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Short communication

# 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 ($^{\bullet}$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, $\Delta 9C_{18}$) 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 $^{\bullet}$OH. The $^{\bullet}$OH-induced photochemical production of DCAs ($C_{2di}$–$C_{9di}$) ($170 \pm 26$ nM h$^{-1}$) was much higher than that induced by the direct effect of UV-B ($33 \pm 22$ nM h$^{-1}$), accounting for approximately 85% of the total (direct + $^{\bullet}$OH-induced) photochemical production of DCAs ($C_{2di}$–$C_{9di}$) ($198 \pm 15$ nM h$^{-1}$). Azelaic acid ($C_{9di}$) was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and $^{\bullet}$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 $^{\bullet}$OH photoproduction (P-OH in nM h$^{-1}$), the production of $C_{9di}$ from 50 μM of oleic acid was evaluated at ∼45 nM (nM $^{\bullet}$OH)$^{-1}$.

*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 [8–10]. Sensitized photooxidation is initiated by powerful oxidizing agents such as ozone ($O_3$), hydroxyl radical ($^{\bullet}$OH) and nitrate radical ($NO_3^{\bullet}$), 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, $\Delta 9C_{18}$) with $O_3$ and $NO_3^{\bullet}$ 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 ($\omega C_9$), azelaic ($C_{9di}$) acids and 1-nonanal ($C_{9ald}$) [13–16] 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 produc-

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tion 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 $\omega C_9$ 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 $^{\bullet}OH$, which is one of the most reactive oxidants ($E = +1.83$ V) [21–23]. Major sources of $^{\bullet}OH$ in natural waters are the nitrate ($NO_3^-$) and nitrite ($NO_2^-$) 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 [24–26]. 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 the aquatic carbon cycle [27,28].

The objective of this study is to assess under laboratory controlled conditions the direct and $^{\bullet}OH$-induced photochemical production of DCAs from oleic acid in aqueous solution (pure water). $NO_3^-$ was chosen as a photosensitizer and source of $^{\bullet}OH$ radicals since: (i) the quantum yield of $^{\bullet}OH$ formation ($\Phi_{OH}$) from $NO_3^-$ photolysis is well known [25,26,29], (ii) $NO_3^-$ is a very poor $^{\bullet}OH$ scavenger ($k < 1.10^5\ s^{-1}$) compared to $NO_2^-$ ($k = 1.10^{10}\ s^{-1}$) in aqueous solutions [25] and (iii) in natural waters $NO_3^-$ is often found in much higher concentrations than $NO_2^-$. The production of $^{\bullet}OH$ from the UV-B photolysis of $NO_3^-$ is described by the equations [30,31]:

$$[NO_3^- + \text{UV-B} \rightarrow NO_3^-]^* \tag{1}$$

$$[NO_3^-]^* \rightarrow NO_2^{\bullet} + O^{\bullet -} \tag{2}$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \tag{3}$$

## 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 $^{\bullet}OH$, a subsample of the oleate solution was amended with $NO_3^-$ (Fluka, 15 μM final concentration). The $NO_3^-$-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, 40 W) 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. Pyrex tubes were wrapped in aluminum foil for the dark controls. Duplicate samples were exposed for each light/$NO_3^-$ 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 $HgCl_2$ (10 mg l$^{-1}$ final concentration) at 4 °C in the dark until measurements.

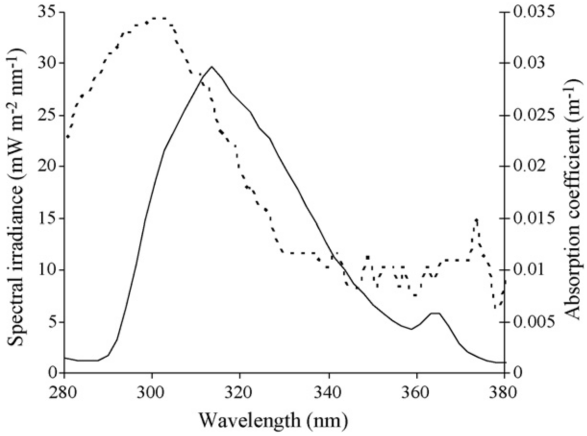

Fig. 1. Spectral irradiance of the UV-B lamps measured with a UV/vis spectroradiometer RAMSES (TriOS, Ger.) covered by cellulose diacetate filter (—) and UV absorption coefficient of 15 μM $NO_3^-$ in Milli-Q water measured using a Shimadzu UV-1605 spectrophotometer equipped with a 10 cm quartz cuvette (- - -).

