Chemistry of fog waters in California’s Central Valley:
1. In situ photoformation of hydroxyl radical and singlet molecular oxygen

Cort Anastasio*, Keith G. McGregor

Atmospheric Science Program, Department of Land, Air and Water Resources, University of California, One Shields Avenue, Davis, CA 95616-8627, USA

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Abstract

The aqueous-phase photoformation of hydroxyl radical (·OH) and singlet molecular oxygen (O₂(1Δg) or ¹O₂) was characterized in winter fog waters collected in Davis, California. All of the samples studied formed ·OH and ¹O₂ upon illumination with simulated sunlight. Nitrite photolysis was a major source of ·OH in these samples, accounting for 47–100% of ·OH photoformation. Compared to calculated rates of gas-to-drop partitioning, in situ photoformation was a significant source of ·OH to all but the smallest fog drops, and was the dominant source of aqueous-phase ¹O₂. Measured lifetimes of ·OH in the fog drops ranged from 0.38 to 1.5 μs. These values are significantly shorter than those predicted based on known drop constituents, indicating that uncharacterized compounds – likely organic – are significant sinks for ·OH in fog waters. Based on measured steady-state concentrations, both ·OH and ¹O₂ are likely to play significant roles in the transformations of trace species in fog drops. Hydroxyl radical appears to be a relatively significant sink for refractory compounds and a minor sink for reactive trace species. Conversely, ¹O₂ will be a minor sink for refractory compounds but a significant sink for certain electron-rich reactive trace species. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reactions in fog and cloud drops can have significant effects upon the composition and chemistry of the troposphere. For example, aqueous-phase reactions involving HOOH or O₃ play a major role in the tropospheric oxidation of SO₂ (Seinfeld and Pandis, 1998). Similarly, the fate of even slightly soluble tropospheric trace species can be heavily influenced by reactions in atmospheric hydrometeors involving oxidants such as hydroxyl radical (·OH) and singlet molecular oxygen (¹O₂). To understand the atmospheric fate of such trace species requires knowledge of oxidant chemistry in both the gas and condensed phases. While reaction pathways and oxidant concentrations in the gas phase are relatively well known (Finlayson-Pitts and Pitts, 2000), our knowledge of the same quantities in condensed phases is scant.

Oxidants in condensed phases can result either from partitioning of gas phase species (i.e., of the oxidants or their precursors) or from photochemical reactions within the drops or particles (e.g., Graedel and Weschler, 1981). Previous papers have documented that this latter in situ photochemistry is a significant source of oxidants such as peroxy radicals, HOOH, ·OH, and ¹O₂ in acidic cloud drops collected in the eastern US (Faust, 1994 and references therein). However, there is much less data regarding oxidant photoformation in fog waters, especially for samples with near-neutral pH values, such as those typically observed in the western US.
To address this gap, we have characterized the in situ photoformation of \( 'OH \) and \( ^1O_2 \) in fog waters collected from Davis, in the northern section of California’s Central Valley. The Central Valley extends for approximately 700 km through the middle of California, with an area of approximately 100,000 km\(^2\) and a population of over 5 million people in agricultural, suburban, and urban areas (Umbach, 1997). In winter the Central Valley often experiences radiation fogs that can last for up to several days (Holets and Swanson, 1981). There were three major goals for this research: (i) to characterize the formation rates, lifetimes, and steady-state concentrations of \( 'OH \) and \( ^1O_2 \) in sunlit fog drops; (ii) to compare the significance of aqueous-phase photoreactions with gas-to-drop partitioning as sources of these oxidants, and (iii) to examine radiation fogs that can last for up to several days (Holets and Swanson, 1981). There were three major goals for this research: (i) to characterize the formation rates, lifetimes, and steady-state concentrations of \( 'OH \) and \( ^1O_2 \) as sinks for tropospheric trace species. This latter point is then explored further, for the specific case of amino acids, in a companion paper (McGregor and Anastasio, 2000).

2. Experimental methods

2.1. Fog and cloud water samples

Sample data are listed in Table 1. Fog water samples were collected at the National Acid Deposition Program site (CA88) at the University of California at Davis, approximately 2 miles west–southwest of the center of the city of Davis, California (CA), USA (38°33'N, 121°38'W). Bulk samples were collected into cleaned high-density polyethylene (HDPE) bottles using a Caltech active strand cloudwater collector (CASCC2; Demoz et al., 1996) located 10 ft above ground. Prior to each fog event, all collection surfaces in the CASCC2 were removed and cleaned (ethanol; Alconox in hot water; Milli-Q rinse; acid rinse; Milli-Q soak and rinse) as described by McGregor (2000). As a check on collection procedures, rinse water samples were taken by spraying Milli-Q water (see below) into the CASCC2 and collecting it as a sample. Within 8 h after collection, bulk fog waters and rinse waters were filtered (0.45 \( \mu \)m unfiltered Tefsep; Micron Separations, Inc.) and then frozen (\(-20^\circ C\)) in HDPE bottles. Size-fractionated fog and cloud water samples were collected (at Davis, CA and Tenerife, Canary Islands, respectively) by researchers from Colorado State University. These samples were frozen immediately after collection, shipped to our laboratory, thawed, and then filtered and stored frozen.

2.2. Materials

Phenol (reagent grade), sodium nitrate (certified American Chemical Society (ACS)), hydrogen peroxide (30\%), acetonitrile (Optima), sodium borate (certified ACS), sulfuric acid (Optima), and perchloric acid (Optima) were all received from Fisher. Benzoic acid (99\%), sodium benzoate (99\%), \( m \)-hydroxybenzoic acid (99\%), furfuryl alcohol (99\%), and deuterium oxide (99.9\% D-atom) were received from Aldrich. Benzene (99.9\%, HPLC grade) was received from Sigma Aldrich, while \( p \)-hydroxybenzoic acid (\( >98\%\)) was obtained from TCI America. All chemicals were used as received. Purified water (”Milli-Q water”) was obtained from a Milli-Q Plus system (Millipore; \( >18.2 \text{ M}\Omega \text{ cm} \)).

