

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

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

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Received: 31 January 2011 – Accepted: 1 February 2011 – Published: 23 February 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

11, 6457–6492, 2011

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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 $\cdot\text{OH}$ 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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1 Introduction

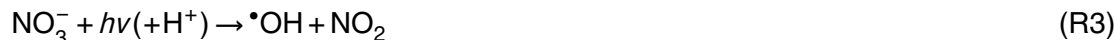
Hydrogen peroxide (HOOH) is a significant oxidant in atmospheric condensed phases such as cloud and fog drops, aqueous particles, and snow. For example, aqueous HOOH is one of the major oxidants that converts reduced sulfur (S(IV)) into sulfuric acid in the atmosphere (Finlayson-Pitts and Pitts, 2000). The two sources of HOOH to cloud and fog drops and aqueous aerosol particles are partitioning from the gas phase and in situ photochemical production (Anastasio et al., 1994; Moller, 2009; Chameides and Davis, 1982). In addition to acting as an oxidant itself, HOOH in solution is also a source of highly reactive hydroxyl radical, both through direct photolysis (Zellner et al., 1990; Chu and Anastasio, 2005):



as well as through the photo-Fenton reaction (Arakaki and Faust, 1998),



Additional sources of aqueous-phase $^{\bullet}\text{OH}$ include nitrite photolysis as well as nitrate photolysis (Chameides and Davis, 1982; Anastasio and McGregor, 2001; Ervens et al., 2003; Chu and Anastasio, 2003, 2007; Dubowski et al., 2001; Qiu et al., 2002):



Hydroxyl radicals react quickly in aqueous drops, with the main sink typically being organic compounds (Herrmann et al., 2005; Faust, 1994; Arakaki and Faust, 1998). This rapid reaction leads to the formation of aqueous alkyl radicals, which then (generally) add oxygen to form organic peroxy radicals (Ervens et al., 2003; von Sonntag and Schuchmann, 1997). For example, in the case of the $^{\bullet}\text{OH}$ -initiated reaction with hydrated acetaldehyde, this sequence is (Ervens et al., 2003):



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The fate of the resulting organic peroxy radicals in aqueous phases depends on the type of peroxy radical (von Sonntag and Schuchmann, 1997). Peroxy radicals with a hydroxyl group on the peroxy-bearing carbon (i.e., alpha-hydroxy peroxy radicals), can undergo fast decomposition to release a more oxidized organic compound and a hydroperoxyl radical (von Sonntag and Schuchmann, 1997). For example, this is the case in the $\cdot\text{OH}$ -initiated oxidations of aqueous formaldehyde and formic acid, two of the more abundant organic compounds found in tropospheric aqueous phase (Chameides and Davis, 1983; Ervens et al., 2003). In the case of the α -hydroxy peroxy radical derived from acetaldehyde in (R5) above, decomposition forms $\text{HO}_2\cdot$ and acetic acid (Ervens et al., 2003):



$\text{HO}_2\cdot$, the hydroperoxyl radical, can dissociate to form superoxide and H^+ ($\text{pK}_a = 4.85$ (Bielski et al., 1985)):



Dismutation of $\text{HO}_2\cdot$ and $\cdot\text{O}_2^-$ can then form hydrogen peroxide (Bielski et al., 1985):



or



Peroxy radicals that do not contain an α -hydroxy group follow a variety of bimolecular pathways that can result in the formation of HOOH, alkoxy radicals, carbonyl compounds and alcohols (von Sonntag and Schuchmann, 1997). This is illustrated below for a generic organic compound R_2CH_2 , starting with hydroxyl radical reaction to form peroxy radicals ($\text{R}_2\text{CHOO}\cdot$):



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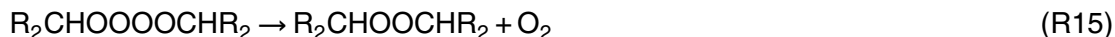
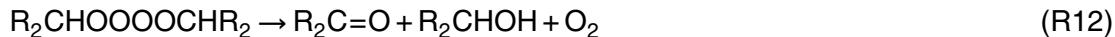
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The two peroxy radicals can then combine to form an intermediate tetroxide,



which can undergo four possible decompositions:



