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Short communication

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

Marc Tedetti [a], Kimitaka Kawamura [b], Masahiro Narukawa [b,1],
Fabien Joux [c], Bruno Charrière [a], Richard Sempéré [a,*]

[a] *Laboratoire de Microbiologie Géochimie et Ecologie Marines (LMGEM), CNRS/INSU, UMR 6117, Centre d'Océanologie de Marseille, Université de la Méditerranée, Campus de Luminy, Case 901, F-13 288 Marseille Cedex 9, France*
[b] *Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo 060-0819, Japan*
[c] *Université Pierre et Marie Curie-Paris-6, CNRS, UMR 7621, F 66650 Banyuls-sur-mer, France*

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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, $\Delta 9C_{18}$) 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 •OH. The •OH-induced photochemical production of DCAs (C_{2di}–C_{9di}) (170 ± 26 nM h^{-1}) was much higher than that induced by the direct effect of UV-B (33 ± 22 nM h^{-1}), accounting for approximately 85% of the total (direct + •OH-induced) photochemical production of DCAs (C_{2di}–C_{9di}) (198 ± 15 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 at ∼45 nM (nM •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 (•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 (ωC_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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[*] Corresponding author. Tel.: +33 4 91 82 92 12; fax: +33 4 91 82 96 41.
E-mail addresses: tedetti@com.univ-mrs (M. Tedetti), kawamura@lowtem.hokudai.ac.jp (K. Kawamura), narukawa@stelab.nagoya-u.ac.jp (M. Narukawa), joux@obs-banyuls.fr (F. Joux), charriere@com.univ-mrs.fr (B. Charrière), sempere@com.univ-mrs.fr (R. Sempéré).

[1] Present address: Solar-Terrestrial Environment Laboratory, Nagoya University, Aichi, Japan.

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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 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 $^{\bullet}OH$, 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 (Φ_{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.

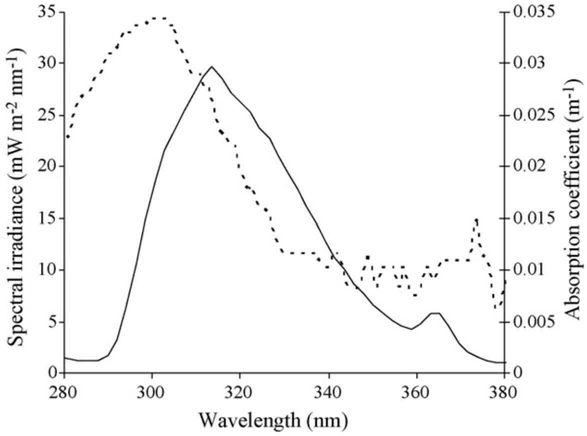

Fig. 1. Spectral irradiance of the UV-B lamps measured with a UV/vis spectroradiometer RAMSES (TriOS, Ger.) covered by cellulose diacetate filter (—) and UV absorption coefficient of 15 μM NO_3^- in Milli-Q water measured using a Shimadzu UV-1605 spectrophotometer equipped with a 10 cm quartz cuvette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

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,