2.3. Equipment

Sample pH was measured using an Orion Ross semimicroelectrode (#8103 BN), or a Microelectrodes Incorporated MI-414–6 cm probe, attached to an Orion 420A pH meter. UV–Vis absorbance spectra were taken in a Shimadzu UV-2501PC UV/Vis spectrophotometer (2 nm slit width; slow scan speed) using Milli-Q water as reference. Anions were determined with a Dionex DX-120 ion chromatograph (AS14 4 mm analytical column, AG14 4 mm guard column, ASRS-II 4 mm suppressor and DS4-I detector). Dissolved organic carbon concentrations in aliquots of sample (preserved with 75 \( \mu \)M HgCl\(_2\) ) were measured using a Shimadzu TOC 5050 Carbon analyzer. Samples were illuminated using either 313 nm light from a 1000 W Hg/Xe monochromatic system (Faust and Allen, 1992) or simulated sunlight from a 1000 W Xe Solar Simulator (Faust, 1993). In both systems samples were maintained at \( \approx 20^\circ C \) using a Neslab RTE 211 recirculating water bath. The isocratic high-pressure liquid chromatograph (HPLC) used in this work consisted of a Shimadzu LC10-AT pump, a Keystone Scientific C-18 Beta Basic reverse-phase column (250 x 3 mm, 5 \( \mu \)m bead) with attached guard column, and a Shimadzu SPD-10AV UV/Visible detector.

2.4. \( 'OH \) measurement

Hydroxyl radicals were characterized using techniques where \( 'OH \) reacts with an added probe (benzene or benzoic acid) to form a stable, measurable product (phenol or \( m \)-hydroxybenzoic acid, respectively). For each sample at least three different probe concentrations (50–1500 \( \mu M \)) were used in separate aliquots of sample. Initial studies used the benzene probe technique (Faust and Allen, 1993; Arakaki and Faust, 1998) with \( \approx 4 \text{ ml} \) of sample in a stirred, airtight 4.5 ml quartz cuvette (Spectrocell). Stock solutions of benzene in Milli-Q water were made within a day of use and concentrations were calculated using the measured absorbance of the solution and the molar absorptivity of aqueous benzene at 254 nm (113 \( \pm \)1.7 M\(^{-1}\) cm\(^{-1}\), average \( \pm \)1 standard error). In later studies a benzoic acid technique (Zhou and Mopper, 1990) was used with \( \approx 250 \mu l \) of sample in a non- airtight quartz tube (GE 021 quartz, 4 mm ID x 58 mm l, 750 \( \mu l \) volume, with PTFE stopper) and added benzoic
Table 1
Collection data and composition of fog and cloud waters

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Collection date</th>
<th>Collection time</th>
<th>LWC a (g m^{-3})</th>
<th>pH</th>
<th>( z_{313} ) b (cm^{-1})</th>
<th>[Cl(^{-})] c (( \mu M ))</th>
<th>[N(III)] c (( \mu M ))</th>
<th>[NO(^{2-})] d (( \mu M ))</th>
<th>[SO(^{2-})] d (( \mu M ))</th>
<th>[DOC] d (( \mu M \cdot C ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk fog waters from Davis, CA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA97-A01</td>
<td>01/30/97</td>
<td>03:55–07:51</td>
<td>0.17</td>
<td>6.7</td>
<td>0.070</td>
<td>10</td>
<td>40</td>
<td>350</td>
<td>30</td>
<td>1200</td>
</tr>
<tr>
<td>DA97-05F</td>
<td>02/03/97</td>
<td>05:45–08:37</td>
<td>0.11</td>
<td>7.0</td>
<td>0.100</td>
<td>20</td>
<td>75</td>
<td>240</td>
<td>19</td>
<td>2500</td>
</tr>
<tr>
<td>DA98-05F</td>
<td>01/22–23/98</td>
<td>22:15–01:15</td>
<td>0.076</td>
<td>6.9</td>
<td>0.091</td>
<td>82</td>
<td>29</td>
<td>940</td>
<td>140</td>
<td>1700</td>
</tr>
<tr>
<td>DA98-06F</td>
<td>01/23/98</td>
<td>01:15–04:30</td>
<td>0.10</td>
<td>6.8</td>
<td>0.132</td>
<td>55</td>
<td>59</td>
<td>1010</td>
<td>140</td>
<td>2400</td>
</tr>
<tr>
<td>DA98-09F</td>
<td>01/25/98</td>
<td>01:25–04:55</td>
<td>0.081</td>
<td>6.7</td>
<td>0.121</td>
<td>19</td>
<td>21</td>
<td>880</td>
<td>64</td>
<td>3100</td>
</tr>
<tr>
<td>DA98-11F</td>
<td>01/25/98</td>
<td>07:00–10:05</td>
<td>0.025</td>
<td>6.1</td>
<td>0.262</td>
<td>71</td>
<td>10</td>
<td>2900</td>
<td>180</td>
<td>3800</td>
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<tr>
<td>DA98-14F</td>
<td>02/13/98</td>
<td>07:00–10:10</td>
<td>0.076</td>
<td>6.7</td>
<td>0.029</td>
<td>34</td>
<td>11</td>
<td>75</td>
<td>82</td>
<td>2400</td>
</tr>
<tr>
<td><strong>Size-segregated fog waters from Davis, CA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>DA99L01F</td>
<td>01/05/99</td>
<td>05:00–06:00</td>
<td>—</td>
<td>6.3</td>
<td>0.024</td>
<td>4.7</td>
<td>15</td>
<td>160</td>
<td>13</td>
<td>680</td>
</tr>
<tr>
<td>DA99S01F</td>
<td>01/05/99</td>
<td>05:00–06:00</td>
<td>—</td>
<td>6.0</td>
<td>0.149</td>
<td>26</td>
<td>6.6</td>
<td>1050</td>
<td>56</td>
<td>4100</td>
</tr>
<tr>
<td><strong>Size-segregated cloud waters from Tenerife, Canary Islands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO97-AL2</td>
<td>07/09/97</td>
<td>00:00–02:00</td>
<td>—</td>
<td>3.7</td>
<td>0.021</td>
<td>4100</td>
<td>&lt;0.72</td>
<td>850</td>
<td>740</td>
<td>1100</td>
</tr>
<tr>
<td>CO97-AS2</td>
<td>07/09/97</td>
<td>00:00–02:00</td>
<td>—</td>
<td>3.4</td>
<td>0.006</td>
<td>530</td>
<td>&lt;0.91</td>
<td>140</td>
<td>380</td>
<td>440</td>
</tr>
<tr>
<td><strong>Rinse waters from bulk fog water collection</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA97R02F</td>
<td>03/30/97</td>
<td>01:50</td>
<td>—</td>
<td>6.4</td>
<td>0.001</td>
<td>1.0</td>
<td>&lt;0.72</td>
<td>0.53</td>
<td>&lt;0.50</td>
<td>100</td>
</tr>
<tr>
<td>DA98R06F</td>
<td>02/13/98</td>
<td>04:00</td>
<td>—</td>
<td>6.0</td>
<td>0.001</td>
<td>1.3</td>
<td>&lt;0.72</td>
<td>0.76</td>
<td>0.49</td>
<td>2700</td>
</tr>
<tr>
<td>DA98R07F</td>
<td>03/02/98</td>
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<td>—</td>
<td>6.5</td>
<td>0.001</td>
<td>1.8</td>
<td>&lt;0.91</td>
<td>2.2</td>
<td>0.55</td>
<td>160</td>
</tr>
<tr>
<td>DA99R01F</td>
<td>01/13/99</td>
<td>17:00</td>
<td>—</td>
<td>5.7</td>
<td>0.000</td>
<td>1.9</td>
<td>&lt;0.83</td>
<td>3.7</td>
<td>7.9</td>
<td>400</td>
</tr>
</tbody>
</table>

