Hydroxyl radical-induced photochemical formation of dicarboxylic acids from unsaturated fatty acid (oleic acid) in aqueous solution

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Abstract

In this study, we assess under laboratory controlled conditions the direct and hydroxyl radical (OH)-induced photochemical production of low molecular weight (LMW) dicarboxylic acids and related compounds (C_2-C_9) (DCAs) from oleic acid (cis-9-octadecenoic, 9C_{18}) in aqueous solution. Nitrate (NO_3^-)-amended and unamended oleate solutions were irradiated under ultraviolet-B radiation (UV-B, 313 nm) for 5 h, with NO_3^- being the source of OH. The OH-induced photochemical production of DCAs (C_{2di}-C_{9di}) (165 ± 32 nM h^{-1}) was much higher than that induced by the direct effect of UV-B (33 ± 31 nM h^{-1}), accounting for 85% of the total (direct + OH-induced) photochemical production of DCAs (C_{2di}-C_{9di}) (194 ± 6 nM h^{-1}). Azelaic acid (C_{9di}) was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and OH-induced photochemical production, respectively) followed by C_{8di}, C_{7di} and C_{6di}, whereas shorter chain compounds (C_{2di}-C_{5di}) were minor produced species. Using our estimate of OH photoproduction (P-OH in nM h^{-1}), the production of C_{9di} from 50 µM of oleic acid was evaluated to ~ 36 nM (nM OH)^{-1}. We propose in this work a chemical mechanism for the reaction of OH with oleic acid in aqueous solution from the cleavage of its double bond, and the subsequent formation of DCAs through oxidation and decarboxylation processes.

Keywords: Oleic acid; dicarboxylic acids; hydroxyl radical; nitrate; UV-B radiation
1. Introduction

Low molecular weight (LMW) dicarboxylic acids and related compounds (C_2-C_9) (DCAs) are ubiquitous water soluble organic compounds that have been detected in a variety of environmental samples including atmospheric aerosols [1], rain waters [2], ice cores [3], marine sediments [4], fresh waters [5] and seawater [6]. Because of their hygroscopic properties, DCAs can act as cloud condensation nuclei and have an impact on the radiative forcing at the Earth’s surface [7]. In atmospheric aerosols, one of the major sources of DCAs is direct and sensitized photooxidation of unsaturated hydrocarbons and fatty acids [8,9,10]. Sensitized photooxidation is initiated by powerful oxidizing agents such as ozone (O_3), hydroxyl radical (OH) and nitrate radical (NO_3), which are produced by the interactions between ultraviolet-B radiation (UV-B: 280-315 nm) and volatile organic compounds and nitrogen oxides.

The reaction of oleic acid (cis-9-octadecenoic, 9C_{18}) with O_3, OH and NO_3 has recently emerged as a model system to better understand the photooxidation processes affecting unsaturated fatty acids in atmospheric aerosols [11,12]. Oleic acid is degraded through an oxidative cleavage of its double bond to produce C_9 compounds, i.e., nonanoic (C_9), 9-oxononanoic (ωC_9) azelaic (C_{9di}) acids and 1-nonanal (C_{9ald}) [13,14,15,16] as well as nitrated carboxylic acids [12]. Secondary photooxidation reactions could initiate the production of lower molecular weight DCAs such as C_{2di}-C_{8di} [9,17,18]. Although the production of DCAs from photooxidation of unsaturated fatty acids has been largely studied in the atmospheric aerosols, little is known about the direct and sensitized photoproduction of DCAs in aqueous solutions. In seawater, it has been shown that oleic acid, which is produced by phytoplankton [19], was directly photooxidized to produce ωC_9 and C_{9ald} [20]. However, there is no report of concentrations of a homologous series of DCAs from these.
photooxidation processes. In natural waters, many photochemical reactions are driven by \( \text{OH} \),
which is one of the most reactive oxidants \( (E = +1.83 \text{ V}) \) [21,22,23]. Major sources of \( \text{OH} \) in
natural waters are the nitrate (\( \text{NO}_3^- \)) and nitrite (\( \text{NO}_2^- \)) photolysis, initiated by UV-B and UV-
A (315-400 nm), respectively, as well as the photolysis of colored dissolved organic matter
(CDOM), initiated by both UV-B and UV-A [24,25,26]. Photochemical oxidation reactions
may substantially modify molecular distribution and bacterial availability of dissolved organic
compounds in natural waters and then play a significant role in aquatic carbon cycle [27,28].