Spectral irradiance of the UV-B lamps was measured with 2 nm resolution using a UV/vis spectroradiometer RAMSES (TriOS, Ger.) covered by a cellulose diacetate filter (Fig. 1). Irradiance received by the samples was controlled by the distance between lamps and tubes. Integrated irradiance over the UV-B range (280–315 nm) was 0.5 W m$^{-2}$. The UV-B irradiance integrated over 5 h irradiation was 9 kJ m$^{-2}$, which approximately corresponds to the exposure of a sample during 1.5 h at solar noon in summer in mid-latitudes.

### 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 $^{\bullet}$OH photoproduction

$^{\bullet}$OH photoproduction (P-OH) from the irradiation of 15 μM $NO_3^-$ was assessed over the UV-B spectral domain (280–315 nm) using the following photochemical equation:

$$\text{P-OH} = J \int_{280\,\text{nm}}^{315\,\text{nm}} E_0(\lambda) \times a(\lambda) \times \Phi_{\text{OH}}(\lambda)\,\mathrm{d}\lambda \qquad (4)$$

where P-OH is the production of $^{\bullet}$OH (mol $l^{-1}$ $h^{-1}$), $E_0(\lambda)$ the spectral irradiance received by the samples (mW $m^{-2}$ $nm^{-1}$, converted into mol photon $m^{-2}$ $h^{-1}$ $nm^{-1}$; Fig. 1), $a(\lambda)$ the absorption coefficient of 15 μM $NO_3^-$ in Milli-Q water ($m^{-1}$; Fig. 1) and $\Phi_{\text{OH}}(\lambda)$ is the quantum yield of $^{\bullet}$OH formation from $NO_3^-$ photolysis in aqueous solution. With regard to the literature data [25,29,33], we assumed here an average $\Phi_{\text{OH}}$ over the spectral domain 280–315 nm equal to 0.6%. $J$ is a unit conversion factor (0.001 $m^3$ $l^{-1}$). Consequently, P-OH in the $NO_3^-$-amended oleate solutions exposed to UV-B was estimated to be ∼1.6 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 + $NO_3^-$) (1165 ± 72 nM) was much higher than that under UV-B alone (T5 UV-B) (314 ± 107 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 ∼36 and 42% of the total DCA concentration in conditions T5 UV-B and T5 UV-B + $NO_3^-$, respectively (Table 1). In some duplicate samples, glutaric acid ($C_{5di}$) was detected but its concentration was too close to detection limit (i.e. ∼1 nM for all the compounds) to be accurately quantified. The concentrations of DCAs reported here are close to those found recently in Mediterranean surface seawater samples (700–730 nM) [6].