aAverage liquid water content during collection period, units of g-H\(_2\)O m\(^{-3}\)-air.
bBase-10 sample absorbance per cm at 313 nm.
cSum of concentrations of dissolved nitrite (NO\(^{2-}\)) and nitrous acid (HNO\(_2\)).
dDissolved (\(<0.45\ \text{\mu M}\)) organic carbon concentration in units of \(\text{\mu mol-C \cdot L}^{-1}\).

acids/phenolic acid/benzoate solution adjusted to the pH of the fog sample. In all experiments fog waters were diluted by ≤ 10% due to the addition of probe. At measured time intervals during illumination, aliquots of sample with probe were removed from the quartz cell and analyzed for phenol or m-hydroxybenzoic acid (m-OHBA) using HPLC. Phenol was analyzed using an eluent of 50% CH\(_3\)CN/50% H\(_2\)O at a flow rate of 0.70 ml min\(^{-1}\) and a detection wavelength of 269 nm. Analysis of m-OHBA utilized an eluent of 30% CH\(_3\)CN/70% H\(_2\)O (adjusted to a pH of 2 with HClO\(_4\)), a flow rate of 0.60 ml min\(^{-1}\), and a detection wavelength of 238 or 297 nm. Concentrations of phenol and m-OHBA were determined based on calibration standards made in Milli-Q water and run during the day of the illumination experiment. There was no significant difference between standards made in Milli-Q water and those made in fog water with added probe.

Initial rates of phenol or m-OHBA formation during illumination (\( R'_i \)) were determined from plots of total concentration of product formed versus illumination time using either a linear regression fit or an exponential fit, depending on the shape of the data. Exponential fits for experiments using the benzene probe were determined by fitting the experimental data to

\[
[\text{PhOH}]_t = [\text{PhOH}]_0 + a(1 - e^{-bt})
\]

using a three-parameter, exponential rise to a maximum fit of Sigma Plot (version 4.0; SPSS Inc.), where \([\text{PhOH}]_t\) is the experimentally measured concentration of phenol at illumination time \(t\), \([\text{PhOH}]_0\) is the initial concentration of phenol, and \(a\) and \(b\) are parameters determined by the fitting procedure. The initial rate of phenol formation was then calculated as the first derivative of Eq. (1) with respect to \(t\) at time zero, i.e.,

\[
R'_i = ab.
\]

An example of the formation of phenol in one experiment, and the regression fits to these data, are shown in Fig. 1a.

For benzoic acid probe experiments with exponential fits, the experimental data was fit to

\[
[m\text{-OHBA}]_t = [m\text{-OHBA}]_0 + \left( \frac{c \times d}{J_{m\text{-OHBA}} - d} \right) \times (e^{-bt} - e^{-bt_{\text{concat}}})
\]
product formation data (for example, from a second-order polynomial) yield initial rates of product formation (and final 'OH results) that are very close to those obtained from the exponential fi ts described above.

Values of $j_{m-OHBA}$ in Eq. (3) were determined using simulated sunlight illumination of 2.0 μM m-OHBA in Milli-Q water adjusted to pH 8.9 or 1.9. These experiments yielded a photolysis rate constant of 0.11 h⁻¹ for destruction of the base form (m-hydroxybenzoate) and revealed that the acid form does not undergo direct photolysis at these wavelengths (rate constant ±1 standard error = 0.0028 ± 0.011 h⁻¹). The 2-nitrobenzaldehyde actinometry rate constant ($j_{2NB,EXP}$, see below) for these experiments was 0.0060 s⁻¹. From these data the apparent rate constant for direct photolysis of m-OHBA ($j_{m-OHBA}$; h⁻¹) was calculated for each solar simulator 'OH experiment using

$$j_{m-OHBA} = 0.11 \text{ h}^{-1} \times (j_{2NB,EXP}/0.0060 \text{ s}^{-1}) \times (1 + 10^{-(\text{pH}/10)} - \text{nK}^{-1}),$$

where $j_{2NB,EXP}$ is the rate constant for photolysis of the actinometer (s⁻¹; see below) measured on the day of sample illumination, pK_1 is the first pK_1 for m-OHBA (4.06; Lide, 1999), and the pH is that of the illuminated sample. Values for $j_{m-OHBA}$ ranged from 0.04 to 0.23 h⁻¹.