The kinetics and product yields from the aqueous reactions of $\cdot OH$ 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 $\cdot OH$ 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 $HO_2\cdot/O_2^-$, so HOOH yields from reaction of $\cdot OH$ with organic will be lower than these values. Unimolecular elimination of $HO_2\cdot$ 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 $\cdot OH$ with 2-butoxyethanol found a yield of $HO_2\cdot$ of 0.25 and a yield of HOOH through pathways other than $HO_2\cdot$ of 0.17, further showing that substantial HOOH can be produced via mechanisms other

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than the $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$ disproportionation reaction (R8 or R9). The yield of HOOH from the $\bullet\text{OH}$ -mediated oxidation of aqueous organic compounds probably varies considerably, depending on the production rate of $\bullet\text{OH}$, concentrations of $\bullet\text{OH}$ and organic compounds, and other environmental conditions (Stemmler and von Gunten, 2000).

5 But this yield is an important parameter since most aqueous $\bullet\text{OH}$ 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 $\bullet\text{OH}$, 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

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snow grains might effectively recycle HOOH. This first possibility has been examined in recent work (Beine and Anastasio, 2011). The efficacy of the second possibility – i.e., HOOH recycling – depends on the yields of HOOH from the reactions of snow grain $\bullet\text{OH}$ with organics. In this mechanism, HOOH in snow or ice is photolyzed to form hydroxyl radicals (Chu and Anastasio, 2005), which then react with organics to form peroxy radicals, which lead to HOOH. If the yields of HOOH are high enough, $\bullet\text{OH}$ reactions with organics could effectively recycle HOOH in snow or ice and significantly extend its lifetime. Recycling of HOOH via $\bullet\text{OH}$ reaction with organics has been proposed to occur in cloud drops (Lelieveld and Crutzen, 1990), but has not been studied on ice.

This work is motivated by two questions: (1) in atmospheric aqueous phases, how efficiently can the reaction of $\bullet\text{OH}$ with organic compounds form HOOH? and (2) in ice and snow, does recycling of HOOH through reaction of $\bullet\text{OH}$ with organic compounds significantly extend the net lifetime of HOOH? To answer these questions we have measured the yield of HOOH from the reaction of $\bullet\text{OH}$ with ten model organic compounds, in both aqueous solution and ice, at various pH values and temperatures.

2 Methods

2.1 Materials

Acetonitrile (HPLC grade), ethylenediamine tetraacetic acid (EDTA, molecular biology grade), formaldehyde (as paraformaldehyde, 95%), glycine (>99%), phenylalanine (>98%), benzoic acid (99%), octanol (99%), octanal (>99%), octanoic acid (>99%), octanedioic acid (>98%), and horseradish peroxidase (HRP) were from Sigma. Para-hydroxyphenylacetic acid (POHPAA) was from TCI. Sulfuric acid (Optima grade), sodium borate (ACS grade), sodium nitrate (ACS grade), sodium formate (ACS grade), potassium hydrogen phthalate (KHP) (ACS grade), and hydrogen peroxide (ACS grade) were from Fisher Chemical. Formaldehyde solution (<1%) was made from paraformaldehyde by stirring in 60°C water for 1 h (Sigma-Aldrich). All

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other chemicals were used as received.

High purity water (“UV Milli-Q water”) was water from a Millipore Milli-Q Plus system that was further treated to remove residual organic compounds by adding hydrogen peroxide (to make a 0.5 mM solution) and then illuminating for 24 h with 254 nm UV light in a Rayonet RPR-200 photoreactor with 4 RPR-2537 bulbs.

2.2 Solution and ice samples

To determine the yield of HOOH from the reaction of OH with an organic compound, we measured the rate of HOOH formation during illumination of two parallel solutions for each experiment: one containing 0.20 mM of model organic compound and one containing 0.20 mM of organic and 0.50 mM nitrate (as the source of $\cdot\text{OH}$). The pH in both solutions was identically adjusted by adding sulfuric acid ($\text{pH} \leq 5$) or sodium borate ($\text{pH} > 5$). Working solutions were made the day of the experiment, and stored in amber glass bottles until use.

