, our experimental yield for HOOH from formaldehyde (0.09, pH 5, 5°C) is much lower than the complete conversion (yield = 0.5) anticipated from the reaction scheme in the model. This suggests that models might overestimate HOOH production from the $\bullet\text{OH}$ oxidation of formaldehyde, and perhaps other organics that form α -hydroxyperoxyl radicals.

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In addition, our work shows a significant pH dependence to HOOH production via $\bullet\text{OH}$ oxidation of organics that does not appear to be in current models of atmospheric aqueous-phase chemistry. We found maximum HOOH yields of 0.35 (pH 2) and 0.24 (pH 5). We believe these values represent reasonable upper-bound estimates for HOOH yields from $\bullet\text{OH}$ reactions with organic compounds in atmospheric aqueous phases, and could be used in combination with the average yields presented earlier to validate model predictions.

Our results indicate that HOOH yields from the reaction of $\bullet\text{OH}$ with organics in ice are generally substantially lower than in atmospheric aqueous phases; thus assuming that reactions of $\bullet\text{OH}$ with organics in ice and snow proceed similarly to aqueous reactions will likely overestimate HOOH production rates. As noted earlier, four of the seven compounds tested in ice produced no HOOH; depending on the mix of compounds in a particular snow pack, it may be that the rate of HOOH production from $\bullet\text{OH}$ radical attack on organics is zero. Looking only at the three compounds that conclusively produced HOOH in ice, the average yield was 0.12 (pH 2) and 0.050 (pH 5). Formaldehyde had the highest yield in ice of 0.25 (pH 2), and 0.13 (pH 5). These values could be used to estimate HOOH production rates from $\bullet\text{OH}$ reaction with organics in ice.

We can also use our ice data to address the second question we raised in our introduction: does recycling of HOOH through reaction of $\bullet\text{OH}$ with organic compounds significantly extend the net lifetime of HOOH in snow and ice? To address this, we consider the net HOOH lifetime in snow for two cases: (1) with photolysis of HOOH only, and (2) with both HOOH photolysis and HOOH recycling via $\bullet\text{OH}$ -mediated reactions of organics. Considering only HOOH photolysis, the rate constant for HOOH loss in surface snow at Summit, Greenland (summer solstice, midday), $j(\text{HOOH}\rightarrow\text{OH})$, is $7 \times 10^{-3}\text{ h}^{-1}$ (Chu and Anastasio, 2005), corresponding to a photolytic lifetime ($1/j$) for hydrogen peroxide of 143 h.

Taking into account HOOH formation via $\bullet\text{OH}$ reactions with organic compounds, the net lifetime (τ) of HOOH is:

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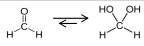





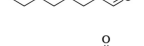
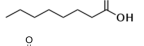
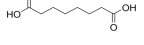
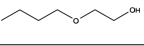
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Table 1. Physical and chemical properties of model organic compounds.

Chemical	Structure	Formula	Molecular weight (g mol ⁻¹)	Water solubility (mol L ⁻¹) [*]	pKa [*]
Formaldehyde		HCHO	30.0	13.3	na
Formate		HCOOH	45.0	22.2	3.8
Glycine		NH ₂ CH ₂ COOH	75.1	3.32	2.4, 9.8
Phenylalanine		HO ₂ CCH(NH ₂)CH ₂ C ₆ H ₅	165.2	0.121	2.2, 9.3
Benzoic Acid		C ₆ H ₅ COOH	122.1	0.0278	4.2
Octanol		CH ₃ (CH ₂) ₇ OH	130.2	0.00415	na
Octanal		CH ₃ (CH ₂) ₆ CHO	128.2	0.00437	na
Octanoic acid		CH ₃ (CH ₂) ₆ COOH	144.2	0.00548	4.9
Octanedioic acid		C ₆ H ₁₂ (COOH) ₂	174.2	0.0689	4.5
2-Butoxyethanol		CH ₃ (CH ₂) ₃ O(CH ₂) ₂ OH	118.2	8.46	na