After determining $R_p^*$ for each probe concentration in a given sample, a plot of 1/$R_p^*$ versus 1/(probe concentration) was made (e.g., Zhou and Mopper, 1990). An example of one of these plots is shown in Fig. 1b. From the linear regression slope and y-intercept of this plot three quantities were determined: (i) the initial rate of 'OH formation ($R_{OH,EXP}$ for simulated sunlight illumination; $R_{OH,313}$ for 313 nm illumination); (ii) the apparent first-order rate constant for 'OH destruction due to natural scavengers in the sample ($k_{OH}$), and (iii) the steady-state 'OH concentration ([OH]EXP):

$$R_{OH,EXP} = (1/\text{intercept} \times Y_{product})^{-1},$$

$$k_{OH} = k_p \times (\text{slope/} \text{y-intercept}),$$

$$[\text{OH}]_{\text{EXP}} = (k_p \times \text{slope} \times Y_{product})^{-1}.$$  

The quantity $Y_{product}$ is the yield of product (e.g., phenol or m-OHBA) from the reaction of 'OH with added probe. As shown in Table 2, the yield of phenol ($Y_{pOH}$) was approximately constant between pH 2.2 and 8.7 and showed no apparent dependence upon ionic strength. A combination of our data (Table 2) and data reported by Arakaki and Faust (1998) yielded an average (±1 standard error) value of $Y_{pOH}$ of 0.73 ± 0.071. The average yield of m-OHBA ($Y_{m-OHBA}$) from the reaction of 'OH with benzoic acid/benzoate was 0.19 ± 0.0068, based on an average consisting of our data (Table 2) and one data point from Zhou and Mopper (1990). Using this same procedure for the para-isomer gave a value for $Y_{p-OHBA}$ of 0.17 ± 0.0017. The quantity $k_p$ in Eqs. (6) and (7) is the
Table 2
Yield of product from reaction of 'OH with benzene and benzoic acid/benzoate

<table>
<thead>
<tr>
<th>Probe</th>
<th>pH</th>
<th>(Y_{\text{POH}})</th>
<th>(Y_{\text{m-OHBA}})</th>
<th>(Y_{\text{p-OHBA}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene(^b)</td>
<td>2.2</td>
<td>0.73</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>0.71</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>0.86</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.64</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>0.69</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>0.66</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>0.69</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Benzoic acid(^d)</td>
<td>1.9</td>
<td>—</td>
<td>0.20</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>—</td>
<td>0.19</td>
<td>0.17</td>
</tr>
</tbody>
</table>

\(^a\)Yields were calculated as (observed product formation rate)/(calculated rate of 'OH formation from HOOH photolysis) from 313 nm illumination of Milli-Q water solutions (see below) using procedures described by Arakaki and Faust (1998). In all experiments > 99% of photoformed 'OH reacted with the added probe. Actinic flux values at 313 nm were \(5.5 \times 10^{-2}\) mol l\(^{-1}\)s\(^{-1}\).

\(^b\)Photolysis solutions contained 100 \(\mu\)M HOOH, 1.7 mM Benzen and either \(\text{H}_2\text{SO}_4\) or borate to adjust pH.

\(^c\)Solutions also contained 0.20 M \(\text{Na}_2\text{SO}_4\) to test the effect of ionic strength on phenol yield.

\(^d\)Photolysis solutions contained 200 \(\mu\)M HOOH, 5 mM benzoic acid/benzoate and either \(\text{HClO}_4\) or borate to adjust pH.

2.5. 'OH formation from photolysis of nitrite, nitrous acid and nitrate

The rate of 'OH formation from the photolysis of \(\text{N(III)}\) (i.e., \(\text{NO}_2^- + \text{HNO}_2\)) in a sample under midday, winter solstice sunlight at Davis was determined as the sum of \(j_{\text{NO}_2^- - \text{OH}[\text{NO}_2^-]} + j_{\text{HNO}_2 - \text{OH}[\text{HNO}_2]}\), where \(j_{\text{NO}_2^- - \text{OH}[\text{NO}_2^-]} (2.6 \times 10^{-5} \text{ s}^{-1})\) and \(j_{\text{HNO}_2 - \text{OH}[\text{HNO}_2]} (2.5 \times 10^{-4} \text{ s}^{-1})\) are, respectively, the rate constants for 'OH formation from nitrite and nitrous acid photolysis with sunlight illumination at \(\theta = 62^\circ\) (values determined by normalizing results of Arakaki and coworkers (1999) to \(j_{\text{NO}_2^- - \text{OH}}\)). Concentrations of nitrate and nitrous acid in the sample were determined from the measured value of total \(\text{Ni(III)}\) ([[\text{Ni(III)}]_T, see Table 1]) and the pK\(_a\) of HNO\(_2\) (3.25; Lide, 1999).

The rate constant for 'OH formation from photolysis of nitrate under midday, winter solstice sunlight in Davis, \(j_{\text{NO}_3^- - \text{OH}}\), was determined experimentally by measuring the formation of m-OHBA in simulated sunlight-illuminated solutions containing 200 or 500 \(\mu\)M nitrate, 7.0 or 15 mM benzoate (respectively), and \(\text{H}_2\text{SO}_4\) or borate to adjust the pH (McGregor, 2000). The average value for \(j_{\text{NO}_3^- - \text{OH}} (\pm 1 \text{ standard error})\) was \((1.4 \pm 0.11) \times 10^{-7} \text{ s}^{-1}\), independent of pH between 1.9 and 8.3 (McGregor, 2000). Previously reported values include \(3.0 \times 10^{-7} \text{ s}^{-1}\) (midday, cloudless sky, 26\(^\circ\)N, season unknown; Zhou 1999).
and Mopper, 1990) and $2.5 \times 10^{-7}$ s$^{-1}$ (sunlight during August, time of day unknown, 47°N; Zepp et al., 1987). Although our value is a factor of ~ 2 lower than these previously measured values, this appears to be due to the fact that our value is normalized to midday wintersonline sunlight at Davis ($\theta = 62^\circ$); under midday summersolstice sunlight in Davis ($\theta = 14^\circ$) our rate would be 1.9 times greater.

Values of $R_{i^\text{--OH},313}$, the rate of 'OH formation (mol$^{-1}$ s$^{-1}$) from photolysis of $i$ (NO$_2^-$, HNO$_2$, or NO$_3^-$) in a sample illuminated with 313 nm light at 20°C, were determined as

$$R_{i^\text{--OH},313} = 2.303 \times I_{313} \times \Phi_{i^\text{--OH},313} \times \epsilon_{i,313} \times l \times [i], \quad (9)$$

where $I_{313}$ is the volume-averaged actinic flux at 313 [(1.4–1.9) $\times 10^{-5}$ mol$^{-1}$ s$^{-1}$] determined by 2NB actinometry (Anastasio et al., 1994); $\Phi_{i^\text{--OH},313}$ is the quantum yield of 'OH from 313 photolysis of nitrate, nitrite (0.064 and 0.015, respectively; Zellner et al., 1990), or nitrous acid (0.35; Fischer and Warneck, 1996); $\epsilon_{i,313}$ is the base-10 molar absorptivity at 313 nm of nitrite (9.8 M$^{-1}$ cm$^{-1}$; Fischer and Warneck, 1996), nitrate (5.29 M$^{-1}$ cm$^{-1}$; Gaffney et al., 1992), or nitrous acid (5.3 M$^{-1}$ cm$^{-1}$; Arakaki et al., 1999); $l$ is the pathlength of the cell (cm), and $[i]$ is the molar concentration of $i$.