The objective of this study is to assess under laboratory controlled conditions the direct
and \( \text{OH} \)-induced photochemical production of DCAs from oleic acid in aqueous solution
(pure water). \( \text{NO}_3^- \) was chosen as photosensitizer and source of \( \text{OH} \) radicals since \( \text{(i)} \)
quantum yield of \( \text{OH} \) formation \( (\Phi_{\text{OH}}) \) from \( \text{NO}_3^- \) photolysis is well known [25,26,29], \( \text{(ii)} \)
\( \text{NO}_3^- \) is very poor \( \text{OH} \) scavenger \( (k < 1.10^5 \text{ s}^{-1}) \) compared to \( \text{NO}_2^- \) \( (k = 1.10^{10} \text{ s}^{-1}) \) in aqueous
solutions [25] and \( \text{(iii)} \) in natural waters \( \text{NO}_3^- \) is often found in much higher concentrations
than \( \text{NO}_2^- \). The production of \( \text{OH} \) from the UV-B photolysis of \( \text{NO}_3^- \) is described by the
equations [30,31]:

\[
[\text{NO}_3^- + \text{UV-B} \rightarrow \text{NO}_3^-]^* \tag{1}
\]

\[
[\text{NO}_3^-]^* \rightarrow \text{NO}_2^- + \text{O}^- \tag{2}
\]

\[
\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^- \tag{3}
\]
2. Materials and methods

2.1. Irradiation experiment

Sodium oleate (99% purity, Sigma, 50 µM final concentration) was added to 0.2-µm filtered Milli-Q water (final resistivity > 18 MΩ cm⁻¹). The pH of Milli-Q water was 6 before adding oleate and 7.6 after the dissolution. To stimulate the production of OH, a subsample of the oleate solution was amended with NO₃⁻ (Fluka, 15 µM final concentration). The NO₃⁻-amended and unamended oleate solutions were then dispensed into precombusted (450°C for 6 h) quartz and glass (Pyrex) tubes (100 ml volume) that were sealed with ultraclean (extensively rinsed with 1 N HCl and Milli-Q water) silicone stoppers wrapped in Teflon foil. The tubes were irradiated for 5 h under two UV-B fluorescent lamps emitting mainly at 313 nm (Q-Panel UVB-313, 40W) at controlled room temperature (15 ± 1°C). Quartz tubes, which were used for the UV-B condition, were wrapped in 95 µm cellulose diacetate filter to remove residual UV-C (200-280 nm) of the lamps (Fig. 1). Pyrex tubes were wrapped in aluminum foil for the dark controls. Duplicate samples were exposed for each light/NO₃⁻ treatment. Subsamples for DCA analysis were collected before (T0) and after (T5) 5-h irradiation and stored in 250-ml precombusted glass bottles poisoned with HgCl₂ (10 mg l⁻¹ final concentration) at 4°C in the dark until measurements.

Irradiance of the UV-B lamps was measured with a IL-1700 broadband radiometer (International Light) equipped with a UV-B probe (SUD240, International Light) covered by cellulose diacetate filter. Irradiance received by the samples was controlled by the distance between lamps and tubes. It was fixed at 4.10⁵ W cm⁻², which approximately corresponds to a natural UV-B irradiance at solar noon in summer in mid-latitudes. Irradiance integrated over 5-h irradiation was 7.45 10¹ J cm⁻².
2.2. Measurement of dicarboxylic acids and related compounds