* Howard and Meylan (1997)

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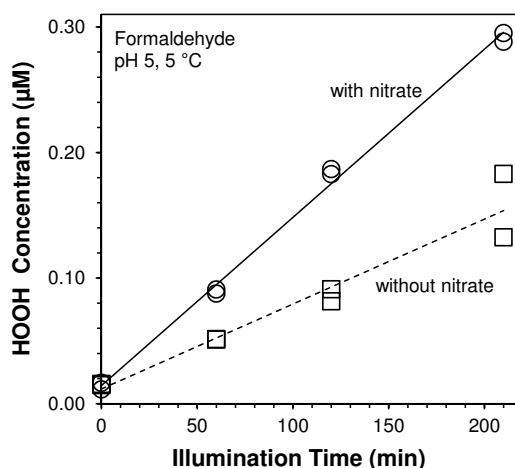


Fig. 1. Production of hydrogen peroxide in illuminated solutions (pH 5, 5 °C) containing 200 µM formaldehyde and either no nitrate (squares) or 500 µM nitrate (circles). Rates of HOOH formation, correlation coefficients (R^2), and $j(2\text{NB})$ values for these two solutions are 0.68 nM min⁻¹, 0.938, and 0.014 s⁻¹, and 1.3 nM min⁻¹, 0.996, and 0.014 s⁻¹, respectively.

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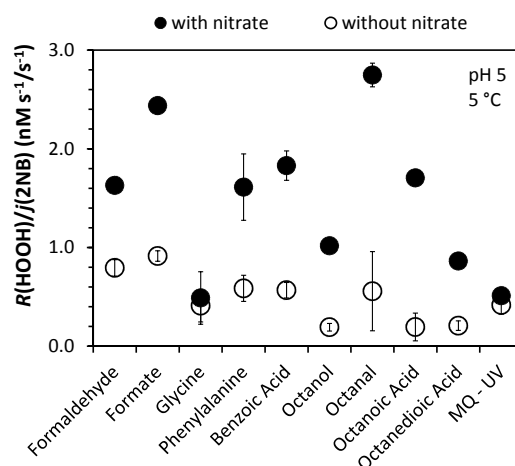


Fig. 2. Production of hydrogen peroxide normalized to measured $j(2\text{NB})$ in illuminated solutions (pH 5, 5 °C) containing 200 µM model organic compound and either no nitrate (open circles) or 500 µM nitrate (closed circles). UV Milli-Q water did not contain a model compound. Error bars (± 1 SE) are the absolute error (net indeterminate error), calculated based on the propagated errors from $R(\text{HOOH})$ and $j(2\text{NB})$. Some points are average values from several experiments with the same compound.

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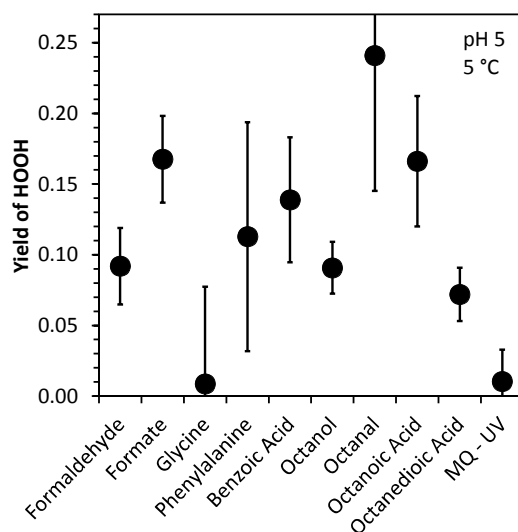


Fig. 3. Yield of hydrogen peroxide from the reaction of $\bullet\text{OH}$ with each model organic compound (pH 5, 5 °C). Error bars (± 1 SE) are the absolute error (net indeterminate error), calculated based on the propagated errors from $R(\text{HOOH})$, $j(2\text{NB})$, and $R(\text{OH})$.