2.6. $1O_2^-$ measurement

For each fog water sample, the photoformation of singlet molecular oxygen ($1O_2^-$) was quantified by measuring the loss of low concentrations ($\leq 2 \mu$M) of furfuryl alcohol (FFA; Haag and Hoigné, 1986; Faust and Allen, 1992) in illuminated solutions containing: (i) 50% fog water and 50% Milli-Q water and (ii) 50% fog water and 50% D$_2$O. All solutions were adjusted to a pH/pD within ± 0.4 units of the original (undiluted) sample pH. During illumination, aliquots of solution were removed at known time intervals and analyzed using the HPLC system described earlier (with eluent of 10% CH$_3$CN/90% H$_2$O, flow rate of 0.60 ml min$^{-1}$, and a detection wavelength of 230 nm). Rate constants for loss of FFA in samples diluted with Milli-Q water or D$_2$O ($k_{\text{FFA},\text{H}_2\text{O}}$ and $k_{\text{FFA},\text{D}_2\text{O}}$, respectively) were determined as the linear regression slopes of plots of $\ln([\text{FFA}]/[\text{FFA}]_0)$ versus illumination time, where [FFA] and [FFA]$_0$ are the concentrations of FFA at time $t$ and time zero, respectively.

Values of $[1O_2^\text{--}],\text{EXP}$, the steady-state concentration of $1O_2^-$ in a given (undiluted) fog water illuminated with simulated sunlight, were determined using

$$[1O_2^\text{--}],\text{EXP} = \frac{k_{\text{FFA},\text{H}_2\text{O}} - k_{\text{FFA},\text{D}_2\text{O}}}{k_{\text{FFA},\text{H}_2\text{O}}/([\text{H}_2\text{O}]\div[\text{D}_2\text{O}]) - 1)}, \quad (10)$$

where: $k_{\text{FFA},\text{H}_2\text{O}}$, is the rate constant for interaction of singlet oxygen with furfuryl alcohol ($1.2 \times 10^8$ M$^{-1}$ s$^{-1}$; Wilkinson et al., 1995); $z_{\text{H}_2\text{O}}$ and $z_{\text{D}_2\text{O}}$ are, respectively, the mole fractions of H$_2$O and D$_2$O used in the D$_2$O-dilution experiment; $D$ is the sample dilution factor used in the experiments (volume of fog sample divided by the total volume of illuminated solution); and $k_{\text{H}_2\text{O}}$ and $k_{\text{D}_2\text{O}}$ are the first-order rate constants for loss of $1O_2^-$ in 100% H$_2$O and 100% D$_2$O solutions, respectively ($2.2 \times 10^8$ s$^{-1}$ and $1.6 \times 10^8$ s$^{-1}$, respectively; Bilski et al., 1997). This equation was derived by combining Eqs. (4) and (7) of Allen et al. (1996) (as discussed by the authors) and then dividing by $D$ in order to correct for the dilution of fog water by H$_2$O or D$_2$O in our experiments. Since solvent quenching by H$_2$O is the dominant sink for singlet oxygen in natural waters, initial rates of $1O_2^-$ formation in the undiluted fog waters ($R_{\text{O}_2^-,\text{EXP}}$) were determined by

$$R_{\text{O}_2^-,\text{EXP}} = [1O_2^-],[\text{EXP}] \times k_{\text{H}_2\text{O}} \quad (11)$$

Values of $R_{\text{O}_2^-,\text{EXP}}$ and $[1O_2^-],[\text{EXP}]$ were normalized to winter-solstice sunlight (to yield values $R_{\text{O}_2^-,\text{WIN}}$ and $[1O_2^-],[\text{WIN}]$, respectively) using the same procedure described for 'OH (Eq. (8)). The average value of ($f_{\text{2NB,W}}/f_{\text{2NB,EXP}}$) for the $1O_2^-$ experiments was 0.35. For each fog water the fraction of FFA loss due to singlet oxygen, $f_{\text{FFA},\text{H}_2\text{O}}$, was calculated from

$$f_{\text{FFA},\text{H}_2\text{O}} = (k_{\text{FFA},\text{H}_2\text{O}},[1O_2^-],[\text{EXP}]) / k_{\text{FFA},\text{H}_2\text{O}}. \quad (12)$$