DCAs were measured by gas chromatography and flame ionization detection (GC/FID) after butyl ester derivatization [32]. The sample (50 ml) was first concentrated down to 3-4 ml using a rotary evaporator under a vacuum, then transferred into a 25 ml pear-shaped flask, further concentrated by the rotary evaporator and finally concentrated to almost dryness under a nitrogen stream. A total of 0.25 ml of 14% BF$_3$/n-butanol was immediately added to the sample and the flask was sealed with a glass stopper, Teflon tape and clamp. The organic acids and reagent were mixed under ultrasonication for 1 min and then heated at 100°C for 30 min to derive dibutyl esters for carboxyl group and dibutoxy acetal for aldehyde group. The derivatives were extracted with 5 ml of n-hexane after adding 3 ml of Milli-Q water and 0.2 ml of acetonitrile. The hexane layer was further washed with Milli-Q water (3 × 3 ml). The esters were dried by using a rotary evaporator, then a nitrogen stream and were finally dissolved in 100 µl of n-hexane prior to GC/FID determination. The dibutyl esters were determined with a Hewlett Packard 5890 gas chromatograph equipped with a split/splitless injector, a fused silica capillary column (HP-5, 25 m × 0.32 mm × 0.52 µm) and an FID detector. Peak identification was performed by a comparison of GC retention times with those of dibutyl ester standards.

2.3. Assessment of OH photoproduction

OH photoproduction (P-OH) from the UV-B irradiation of 15 µM NO$_3^-$ was assessed using the following photochemical equation:

$$P\text{-OH}(313) = E_0(313) \times a(313) \times \Phi_{\text{OH}}(313)$$

(4)

Where P-OH(313) is production of OH at 313 nm (in nM h$^{-1}$), $E_0(313)$ is irradiance received by the samples at 313 nm (4.10$^{-5}$ W cm$^{-2}$ which corresponds to 0.0072 mol photon m$^{-2}$ h$^{-1}$), $a(313)$ is absorption coefficient of 15 µM NO$_3^-$ at 313 nm (0.027 m$^{-1}$; Fig. 2) and $\Phi_{\text{OH}}(313)$ is quantum yield of OH formation from NO$_3^-$ photolysis at 313 nm used from [29] (1.3% at
20°C and pH 6.2-8.2) that we corrected by temperature effect according to the following formula [33]:

\[
\Phi_{\text{OH}}(288 \text{ K}) = \Phi_{\text{OH}}(298 \text{ K}) \exp \left( \frac{1800 \pm 480}{298 - 1/288} \right)
\]

The value of \( \Phi_{\text{OH}}(313) \) we used for 15°C was 1.05%. Consequently, P-OH in the NO\(^3\)-amended oleate solutions exposed to UV-B was estimated to be \( \sim 2 \text{ nM h}^{-1} \).

3. Results and Discussion

Table 1 presents the concentrations of DCAs (C\(_{2di}\)-C\(_{9di}\), \( \omega \)C\(_{9}\)) detected in the oleate solutions before and after 5-h irradiation. We observed that the total concentration of DCAs after irradiation under UV-B in the presence of NO\(^3\) (T5 UV-B + NO\(^3\)) (1140 ± 30 nM) was much higher than that under UV-B alone (T5 UV-B) (314 ± 156 nM) (Table 1). 9-oxononanoic acid (\( \omega \)C\(_{9}\)) was not detected in the different samples, whereas azelaic acid (C\(_{9di}\)) was found as the dominant species, accounting for \( \sim 36\% \) and \( 42\% \) of the total DCA concentration in conditions T5 UV-B and T5 UV-B + NO\(^3\), respectively (Table 1). These concentrations are closed to that found recently in Mediterranean surface seawater samples (700-730 nM) [6].