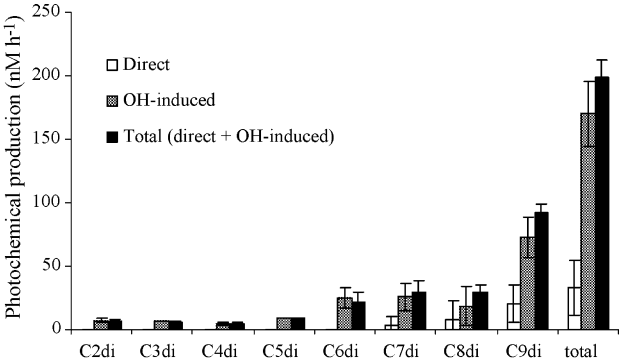

Fig. 2. Direct ($[DCA]_{T5\ UV\text{-}B} - [DCA]_{T5\ dark}$), $^{\bullet}$OH-induced ($[DCA]_{T5\ UV\text{-}B+NO_3^-} - [DCA]_{T5\ UV\text{-}B}$) and total (direct + $^{\bullet}$OH-induced) ($[DCA]_{T5\ UV\text{-}B+NO_3^-} - [DCA]_{T5\ dark+NO_3^-}$) photochemical production of DCAs ($C_{2di}$–$C_{9di}$) (nM $h^{-1}$) from UV-B irradiation of 50 μM oleic acid in aqueous solution.

In order to evaluate the photochemical production of DCAs (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 control" and then divided by a factor 5. Direct (UV-B-induced), $^{\bullet}$OH-induced and total (direct + $^{\bullet}$OH-induced) photochemical productions of DCA were determined by subtracting the DCA concentration in UV-B by that in dark ($[DCA]_{T5\ UV\text{-}B} - [DCA]_{T5\ dark}$), the DCA concentration in UV-B + $NO_3^-$ by that in UV-B ($[DCA]_{T5\ UV\text{-}B+NO_3^-} - [DCA]_{T5\ UV\text{-}B}$) and the DCA concentration in UV-B + $NO_3^-$ by that in dark + $NO_3^-$ ($[DCA]_{T5\ UV\text{-}B+NO_3^-} - [DCA]_{T5\ dark+NO_3^-}$), respectively. The photochemical production of total DCAs ($C_{2di}$–$C_{9di}$) was then obtained by summing the photochemical productions of each DCA (Fig. 2).

Table 1

Concentrations (nM) of dicarboxylic acids ($C_{2di}$–$C_{9di}$) 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

| Compounds | T0 | T0 + $NO_3^-$ | T5 dark | T5 dark + $NO_3^-$ | T5 UV-B | T5 UV-B + $NO_3^-$ |
|---|---|---|---|---|---|---|
| Oxalic acid, $C_{2di}$ | 25 | 41 | 33 ± 15[a] | 27 ± 6 | 23 ± 7 | 60 ± 5 |
| Malonic acid, $C_{3di}$ | 14 | 9 | 18 ± 21[a] | 8 ± 4 | 5 ± 1 | 39 ± 1 |
| Succinic acid, $C_{4di}$ | 14 | 11 | 7 ± 0 | 10 ± 0 | 8 ± 1 | 31 ± 7 |
| Glutaric acid, $C_{5di}$ | 10 | 2 | 3[b] | 6[b] | 2 ± 1[a] | 49[b] |
| Adipic acid, $C_{6di}$ | 116 | 102 | 97 ± 4 | 92 ± 6 | 72 ± 14 | 198 ± 38 |
| Pimelic acid, $C_{7di}$ | 30 | 22 | 10 ± 8[a] | 6 ± 4[a] | 27 ± 32[a] | 156 ± 42 |
| Suberic acid, $C_{8di}$ | 31 | 25 | 21 ± 20[a] | 9 ± 6[a] | 63 ± 68[a] | 156 ± 30 |
| Azelaic acid, $C_{9di}$ | 37 | 39 | 11 ± 2 | 14 ± 1 | 114 ± 75[a] | 476 ± 30 |
| 9-Oxononanoic, $\omega C_9$ | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 277 | 251 | 200 ± 34 | 172 ± 12 | 314 ± 107 | 1165 ± 72 |

For T5 conditions, averaged concentrations are given with a standard deviation based on duplicate samples exposed in the same light/$NO_3^-$ conditions. $\omega C_9$ was not detected in the different samples.

[a] High variability within duplicate samples but both concentrations were ≫ detection limit (i.e. ∼1 nM for all the compounds).

[b] Concentration is given for only one duplicate sample. In the second one, the compound ($C_{5di}$) was detected but its concentration was too close to detection limit (1 nM) to be accurately quantified.