3. Results and discussion

3.1. Samples

Chemical characteristics of the samples studied are listed in Table 1. As noted for previous samples (e.g., Anastasio, 1994; Collett et al., 1999), the Central Valley fog waters studied here had near-neutral pH values, high concentrations of nitrate and dissolved organic carbon (DOC), and high absorbance values at 313 nm. The composition of the Tenerife samples was quite different, reflecting a polluted marine cloud with acidic pH values, high chloride, nitrate, and sulfate concentrations, and, relative to the fog waters, low organic carbon and absorbance values. The low concentrations and absorbance values of the rinse waters (Table 1) suggest that collection and processing of the bulk fog waters had no significant effect upon their composition or chemistry. (The apparent high DOC concentration in rinse water DA98R06F appears to be due to the contamination of the aliquot removed for DOC analysis, and not high levels of DOC in the actual sample, based on the fact that values for other parameters, including $z_{313}$, were low in this sample.)
Table 3
Hydroxyl radical results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drop size</th>
<th>Probe</th>
<th>Light</th>
<th>( R_{OH,WIN} ) (µM h⁻¹)</th>
<th>( 10^{-6} k_{OH} ) (s⁻¹)</th>
<th>( 10^{16} [OH]_{WIN} ) (M)</th>
<th>( f_{NMB} )</th>
<th>( f_{NV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA97-A01</td>
<td>B</td>
<td>BA</td>
<td>Sol</td>
<td>(3.5 ± 1.3)</td>
<td>1.5 ± 0.68</td>
<td>6.4 ± 1.6</td>
<td>1.08</td>
<td>0.05</td>
</tr>
<tr>
<td>DA98-05F</td>
<td>B</td>
<td>BA</td>
<td>Sol</td>
<td>(6.7 ± 0.33)*</td>
<td>2.6 ± 0.13</td>
<td>(7.2 ± 0.51)*</td>
<td>0.72b</td>
<td>0.65b</td>
</tr>
<tr>
<td>DA98-06F</td>
<td>B</td>
<td>BA</td>
<td>Sol</td>
<td>(4.4 ± 1.5)</td>
<td>1.9 ± 0.87</td>
<td>6.6 ± 2.0</td>
<td>0.63</td>
<td>0.10</td>
</tr>
<tr>
<td>DA98-09F</td>
<td>B</td>
<td>BA</td>
<td>Sol</td>
<td>(3.9 ± 0.16)</td>
<td>1.9 ± 0.09</td>
<td>5.7 ± 0.15</td>
<td>1.45</td>
<td>0.13</td>
</tr>
<tr>
<td>DA99-14F</td>
<td>B</td>
<td>BA</td>
<td>Sol</td>
<td>(13 ± 5.1)*</td>
<td>1.8 ± 0.86</td>
<td>(39 ± 24)*</td>
<td>0.13b</td>
<td>0.69b</td>
</tr>
<tr>
<td>DA99L01F</td>
<td>L</td>
<td>BA</td>
<td>Sol</td>
<td>1.2 ± 0.23</td>
<td>0.68 ± 0.28</td>
<td>4.7 ± 1.7</td>
<td>0.90</td>
<td>0.03</td>
</tr>
<tr>
<td>DA99S01F</td>
<td>S</td>
<td>BA</td>
<td>Sol</td>
<td>0.88 ± 0.14</td>
<td>0.73 ± 0.19</td>
<td>3.4 ± 0.70</td>
<td>1.58</td>
<td>0.09</td>
</tr>
<tr>
<td>CO97-AL2</td>
<td>L</td>
<td>BA</td>
<td>Sol</td>
<td>1.3 ± 0.27</td>
<td>0.77 ± 0.25</td>
<td>4.8 ± 1.2</td>
<td>0.47</td>
<td>0.40</td>
</tr>
<tr>
<td>CO97-AS2</td>
<td>S</td>
<td>BA</td>
<td>Sol</td>
<td>1.1 ± 0.13</td>
<td>0.38 ± 0.10</td>
<td>7.7 ± 1.9</td>
<td>&lt; 0.21</td>
<td>0.38</td>
</tr>
<tr>
<td>DA97R02F</td>
<td>—</td>
<td>BA</td>
<td>Sol</td>
<td>&lt; 0.02†</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Listed uncertainties are 1 standard error, based on propagated relative standard errors from plots of \( 1/R_p^2 \) versus \( 1/|\text{probe concentration}| \).

Drop sizes: B = bulk samples (large and small drops, \( \geq 3.5 \mu m \) diameter); L = large drops (\( \geq 23 \mu m \) diameter); S = small drops (4–23 µm diameter).

Probe used in experiment: BA = benzoic acid/benzoate; C6H6 = benzene.

Light used to illuminate sample: Sol = simulated sunlight; 313 = 313 nm illumination.

Fraction of \( \cdot OH \) photoformation attributable to N(III) (i.e., nitrite and nitrous acid) = \( (J_{NO_2}\cdotOH[NO_2^-] + J_{HNO_2}\cdotOH[HNO_2])/ (R_{OH,WIN}) \). See experimental section for details.

Fraction of \( \cdot OH \) photoformation attributable to nitrate = \( (J_{NO_3}\cdotOH[NO_3^-])/ (R_{OH,WIN}) \). See experimental section for details.

These values were calculated from 313 nm data by assuming \( [OH]_{WIN} \) is constant at all wavelengths; listed values are therefore likely overestimated.

Calculated for 313 nm data, i.e., as \((R_{I\cdotOH,313})/(R_{OH,313})\); see text.

Rinse water.

1.2 mM benzoate was added to DA97R02F and illuminated (\( j_{NB,EXP} = 0.0091 \) s⁻¹) for 90 min in a 1.0 cm quartz cuvette; no detectable \( m\)-OHBA was formed.

3.2. Hydroxyl radical with simulated sunlight

As shown in Table 3, winter-sunlight normalized rates of \( \cdot OH \) formation for the fog and cloud waters only varied by a factor of \(~ 5\) despite the compositional differences described above. For the bulk fog waters, the average value of \( R_{OH,WIN} \) was 3.3 µM h⁻¹, while rates for the size-segregated fog waters were approximately three times lower than this. Although only two sets of size-fractionated samples were studied, the results suggest that there is somewhat higher rate of \( \cdot OH \) formation in smaller drops compared to larger drops (Table 3). It should be noted that, as with the Davis fog waters, the rates of \( \cdot OH \) formation in the Tenerife cloud waters (Table 3) were normalized to Davis winter-solstice sunlight and that actual rates under midday, summer sunlight in Tenerife would be approximately two times higher. There was no detectable formation of \( \cdot OH \) in the collector rinse water studied (Table 3), suggesting again that there was no appreciable contamination in the bulk fog waters due to the sample collection or processing.

As shown by the values of \( f_{NMB} \) in Table 3, nitrite was the primary chromophore responsible for the photoformation of \( \cdot OH \) in the fog waters illuminated with simulated sunlight, accounting for 47–100% of \( \cdot OH \) photoformation. Concentrations of NO\(_3^-\) in these samples ranged from 6.6–75 µM (Table 1; note that NO\(_3^-\) is the dominant N(III) species at the pH values of the fog waters). In contrast, concentrations of N(III) in the Tenerife cloud waters were below detection limits (Table 1) and N(III) was, at most, a minor source of \( \cdot OH \) in these samples (Table 3). This difference in N(III) concentrations between the fog and cloud waters reflects the greater partitioning of N(III) (\( pK_a = 3.25; Lide, 1999 \)) into the higher-pH fog waters as well as any differences in gas phase concentrations of HONO. The concentrations of N(III) in our samples, and the concentration differences between the fog and cloud waters, are comparable to values reported previously for hydrometeors from Japan and Europe (Lammel and Cape, 1996). In addition, our results for \( f_{NMB} \) in the fog waters are similar to those reported recently for dew waters (mean pH = 6.1) collected in Hiroshima, Japan, where NO\(_3^-\) was responsible for, on average, 99% of photoformed \( \cdot OH \) (Arakaki et al., 1999).

