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Heterogeneous photochemistry of dicarboxylic acids on mineral dust

Milena Ponczek, Nathalie Hayeck[&], Corinne Emmelin, Christian George*

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France

[&] Now at the Chemistry Department, Faculty of Arts and Sciences, American University of Beirut, Beirut, Lebanon

*correspondence to: christian.george@ircelyon.univ-lyon1.fr

Abstract

Dicarboxylic acids have low volatilities and hence are present mostly in the particulate phase, including the surface of dust particles. Mineral dust, globally the most emitted aerosol, has photocatalytic properties that can initiate photo-induced heterogeneous chemistry of organic compounds, which is still poorly characterized. We investigated the photochemistry of five dicarboxylic acids (DCA) i.e., succinic (butanedioic) acid, glutaric (pentanedioic) acid, adipic (hexanedioic) acid, pimelic (heptanedioic) acid and suberic (octanedioic) acid on Arizona test dust (ATD) particles upon UV-A light irradiation ($0 - 1.4 \text{ mW cm}^{-2}$). Gas-phase products were monitored by a high-resolution proton-transfer-reaction mass spectrometer (PTR-ToF-MS), and surface sorbed products were extracted and analyzed by ultra-high-performance liquid chromatography coupled to a heated electrospray ionization high-resolution mass spectrometer (UHPLC-HESI-HRMS). Monoacids and aldehydes were the main observed and quantified gaseous products. In contrast, shorter chain DCA and highly oxygenated products were found at the surface of the dust particles. Interestingly, the photochemistry of these DCAs presented an even-odd alternation concerning their heterogeneous reactivity, with odd-numbered carbon diacids being more reactive than their even-numbered homologous ones. We present and discuss a reaction mechanism for the C_4 - C_8 DCA heterogeneous photooxidation catalysed by TiO_2/Fe_2O_3 -rich dust particles. Our results suggest that photochemical processing on dust surfaces should be regarded as a possible efficient pathway for altering their surface properties impacting ice nucleation and cloud condensation properties.

1 Introduction

Dicarboxylic acids (DCA) are ubiquitous in the atmosphere and are especially abundant in aerosols (Kawamura and Bikkina, 2016). In fact, due to the presence of two carboxylic groups, they are less volatile and more soluble in water when compared to the respective monoacids. Oxalic acid (C_2) is the most abundant diacid, followed by malonic (C_3) and succinic (C_4) acids (Kawamura et al., 1996). Dicarboxylic acids and related compounds (oxo and keto acids, and other dicarbonyls) are emitted from anthropogenic and natural primary sources such as fossil

32 fuel combustion, biomass burning, cooking, and oceans. They are also widely used in hydraulic fluids,
33 agricultural chemicals, pharmaceuticals, dyes, complexing agents, and as intermediates in the manufacture of
34 esters and polyamides (Helmi Rozaini, 2012), increasing the possibilities of fugitive emissions during
35 transportation or storage. Although direct emissions contribute to the diacids abundance, several studies have
36 shown that low molecular weight (LMW) diacids are also produced in the troposphere by photochemical chain
37 reactions implying unsaturated hydrocarbons and fatty acids, as well as their oxidation products (Kawamura et
38 al., 1996; Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005). These results are supported by the
39 observation of diurnal and seasonal variation where an increase of DCA concentration in the afternoon and
40 summer times coincides with higher levels of atmospheric oxidants (Kawamura and Bikkina, 2016).

41 Except for the ketoacids, carboxylic acids do not absorb significantly at wavelengths greater than 250 nm, and
42 generally, do not undergo photolysis in the troposphere (Mellouki et al., 2015). Additionally, they have weak
43 reactivity in the gaseous phase, thus, their removal from the atmosphere is mainly through heterogeneous
44 processes (i.e., dry and wet depositions) (Chebbi and Carlier, 1996). Water-soluble C₂–C₉ DCAs have low vapor
45 pressure which favors their adsorption onto airborne particles (Yang et al., 2008), including mineral aerosols,
46 particularly over Asia or over oceans (Pan et al., 2017; Sullivan et al., 2007). Indeed, Russell et al. reported the
47 presence of complex mixtures of carbonyl compounds on dry particles from the Caribbean marine boundary
48 layer (Russell et al., 2002). Corroborating this result, oxalic acid was found in Asian mineral dust particles for
49 both sub and super-micron diameters (Sullivan and Prather, 2007). Oxalic, succinic, malic, glutaric and adipic
50 acids were also shown to be adsorbed on mineral dust particles collected in Israel (Falkovich et al., 2004).
51 Moreover, the presence of DCA alters mineral dust hygroscopic properties (Russell et al., 2002), and
52 consequently their possible ability to act as ice nucleation and cloud condensation nuclei (Keskinen et al., 2014;
53 Niedermeier et al., 2010; Tang et al., 2016).