In order to evaluate the photochemical production of DCAs (in nM h\(^{-1}\)) from the 5-h irradiation of oleic acid, the concentrations reported in Table 1 for UV-B conditions were corrected for the corresponding “dark” and then divided by a factor 5. Direct (UV-B-induced), OH-induced and total (direct + OH-induced) photochemical productions of DCA were determined by subtracting the DCA concentration in UV-B by that in dark ([DCA]\(_{T5 \text{ UV-B}}\) - [DCA]\(_{T5 \text{ dark}}\)), the DCA concentration in UV-B + NO\(^3\) by that in UV-B ([DCA]\(_{T5 \text{ UV-B + NO3}}\) - [DCA]\(_{T5 \text{ UV-B}}\)) and the DCA concentration in UV-B + NO\(^3\) by that in dark + NO\(^3\) ([DCA]\(_{T5 \text{ UV-B + NO3}}\) - [DCA]\(_{T5 \text{ dark + NO3}}\)), respectively. The photochemical productions of each DCA were then summing to obtain the photochemical production of total DCAs (C\(_{2di}\)-C\(_{9di}\)) (Fig. 3).
Clearly, the OH-induced photochemical production of DCAs (165 ± 32 nM h⁻¹) was much higher than that induced by the direct effect of UV-B (33 ± 31 nM h⁻¹), accounting for 85% of the total (direct + OH-induced) photochemical production of DCAs (194 ± 6 nM h⁻¹) (Fig. 3). Consequently, the UV-B photolysis of NO₃⁻ and the subsequent production of OH (P-OH ~ 2 nM h⁻¹) and its reaction with oleic acid is much more efficient in producing DCAs (from C₉di to C₉di) than the direct effect of UV-B on oleic acid, the latter leading only to the production of DCAs from C₉di to C₇di (Fig. 3). C₉di was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and OH-induced photochemical production, respectively) followed by C₈di, C₇di and C₆di, whereas shorter chain compounds (C₄di–C₅di) were minor species (OH-induced production) or not detected as photoproducts (direct production) (Fig. 3). The OH-induced photochemical degradation of oleic acid led to a C₉di production of 72 ± 16 nM h⁻¹ (Fig. 3). Therefore, using our P-OH calculated value of 2 nM h⁻¹, the production of C₉di from 50 µM of oleic acid in aqueous solution can be assessed to ~ 36 nM (nM OH)⁻¹.

The total photochemical production of DCAs (C₂di–C₉di) for 5-h irradiation (971 nM) represents 7.4 µM C and thus account for 0.8% of the initial concentration of oleic acid (900 µM C). In addition to DCAs (C₂di–C₉di), many other intermediates and photochemically stable compounds are likely produced from the OH-induced degradation of oleic acid in aqueous solution. For atmospheric aerosols, some authors reported the photoproduction of C₉, ωC₉, C₉di and C₉aldr as well as nitrated carboxylic acids from the reaction of oleic acid with OH, O₃ or NO₃ [12,13,14,15,16]. In this study, C₉ and C₉aldr could not be determined using our GC/FID technique. However, ωC₉ was found to be below the detection limit in the samples, suggesting that this compound, once produced from oleic acid, was immediately oxidized into C₉di.

A chemical mechanism for the reaction of OH radicals with oleic acid in aqueous solution and the subsequent formation of DCAs (C₂di–C₉di) is proposed in Figure 4. Both the
action of OH that is produced by the UV-B photolysis of NO$_3^-$, and dissolved oxygen (O$_2$) in the aqueous solution, leads to the cleavage of the double bond of oleic acid and to the production of two C$_9$ compounds, i.e., $\omega$C$_9$ and C$_{9\text{di}}$. From the action of both $^\bullet$OH and O$_2$, $\omega$C$_9$ is oxidized into C$_{9\text{di}}$. The oxidation of DCAs is assumed occurring via H-atom abstraction by OH followed by the O$_2$-induced formation of peroxy radical. From C$_{9\text{di}}$, other DCAs (C$_{8\text{di}}$ to C$_{2\text{di}}$) are then produced through oxidation and decarboxylation processes involving the formation of hydroxy diacid, keto diacid, $\omega$ketoacid and diacid (C$_{{n-1}\text{di}}$).

This study clearly shows that OH efficiently produces DCAs, especially C$_{9\text{di}}$, from unsaturated fatty acids in aqueous solution. As regard to the experimental conditions we used, including pH, temperature, irradiance as well as NO$_3^-$ and oleate concentrations, we can expect to have, qualitatively, similar C$_{2\text{di}}$–C$_{9\text{di}}$ photochemical production in various natural waters including fresh, river and rain waters. However, in seawater, OH, which reacts almost exclusively with bromide ion (Br$^-$) to generate the less reactive dibromide anion (Br$_2^-$), is unlikely as efficient in degrading unsaturated fatty acids [22,34].
Acknowledgments

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References


Figure legends

**Figure 1.** Transmittance of light via cellulose diacetate filter.

**Figure 2.** UV absorption spectrum of 15 µM NO$_3^-$ in Milli-Q water measured using a Shimadzu UV-1605 spectrophotometer equipped with a 10-cm quartz cuvette.