Despite the fact that concentrations of NO\(_3^-\) were \( \sim 3\)–300 times higher than those of N(III) (Table 1), nitrate was generally a minor source of photoformed...
'OH for fog and cloud waters illuminated with simulated sunlight (Table 3). In six of these samples nitrate was responsible for $\leq 14\%$ of the 'OH formed, while in the remaining two samples $\text{NO}_3^-$ accounted for $\approx 40\%$ of the 'OH. At 313 nm, nitrate was the dominant 'OH-producing chromophore in the two fog waters examined, accounting for 65--69\% of photoformed 'OH (Table 3). However, based on the results discussed above, it is clear that shorter wavelengths such as 313 nm are typically responsible for only a minor portion of the overall photoformation of 'OH in sunlight.

Values of the first-order rate constant for destruction of 'OH due to natural scavengers ($k_{\text{OH}}$) varied by less than a factor of four in the Davis fog waters, with an average value of $1.4 \times 10^6$ s$^{-1}$ (Table 3). The average lifetime of 'OH in the fog samples (defined as $\tau = 1/k_{\text{OH}}$) was 0.90 $\mu$s. This fog water value for $k_{\text{OH}}$ is approximately five times higher than the average value measured for Whiteface Mountain, NY cloud waters (Arakaki and Faust, 1998), reflecting a greater concentration of 'OH sinks, or more reactive 'OH sinks, in the fog waters. The size-segregated Tenerife cloud waters had values of $k_{\text{OH}}$ within a factor of 2 of the fog water values, although the difference between the two Tenerife samples was large (Table 3).

Based on measured concentrations (Table 1) and published rate constants (Ross et al., 1994), nitrite was a significant sink for 'OH in the fog waters, accounting for 8.6--31\% of $k_{\text{OH}}$, but chloride, nitrate and sulfate were insignificant, accounting for <1\% of the loss of 'OH. Using median fog water concentrations from Collett et al. (1999) and Anastasio (1994), we estimate that formate and hydrated formaldehyde together account for $\sim 10$--40\% of 'OH destruction in the fog waters, S(IV) is a minor 'OH sink (accounting for <5\% of $k_{\text{OH}}$), and hydroxymethanesulfonate, acetate, ammonium, iron, and copper are all insignificant sinks for 'OH. Although incomplete, these data suggest that there are other important sinks for 'OH that are currently unknown. Arakaki and Faust (1998) found an excellent correlation between $k_{\text{OH}}$ and $[\text{DOC}]$ and suggested that organic compounds were an important sink for 'OH. Even though a plot of $k_{\text{OH}}$ versus $[\text{DOC}]$ for our limited number of fog waters showed a very weak relationship ($R^2 = 0.03$), the high concentrations of DOC in the Davis fogs (Table 1) suggest that unidentified carbon compounds might account for a significant component of $k_{\text{OH}}$.

Measured steady-state concentrations of 'OH in winter sunlight, $[\text{OH}]_{\text{WIN}}$, were surprisingly constant in the bulk and size-segregated fog waters, ranging only from $(3.4$--$6.6) \times 10^{-16}$ M for those samples studied with simulated sunlight (Table 3). This result indicates that the concentrations of 'OH-forming chromophores (e.g., $\text{NO}_2^-$) and 'OH sinks are generally correlated. For the Tenerife cloud samples the large drops had a higher 'OH steady state, primarily due to a much smaller value of $k_{\text{OH}}$, but values of $[\text{OH}]_{\text{WIN}}$ for both cloud samples were within a factor of 2 of the fog waters (Table 3). As noted previously for $R_{\text{OH}}$, the values of $[\text{OH}]$ in the Tenerife samples under summer solstice sunlight would be approximately two times greater than reported values of $[\text{OH}]_{\text{WIN}}$.

### 3.3. Hydroxyl radical with 313 nm light

As shown in Table 3, two Davis bulk fog waters, DA97-A01 and DA98-09F, were studied with 313 nm illumination. Apparent quantum yields for 'OH formation at 313 nm, $\Phi_{\text{OH,313}}$, for these two samples were $(0.64 \pm 0.03) \times 10^{-3}$ and $(1.0 \pm 0.39) \times 10^{-3}$, respectively (where the uncertainties are one standard error). These values are $\sim 2$--3 times smaller than the apparent quantum yields measured for New York cloud waters with 313 nm illumination (Arakaki and Faust, 1998). However, because the $\Phi_{313}$ values of the Davis fog waters are $\sim 10$ times higher than the New York cloud waters, and since the rate of 'OH formation is proportional to the product $\Phi_{\text{OH,313}} \times \Phi_{\text{313}}$ (Anastasio et al., 1994), 'OH formation rates at 313 nm in the Davis fog waters will be $\sim 3$--5 times greater than those in the New York cloud waters. The two values of $R_{\text{OH,WIN}}$ calculated from $\Phi_{\text{OH,313}}$ appear to be overestimated by a factor of 2 based on data from DA97-A01 (Table 3). This suggests that $\Phi_{\text{OH}}$ is not constant for all wavelengths (as assumed in the calculation) but rather that it decreases with increasing wavelength.

### 3.4. Singlet molecular oxygen ($^1\text{O}_2$)

Winter-solstice normalized rates of $^1\text{O}_2$ formation in six bulk fog waters from Davis were in the range $(0.86$--$4.8) \times 10^{-4}$ M h$^{-1}$, while steady-state concentrations ranged from $(1.1$--$6.1) \times 10^{-13}$ M and had an average value of $2.2 \times 10^{-13}$ M (Table 4). These values are similar to previously reported levels in cloud waters from NC, NY, VA and WA (Faust and Allen, 1992). For example, adjusting the Durham, NC equinox-normalized steady-state concentrations of Faust and Allen ($\theta = 36^\circ$; $j_{2\text{NB}} = 0.0101$ s$^{-1}$) to our measured value of $j_{2\text{NB,WIN}}$ (0.0070 s$^{-1}$) yields a range of $[^1\text{O}_2^\text{WIN}]$ values of $(0.19$--$7.6) \times 10^{-13}$ M and an average value of $2.6 \times 10^{-13}$ M for the cloud waters. This similarity between the cloud and fog waters is somewhat surprising given that organic chromophores are likely an important source of $^1\text{O}_2$ in atmospheric waters (Faust and Allen, 1992) and, in general, organic carbon concentrations in Davis fogs are typically about twice as high as levels in continental cloud waters (Anastasio, 1994).