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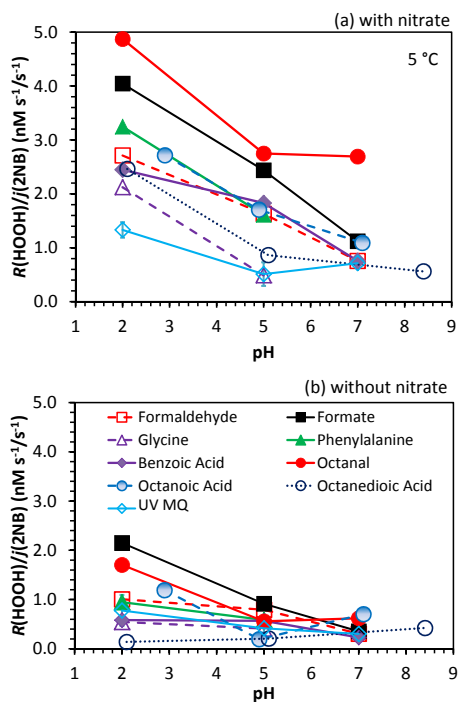


Fig. 4. pH dependence of hydrogen peroxide production (5 °C, normalized by $j(2\text{NB})$) for illuminated solutions containing: **(a)** model compound (200 μM) and nitrate (500 μM), and **(b)** model compound only. UV Milli-Q water did not contain a model compound. Error bars (blue) are the 95% confidence interval of UV Milli-Q water result.

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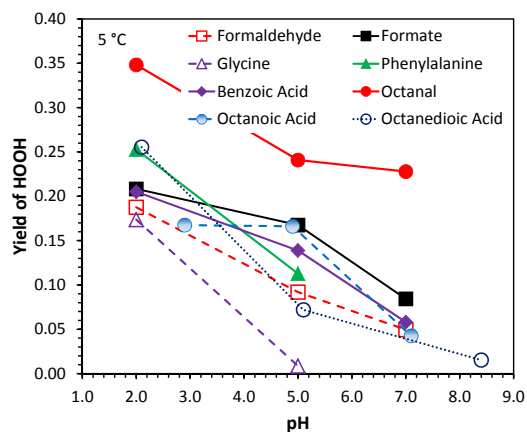


Fig. 5. pH dependence of the HOOH yield from reaction of $\bullet\text{OH}$ with each model compound at 5°C.

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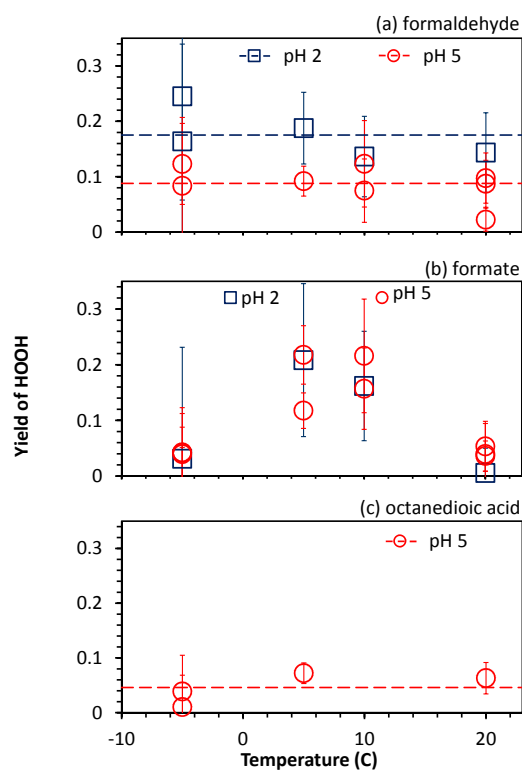


Fig. 6. Temperature dependence of the HOOH yield for three model compounds at pH 2 (blue squares) and pH 5 (red circles). The average HOOH yields for formaldehyde were 0.18 (pH 2) and 0.088 (pH 5), while the average yield for octanedioic acid is 0.046 (pH 5). Error bars are the net indeterminate error (propagated standard error).

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