Aqueous samples were illuminated in airtight FUV quartz cuvettes (2 cm path length, 8 cm volume, Spectrocell). Ice samples were frozen in either capped air-tight 1 cm FUV cuvettes (Spectrocell) or 1 ml PTFE beakers (Fisher Scientific). For beaker samples, 0.5 ml aliquots of test solution were placed in each beaker and covered with Parafilm. For cuvettes, 1 ml of sample was placed in each 3-ml cuvette and capped. Samples were then frozen for 1 h at -10°C in a custom, Peltier-cooled, freeze chamber (Paige Instruments). Cuvettes were frozen horizontally. Each method gave similar results in this investigation, with different possible advantages for other work: beakers allowed more time points to be collected (because more beakers than cuvettes could be fit in our illumination system) and had a photon flux approximately two times that of cuvettes, while cuvette samples were sealed with caps, preventing exchange of materials between the ice sample and room air.

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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 ($j(2NB)$) 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). $j(2NB)$ values at every beaker or cuvette position were measured several times over the course of this study and a correction factor ($F_{2NB,x}$) was determined for each beaker position (x) relative to the position of maximum intensity (the reference position, "ref"):

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

Values of $F_{2NB,x}$ ranged from 0.71 to 1, i.e., corrections were relatively minor. The $j(2NB)$ 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

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

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 $j(2NB)$ 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, $j(2NB)$ 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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0.013 s⁻¹ above a bare field at midday on the summer solstice in Davis, CA (Anastasio and McGregor, 2001).

2.5 Calculation of HOOH yield

We define the HOOH yield as the ratio of the rate of HOOH formation to the rate of [•]OH radical production:

$$\text{Yield} \equiv \frac{R(\text{HOOH})}{R(\text{OH})} = \frac{R(\text{HOOH})/j(2\text{NB})}{R(\text{OH})/j(2\text{NB})} \quad (3)$$

where $R(\text{HOOH})$ is the measured rate of production of hydrogen peroxide (Sect. 2.6) and $R(\text{OH})$ is the calculated rate of production of hydroxyl radical from nitrate (Sect. 2.7), both normalized to $j(2\text{NB})$. Because two molecules of [•]OH are required to produce one molecule of HOOH (e.g. Reactions R3, R10, R11, R13), complete conversion of [•]OH to HOOH via reaction with organics should give a yield of 0.5, i.e., this is the expected upper bound. Uncertainty in the yield was expressed by propagating the standard errors of $R(\text{HOOH})$ and $R(\text{OH})$.

2.6 Measurement of HOOH concentration, $R(\text{HOOH})$, and $R(\text{HOOH})/j(2\text{NB})$

Hydrogen peroxide concentrations were determined with the HPLC post-column fluorescence method of Kok et al. (1995), using instrumentation previously described in Chu and Anastasio (2005): only PEEK or Teflon components were used between the sample injector and the detector. A standard curve for hydrogen peroxide in UV Milli-Q water was run each day. Illuminated samples were removed and analyzed for HOOH at known illumination times up to 6 h. Ice samples were thawed in the dark at room temperature immediately before analysis.

The rate of HOOH formation, $R(\text{HOOH})$, for each illuminated sample pair (i.e., with and without nitrate) was determined by performing a linear regression on the data points of $[\text{HOOH}]_{\text{corrected}}$ versus illumination time. Dark (not illuminated) samples were

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run with each experiment. With some exceptions, these samples did not show HOOH production rates greater than zero, and deviations from zero were always much smaller than illuminated production rates. Consequently, we did not include a correction for dark samples in our $R(\text{HOOH})$ values.

Values of $R(\text{HOOH})$ for each sample pair (with and without nitrate) were divided by the measured $j(2\text{NB})$ value for each sample to correct for any difference in light flux in the parallel samples. To subtract any background production from direct photoreaction of the organic compound, $R(\text{HOOH})/j(2\text{NB})$ for the sample without nitrate was subtracted from the value of $R(\text{HOOH})/j(2\text{NB})$ determined for the sample with nitrate. Listed uncertainties in values of the net $R(\text{HOOH})/j(2\text{NB})$ are ± 1 standard error, determined from the SE of the slope of $[\text{HOOH}]_{\text{corrected}}$ versus illumination time and including propagated errors from $j(2\text{NB})$.