There was no detectable loss of FFA in the collector rinse water tested (Table 4), indicating that the presence of singlet-oxygen-generating chromophores in our
samples were not a result of sample collection or handling. Calculation of $f_{\text{FFA/O}_2}$ revealed that 35–89% of FFA loss in the fog waters was due to $^{1}\text{O}_2$ (Table 4). This wide range indicates that, rather than assuming a constant value for $f_{\text{FFA/O}_2}$, the use of FFA as a probe for $^{1}\text{O}_2$ in hydrometeors should be coupled with D$_2$O experiments so that values of $R_{\text{O}_2}$ and $[^3\text{O}_2]$ can be more accurately determined.

### 3.6. Importance of aqueous $^{\cdot}\text{OH}$ and $^{1}\text{O}_2$ as sinks for tropospheric trace species

The overall atmospheric lifetimes for compounds that partition appreciably into aqueous drops is determined in part by aqueous phase reactions such as oxidation by $^{\cdot}\text{OH}$ and $^{1}\text{O}_2$. In fog drops with a typical $^{\cdot}\text{OH}$ concentration of $5 \times 10^{-16}$ M (Table 3), the lower bound for the lifetime of a trace species, with respect to reaction with $^{\cdot}\text{OH}$, is approximately 55 h (assuming a diffusion-limited second-order rate constant of $1 \times 10^{10}$ M$^{-1}$ s$^{-1}$; Ross et al., 1994). Because the effective concentration of $^{\cdot}\text{OH}$ (aq) will be higher as a result of gas-to-drop partitioning, and since the importance of this partitioning increases with decreasing drop size, the lifetime of trace aqueous species with respect to reaction with $^{\cdot}\text{OH}$ will be lower in smaller drops.

Singlet oxygen reacts rapidly with a number of atmospheric pollutants such as furans, phenols, polycyclic aromatic hydrocarbons, and reduced sulfur species (Wilkinson et al., 1995). At our average fog water $^{1}\text{O}_2$ concentration of $2.2 \times 10^{-13}$ M (Table 4), examples of lifetimes for a range of electron-rich trace species include: 2,3-dimethyl, 2-butene (12 h); 9,10-dimethylanthracene (4.2 h); 2,6-dimethoxyphenol (35 h); 2,5-dimethylfuran (1.5 h); indole (18 h), and diethyl sulfide (63 h). As shown in a companion paper (McGregor and Anastasio, 2000), $^{1}\text{O}_2$ can also be a significant sink for some amino acids in fog drops.

### Table 4

Singlet oxygen ($^{1}\text{O}_2$) in bulk fog waters studied with simulated sunlight

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{10^4}R_{\text{O}_2,\text{WIN}}$ (M h$^{-1}$)</th>
<th>$^{10^{13}}[^3\text{O}<em>2]</em>{\text{WIN}}$ (M)</th>
<th>$f_{\text{FFA/O}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA97-A01</td>
<td>1.1 ± 0.23</td>
<td>1.4 ± 0.29</td>
<td>$0.37 \pm 0.082$</td>
</tr>
<tr>
<td>DA97-05F</td>
<td>1.0 ± 0.39</td>
<td>1.3 ± 0.50</td>
<td>0.35 ± 0.13</td>
</tr>
<tr>
<td>DA98-05F</td>
<td>1.5 ± 0.38</td>
<td>1.9 ± 0.49</td>
<td>0.57 ± 0.15</td>
</tr>
<tr>
<td>DA98-06F</td>
<td>1.3 ± 0.65</td>
<td>1.6 ± 0.83</td>
<td>0.46 ± 0.24</td>
</tr>
<tr>
<td>DA98-11F</td>
<td>4.8 ± 0.61</td>
<td>6.1 ± 0.81</td>
<td>0.89 ± 0.12</td>
</tr>
<tr>
<td>DA98-14F</td>
<td>$0.86 \pm 0.19$</td>
<td>1.1 ± 0.25</td>
<td>0.68 ± 0.34</td>
</tr>
<tr>
<td>DA97R02F</td>
<td>$\leq 0.08^c$</td>
<td>$\leq 0.1^d$</td>
<td>—</td>
</tr>
</tbody>
</table>

*a Listed uncertainties are 1 standard error.
*b The fraction of FFA lost due to reaction with $^{1}\text{O}_2$; see Eq. (12).
*c Rinse water.
*d Upper bounds based on simulated sunlight illumination ($f_{\text{2NB,EXP}} = 0.021$ s$^{-1}$) of sample where there was no detectable loss of FFA after 120 min of illumination.
4. Conclusions

Based on our measured rates, the aqueous-phase photoformation of \( \cdot \text{OH} \) in fog waters from Davis, CA is a significant source of \( \cdot \text{OH} \) to these hydrometeors, especially for larger drops. This photoformed \( \cdot \text{OH} \), in conjunction with \( \cdot \text{OH} \) partitioned from the gas phase, can be an important sink for recalcitrant drop constituents. Nitrite was the dominant source of photoformed \( \cdot \text{OH} \) in the fog drops, while nitrate was typically a minor source. Our measured lifetimes for \( \cdot \text{OH} \) (0.38–1.5 \( \mu \)s) are significantly shorter than those contained within computer models of cloudy/foggy atmospheres (e.g., Jacob et al., 1989), indicating that these models are missing sinks for \( \cdot \text{OH} \). Unidentified dissolved organic compounds are likely to be an important component of this missing \( \cdot \text{OH} \) sink.

In situ photoformation is the dominant source of singlet molecular oxygen to Central Valley fog drops, and it might also be a significant source of \( ^{1}\text{O}_2^* \) to the gas phase, subject to mass transport limitations on evaporation. While \( ^{1}\text{O}_2^* \) is a much more selective oxidant compared to \( \cdot \text{OH} \), it is likely an important sink for a number of electron-rich trace constituents in hydrometeors. Overall, it is clear from our results that a comprehensive understanding of the chemistry of foggy/cloudy atmospheres will require inclusion of aqueous-phase oxidant photoformation. Similar photooxidations in aqueous aerosols probably also significantly affect the chemistry of tropospheric particulate matter.

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