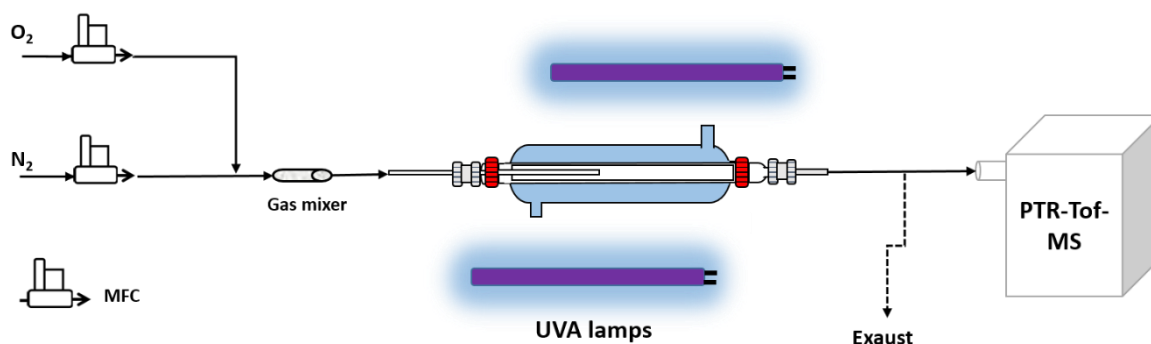
54 Mineral dust is the most abundant emitted aerosol accounting for a range between 1000-3000 Tg released into
55 the atmosphere every year (Formenti et al., 2011). Recently, the photo-induced heterogeneous chemistry
56 initiated by near-UV/Vis light-absorbing species (such as TiO₂, Fe₂O₃) present in mineral aerosol was evinced
57 (Ndour et al., 2009; Ponczek and George, 2018; Romanias et al., 2016; Styler and Donaldson, 2012, 2011) and
58 reviewed (Chen et al., 2012; George et al., 2015; Usher et al., 2003). All these studies reveal a new and
59 potentially important pathway of organic compounds processing in the atmosphere.

60 There are few studies of the kinetics and products identification for the atmospheric photooxidation of aqueous
61 phase chemistry of dicarboxylic acids (Charbouillot et al., 2012; Pavuluri et al., 2015; Yang et al., 2008).
62 However, similar knowledge for heterogeneous reactions on typical mineral dust is still very limited. In this
63 study, we assessed the photoreactivity of five dicarboxylic acids namely, succinic (butanedioic) acid, glutaric
64 (pentanedioic) acid, and adipic (hexanedioic) acid, pimelic (heptanedioic) acid and suberic (octanedioic) acid
65 on Arizona test dust (ATD) particles. The heterogeneous processing on the dust surface was investigated under

66 UV-A irradiation. We discussed the similarities and discrepancies among these homologous compounds and
67 proposed a general mechanism for DCA reactions on ATD.

68 **2 Experimental Section**

69 Experiments were carried out in a horizontal coated wall flow tube reactor, previously described in detail
70 (Jammoul et al., 2008; Ponczek and George, 2018), where the acid-coated dust samples were immobilized on
71 the internal walls of a Pyrex tube insert. The reactor had an outer jacket and was maintained at a constant
72 temperature of 293 K by circulating thermostated water from a chiller bath (Huber CC 130). Seven lamps
73 (Phillips 20W) surround the reactor and could be switched on and off modifying the light intensity (from 0 to
74 1.4 mW cm^{-2} for wavelengths in the range of 300-400 nm). A schematic of the experimental set-up is depicted
75 in Figure 1.