2.7 Calculation of $R(\text{OH})$

We used 0.50 mM nitrate as a photochemical source of hydroxyl radical (Reaction R3 (Chu and Anastasio, 2003)). In order to be able to calculate the rate of $\bullet\text{OH}$ formation in each sample, we first measured the rate constant for $\bullet\text{OH}$ formation from nitrate photolysis, $j(\text{NO}_3^- \rightarrow \text{OH})$, in our illumination systems using pH 5 solutions containing 0.20 mM sodium benzoate and illuminated at 5°C. Hydroxyl radical was trapped using sodium benzoate to form para-hydroxybenzoic acid (*p*-HBA), which was quantified by HPLC and converted to an $\bullet\text{OH}$ equivalent using a *p*-HBA yield of 19% (Chu and Anastasio, 2007). $j(2\text{NB})$ was measured in the same system on the same day. The average ($\pm 1\sigma$) measured value (i.e., $(j(\text{NO}_3^- \rightarrow \text{OH})/j(2\text{NB}))_{\text{ref}}$) in our systems was $(1.8 \pm 0.39) \times 10^{-5} \text{ s}^{-1}/\text{s}^{-1}$ ($n = 6$); there was no difference in this value between the two illumination systems. This ratio was adjusted to values at other temperatures using the temperature dependence of the quantum yield for $\bullet\text{OH}$ formation from nitrate photolysis (Chu and Anastasio, 2003):

$$\ln(\Phi_{\text{OH}}) = (2400 \pm 480) \frac{1}{T} + (3.6 \pm 0.8) \quad (4)$$

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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 $\cdot\text{OH}$ 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 have 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 ($0.80 \text{ nM s}^{-1}/\text{s}^{-1}$), is slightly higher than the 95% upper confidence limit (UCL) for HOOH production by UV Milli-Q water ($0.64 \text{ nM s}^{-1}/\text{s}^{-1}$).

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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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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, $\bullet\text{OH}$ 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 $\bullet\text{O}_2^-$. 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 $\bullet\text{OH}$ 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 $\bullet\text{OH}$ 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 $\text{HO}_2^\bullet/\bullet\text{O}_2^-$. 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 $\bullet\text{OH}$ 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 $\bullet\text{OH}$ 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 $\bullet\text{OH} + 2$ -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 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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$$\tau(\text{HOOH}) = \frac{[\text{HOOH}]}{(1 - 2 \times \text{Yield}) \times R_d(\text{HOOH})}, \quad (6)$$

where [HOOH] is the bulk concentration of HOOH (typically 10 μM for surface snow at Summit), $R_d(\text{HOOH})$ is the rate of HOOH photolysis ($R_d(\text{HOOH}) = j(\text{HOOH} \rightarrow \text{OH}) \times [\text{HOOH}]$), and “Yield” is the yield of HOOH from reaction of $\cdot\text{OH}$ with snowgrain organics. Using an HOOH yield in ice of 0.10 (e.g., Fig. 6) results in a net lifetime of HOOH of 179 h. Thus recycling of HOOH via the reaction of $\cdot\text{OH}$ with organics can increase the lifetime of HOOH by approximately 25%. However, since (as noted earlier), it would take approximately 5 mo to bury surface snow at Summit, the modest impact of HOOH recycling appears insufficient to explain the preservation of HOOH in polar snowpacks.

Supplementary material related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/11/6457/2011/
acpd-11-6457-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/6457/2011/acpd-11-6457-2011-supplement.pdf).

Acknowledgements. We thank Kelley Patten for assisting with experiments, and the National Science Foundation for funding this research (ANT-0636985).

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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 ₈ 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)