**Figure 3.** Direct ([DCA]$_{T5\text{ UV-B}}$ - [DCA]$_{T5\text{ dark}}$), OH-induced ([DCA]$_{T5\text{ UV-B + NO3-}}$ - [DCA]$_{T5\text{ UV}}$) and total (direct + OH-induced) ([DCA]$_{T5\text{ UV-B + NO3-}}$ - [DCA]$_{T5\text{ dark + NO3-}}$) photochemical production of DCAs (C$_{2\text{di}}$-C$_{9\text{di}}$) (in nM h$^{-1}$) from UV-B irradiation of 50 µM oleic acid in aqueous solution.

**Figure 4.** Proposed chemical mechanism for the reaction of OH with oleic acid in aqueous solution and the subsequent formation of DCAs (C$_{2\text{di}}$-C$_{9\text{di}}$) through oxidation and decarboxylation processes.
Table I. Concentrations (in nM) of dicarboxylic acids ($C_{2\text{di}}$-$C_{9\text{di}}$) and oxocarboxylic acid ($\omega C_9$) in the $NO_3^-$-amended and unamended oleate solutions before (T0) and after (T5) 5-h irradiation under UV-B lamps or in the dark.

<table>
<thead>
<tr>
<th>compounds</th>
<th>T0</th>
<th>T0 + $NO_3^-$</th>
<th>T5 dark</th>
<th>T5 dark + $NO_3^-$</th>
<th>T5 UV-B</th>
<th>T5 UV-B + $NO_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic acid, $C_{2\text{di}}$</td>
<td>25</td>
<td>41</td>
<td>33 ± 15</td>
<td>27 ± 6</td>
<td>23 ± 7</td>
<td>60 ± 5</td>
</tr>
<tr>
<td>malonic acid, $C_{3\text{di}}$</td>
<td>14</td>
<td>9</td>
<td>18 ± 21</td>
<td>8 ± 4</td>
<td>5 ± 1</td>
<td>39 ± 1</td>
</tr>
<tr>
<td>succinic acid, $C_{4\text{di}}$</td>
<td>14</td>
<td>11</td>
<td>7 ± 0</td>
<td>10 ± 0</td>
<td>8 ± 1</td>
<td>31 ± 7</td>
</tr>
<tr>
<td>glutaric acid, $C_{5\text{di}}$</td>
<td>10</td>
<td>2</td>
<td>2 ± 2</td>
<td>3 ± 4</td>
<td>2 ± 1</td>
<td>24 ± 35</td>
</tr>
<tr>
<td>adipic acid, $C_{6\text{di}}$</td>
<td>116</td>
<td>102</td>
<td>97 ± 4</td>
<td>92 ± 6</td>
<td>72 ± 14</td>
<td>198 ± 38</td>
</tr>
<tr>
<td>pimelic acid, $C_{7\text{di}}$</td>
<td>30</td>
<td>22</td>
<td>10 ± 8</td>
<td>6 ± 4</td>
<td>27 ± 32</td>
<td>156 ± 42</td>
</tr>
<tr>
<td>suberic acid, $C_{8\text{di}}$</td>
<td>31</td>
<td>25</td>
<td>21 ± 20</td>
<td>9 ± 6</td>
<td>63 ± 68</td>
<td>156 ± 30</td>
</tr>
<tr>
<td>azelaic acid, $C_{9\text{di}}$</td>
<td>37</td>
<td>39</td>
<td>11 ± 2</td>
<td>14 ± 1</td>
<td>114 ± 75</td>
<td>476 ± 30</td>
</tr>
<tr>
<td>9-oxononanoic, $\omega C_9$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>277</td>
<td>251</td>
<td>199 ± 7</td>
<td>169 ± 5</td>
<td>314 ± 156</td>
<td>1140 ± 30</td>
</tr>
</tbody>
</table>

For T5 conditions, averaged concentrations are given with a standard deviation based on duplicate samples exposed in the same light/$NO_3^-$ conditions.
Figure 1
Figure 2
Figure 3
Figure 4