76

77 **Figure 1: Schematic of experimental set-up**

78

79 **2.1 Sample preparation and tube coating**

80 All chemicals were used as received without any further treatment. Succinic, Glutaric and Adipic acids were
81 purchased from Sigma Aldrich (>99% for all); Pimelic (>98%) and Suberic acids (99%) were purchased from
82 Alfa Aesar, Arizona test dust, a real sand from Salt River Valley, Arizona, U.S., was commercially provided by
83 Powder Technology Inc. (ISO 12103-1, A1 Ultrafine Test Dust, ATD); it is well-characterized regarding its
84 composition and chemical and thermal stability (Cwiertny et al., 2008; Vlasenko et al., 2005). ATD composition
85 is shown in the Supplement Material.

86 To prepare the DCA coated dust samples, acids were added as internal mixtures during the coating process at a
87 10% w/w ratio in ATD. To do so, an aqueous solution of the respective acid was mixed with an ATD suspension
88 in ethanol (absolute, 99% Sigma Aldrich). The final suspension was then transferred to the tube inserts coating
89 their inner walls, similar to the coating process described previously (Ponczek and George, 2018). The tubes
90 were left in an oven at 373 K for 1 h to evaporate the solvents (ethanol and water) except the DCA which boiling
91 points are between 473 and 673 K.

92 2.2 Experiment procedure

93 After coating, the freshly prepared insert was placed in the flow tube reactor, under a flow of 300 ml min⁻¹ of
94 synthetic air (N₂ and O₂ mixture in the ratio 79:21) as a carrier gas. To investigate photooxidation reactions,
95 each sample followed the same illumination sequence: 30 min off (for background measurement); 1 h under
96 irradiation, 1 h lights off, 1 h under irradiation.

97 The gas-phase products were monitored online by coupling the reactor outlet to a high-resolution proton-
98 transfer-reaction mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik GmbH). The instrument settings
99 used were: drift voltage of 600 V, drift temperature of 333 K and drift pressure of 2.42 mbar, resulting in an
100 E/N ratio of about 125 Td (1 Td = 10⁻¹⁷ V cm²). The reactor's outlet and the PTR sample inlet tubing were
101 constantly heated to 333 K to minimize adsorption and loss of products. Spectra were acquired at a time
102 resolution of 5 s for regular experiments and 10 s for the long-term experiments. VOC mixing ratios were
103 calculated from the H₃O⁺ mode using the built-in feature of PTR-ToF-MS Viewer Software v. 3.1.0.31 (Ionicon
104 Analytik GmbH), considering default values for the proton transfer reaction rate constant ($k = 2 \times 10^{-9}$
105 cm³ s⁻¹) for all VOCs. It should be noted that uncertainties in the absolute mixing ratios can be estimated to
106 be about 30% (Brüggemann et al., 2017; Hartungen et al., 2004).

107 2.3 Surface Products – Sample Extraction and LC-MS Analysis

108 After irradiation, surface sorbed products were extracted from the dust as follows. First, 10 ml of solvent (9:1
109 v/v of acetonitrile–water - Optima® LC/MS, Fischer Scientific, USA) was added to the coated tube and
110 sonicated for 10 min. Then, the suspension in the tube was left in a rotating device overnight (for approx. 15 h)
111 providing good contact solvent–dust. After that, the suspension was transferred to a 30 mL amber vial and left
112 to decant. The supernatant was, next, transferred to another amber vial and filtered using 0.2 µm GHP membrane
113 (13 mm, Pall Corporation, USA), and evaporated almost to dryness under a mild nitrogen flow. The extracts
114 were then reconstituted in 1 mL of a 50:50 volume mixture of water and acetonitrile (ACN).

115 For the analysis, the appropriate amount of the final reconstituted extract sample (see Table S1) was diluted by
116 adding 500 µL of acetonitrile and 500 µL of water. 5 µL of diluted solutions were analyzed by reversed phase
117 ultra-high-performance liquid chromatography UHPLC (Dionex 3000, Thermo Scientific, USA) coupled to an
118 Orbitrap high-resolution mass spectrometer (Thermo Scientific, USA) using heated negative electrospray
119 ionization (- HESI). Each sample was analysed in triplicate.

120 Analytes were separated using a Waters Acquity HSS T3 column (1.8 µm, 100 × 2.1 mm) with mobile phases
121 consisting of (A) 0.1% formic acid in water (Optima® LC/MS, Fischer Scientific, USA) and (B) 0.1% formic
122 acid in acetonitrile (Optima® LC/MS, Fischer Scientific, USA). Gradient elution was performed by the A/B
123 mixture at a total flow rate of 300 µL min⁻¹ as detailed elsewhere (Wang et al., 2016). Further information
124 regarding the chromatographic and mass spectrometric methods is available in the Supplementary Material.