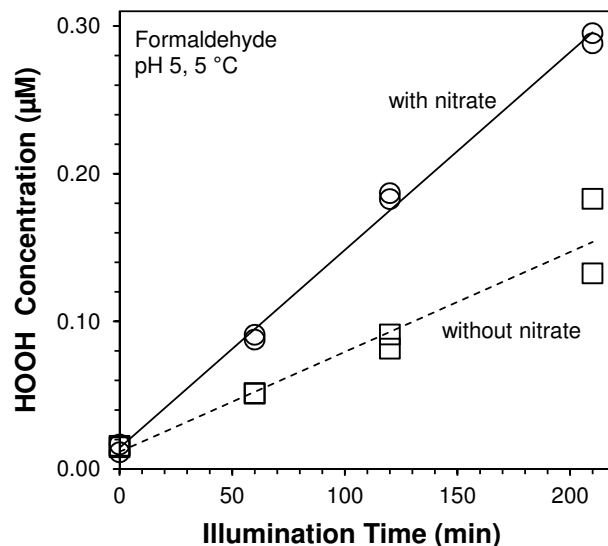
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Fig. 1. Production of hydrogen peroxide in illuminated solutions (pH 5, 5 °C) containing 200 µM formaldehyde and either no nitrate (squares) or 500 µM nitrate (circles). Rates of HOOH formation, correlation coefficients (R^2), and $j(2\text{NB})$ values 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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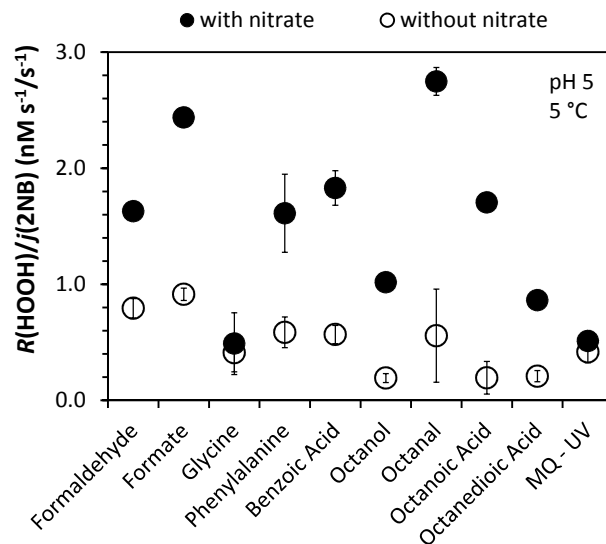


Fig. 2. Production of hydrogen peroxide normalized to measured $j(2\text{NB})$ in illuminated solutions (pH 5, 5 °C) containing 200 μM model organic compound and either no nitrate (open circles) or 500 μM nitrate (closed circles). UV Milli-Q water did not contain a model compound. Error bars (± 1 SE) 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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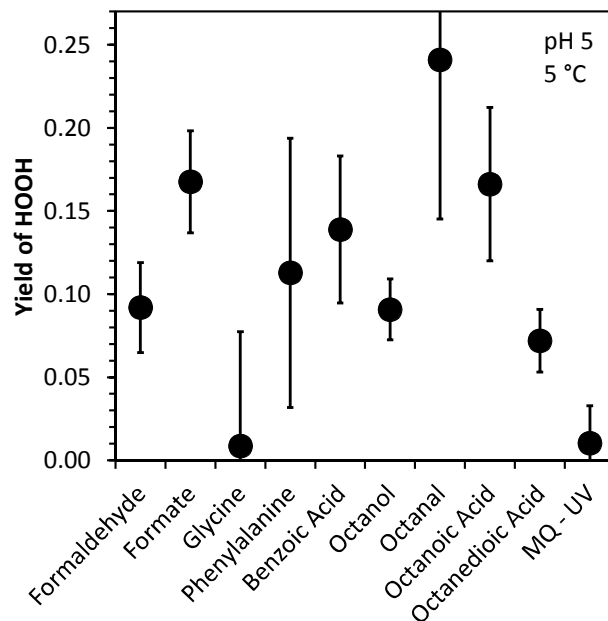


Fig. 3. Yield of hydrogen peroxide from the reaction of $\cdot\text{OH}$ with each model organic compound (pH 5, 5 °C). Error bars (± 1 SE) are the absolute error (net indeterminate error), calculated based on the propagated errors from $R(\text{HOOH})$, $j(2\text{NB})$, and $R(\text{OH})$.