Clearly, the $^\bullet$OH-induced photochemical production of DCAs ($170 \pm 26$ nM h$^{-1}$) was much higher than that induced by the direct effect of UV-B ($33 \pm 22$ nM h$^{-1}$), accounting for approximately 85% of the total (direct + $^\bullet$OH-induced) photochemical production of DCAs ($198 \pm 15$ nM h$^{-1}$) (Fig. 2). $C_{9di}$ was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and $^\bullet$OH-induced photochemical production, respectively) followed by $C_{8di}$, $C_{7di}$ and $C_{6di}$, whereas shorter chain compounds ($C_{2di}$–$C_{5di}$) were minor species ($^\bullet$OH-induced production) or not detected as photoproducts (direct production) (Fig. 2). The $^\bullet$OH-induced photochemical degradation of oleic acid led to a $C_{9di}$ production of $72 \pm 16$ nM h$^{-1}$ (Fig. 2). Therefore, using our P-OH calculated value of 1.6 nM h$^{-1}$, the production of $C_{9di}$ from 50 μM of oleic acid in aqueous solution can be assessed to ~45 nM (nM $^\bullet$OH)$^{-1}$. The total photochemical production of DCAs ($C_{2di}$–$C_{9di}$) for 5 h irradiation (992 nM) represents 7.6 μM C and thus accounts for 0.8% of the initial concentration of oleic acid (900 μM C).

These results show that the reaction of $NO_3^-$ photolysis-induced $^\bullet$OH with oleic acid is efficient in producing DCAs (from $C_{9di}$ to $C_{2di}$) whereas the direct effect of UV-B on oleic acid does not lead to significant productions of DCAs (Fig. 2). $C_9$ and $C_{9ald}$ could not be determined using our GC/FID technique whereas $\omega C_9$ was not detected in the different samples (Table 1). For the $NO_3^-$-amended oleate samples, both the action of $^\bullet$OH and dissolved oxygen ($O_2$) in the water could lead to the cleavage of the double bond (initiated by $^\bullet$OH addition) and to the production of $\omega C_9$. The latter could be then oxidized into $C_{9di}$ via H-atom abstraction by $^\bullet$OH followed by the $O_2$-induced formation of peroxy radical (ROO$^\bullet$). From $C_{9di}$, other DCAs ($C_{8di}$ to $C_{2di}$) could be then produced through oxidation and decarboxylation processes involving the formation of hydroxy diacid, keto diacid, ωketoacid and diacid ($C_{n-1di}$). This chemical mechanism might be efficient in oxidizing $\omega C_9$ into $C_{9di}$ and in a less extend, in producing other DCAs up to $C_{2di}$ since the main scavenger of $^\bullet$OH in natural waters (i.e. bromide ion, $Br^-$) was not present in our solution. This probably allowed high reaction rates between $^\bullet$OH and oleic acid-derived photoproducts. Therefore, in aqueous solution in the presence of $^\bullet$OH, $\omega C_9$ may be a short-lived intermediate photoproduct because of the $^\bullet$OH-induced H-atom abstraction process. By contrast, in atmospheric aerosols, ozonolysis of oleic acid always results in a significant amount of $\omega C_9$, which is a stable, long-lived species because it does not secondary react with $O_3$ [14–16]. Moreover, in seawater it has been shown that without any production of $^\bullet$OH, the direct action of UV-B and $O_2$ led to the cleavage of the double bond of oleic acid and to the production of $\omega C_9$ as well as $C_{9ald}$ [20].

This study clearly shows that $^\bullet$OH efficiently produces DCAs, especially $C_{9di}$, from unsaturated fatty acids in aqueous solution. With 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 $C_{2di}$–$C_{9di}$ photochemical production in various natural waters including fresh, river and rain waters. However, in seawater, $^\bullet$OH, which reacts almost exclusively with $Br^-$ to generate the less reactive dibromide anion ($Br_2^{\bullet -}$), is unlikely to be as efficient in degrading unsaturated fatty acids [22,34].

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