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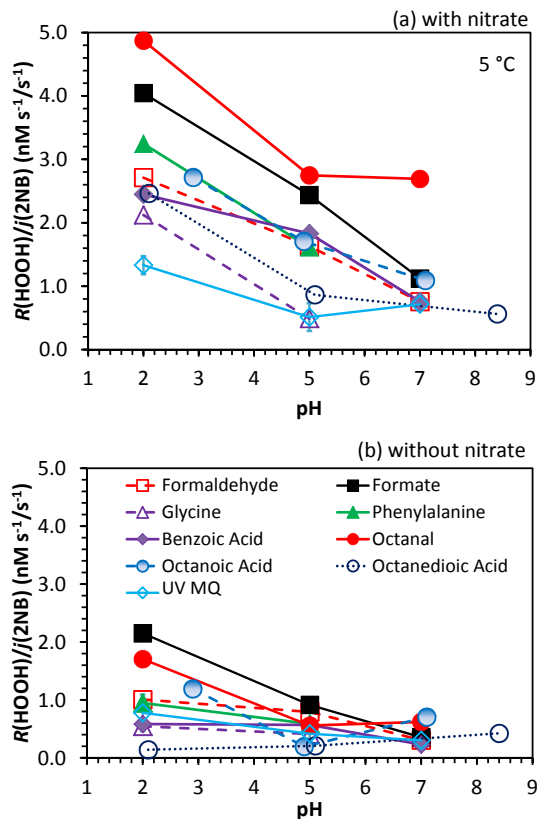
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Fig. 4. pH dependence of hydrogen peroxide production (5°C , normalized by $j(2\text{NB})$) for illuminated solutions containing: **(a)** model compound ($200\ \mu\text{M}$) and nitrate ($500\ \mu\text{M}$), and **(b)** model compound only. UV Milli-Q 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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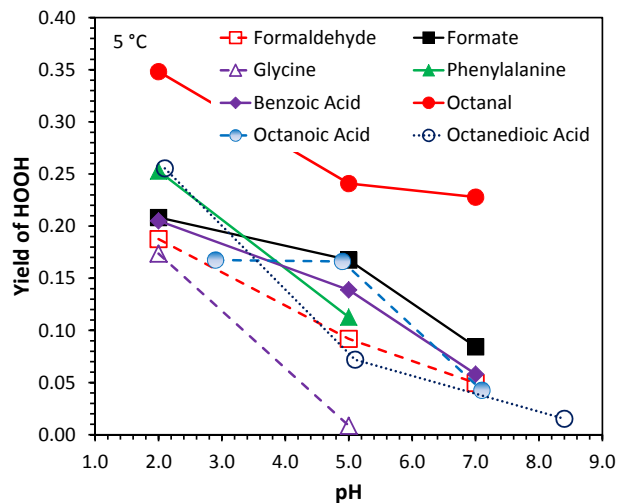
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Fig. 5. pH dependence of the HOOH yield from reaction of $\cdot\text{OH}$ with each model compound at 5 °C.

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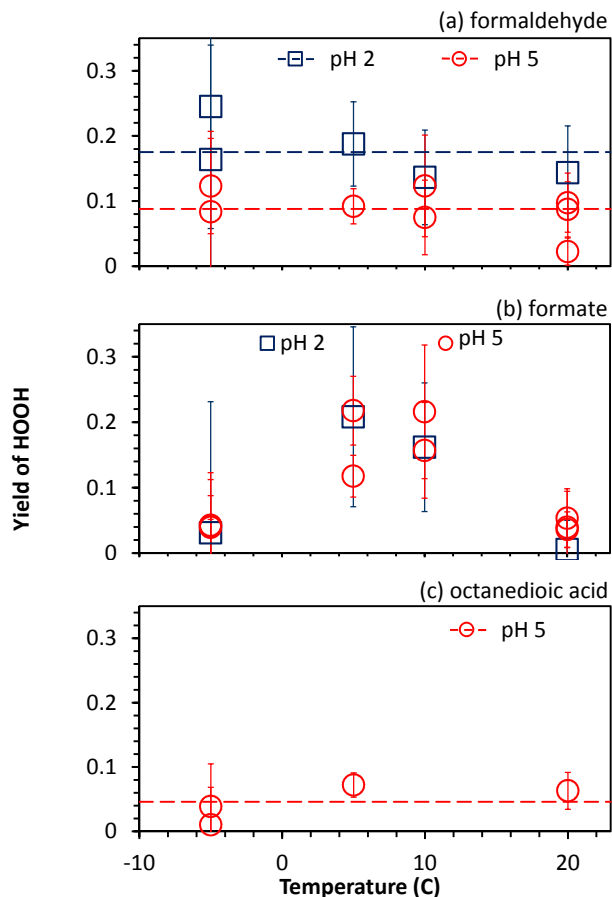
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Fig. 6. Temperature dependence of the HOOH yield for three model compounds at pH 2 (blue squares) and pH 5 (red circles). The average HOOH yields for formaldehyde were 0.18 (pH 2) and 0.088 (pH 5), while the average yield for octanedioic acid is 0.046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

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