125 The chromatograms were analyzed with MZMine 2.21 for a non-target screening of potential products. The
126 software algorithm identifies the products assuming that the extracted ions in the range of 50–750 m/z were
127 formed by the loss of a proton from the analytes; adducts formation with acetonitrile ($[M+ACN]^+$) was also
128 verified. To refine these results, the major products identified by MZMine were re-evaluated and each
129 corresponding peak was manually checked using the software Xcalibur 2.2 (Thermo, USA), thus excluding
130 possible peaks detected erroneously by the automatic screening.

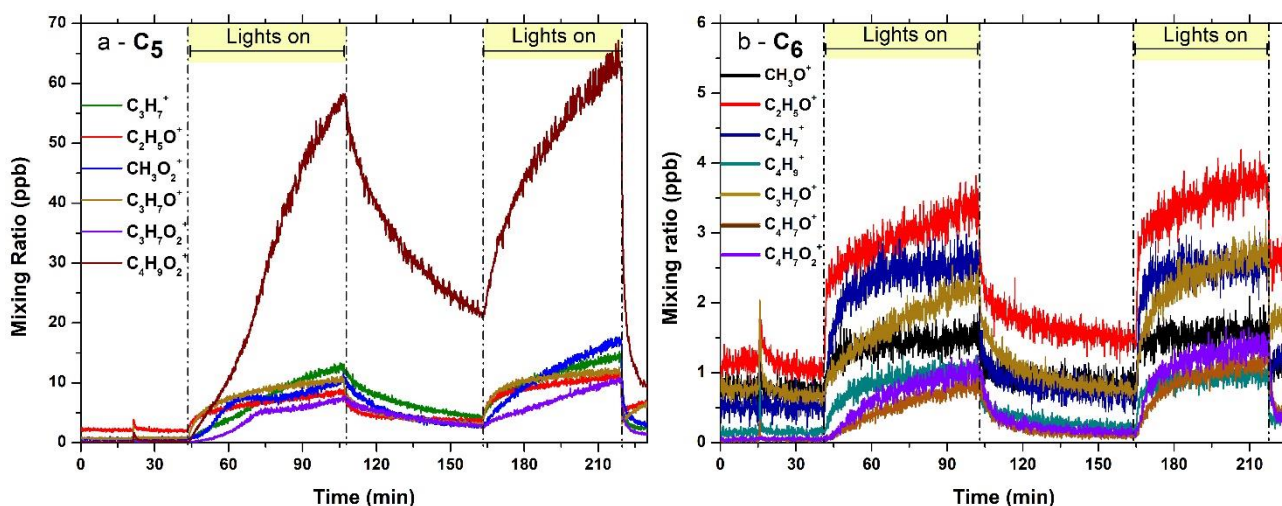
131 Chromatograms of each sample (extracted from the irradiated tube after the experiment) were compared to the
132 results of a replicate tube prepared under the same conditions but left in the dark. Additionally, two procedural
133 blanks consisting of coated tubes with only Arizona test dust (and no acid) one left in the dark and the other
134 irradiated were run in parallel to the samples.

135 Standard solutions of the studied acids were also analyzed to validate their identification in the samples using
136 their corresponding retention time in addition to the high-resolution mass spectra. Experiments using succinic
137 acid have not been analysed by LC-MS since this acid is too small and too polar to be sufficiently retained by
138 our C18-column, as probably are its oxidation products.

139 3 Results and Discussion

140 For all dicarboxylic acids / ATD films, illumination resulted in the immediate increase of various signals
141 detected by the PTR-ToF-MS. However, each acid presented different time responses, product distributions and
142 yields. Typical results for glutaric (C_5) and adipic (C_6) acids are shown in Figure 2.

143



144

145 **Figure 2: Gas-phase products observed by PTR-ToF-MS for irradiated ATD films coated with (a) Glutaric acid**
146 **(C₅) and (b) Adipic acid (C₆)**

147

148 We can observe from Figure 2, that glutaric (C₅) and adipic (C₆) acids presented very different OVOCs
149 (oxygenated volatile organic compounds) production profiles. Glutaric acid had a main product C₄H₉O₂⁺ (*m/z*
150 89.059), which increased rapidly and reached concentrations above 50 ppb. While for adipic acid, we did not
151 observe a foremost compound and products were more evenly distributed. The mixing ratios time profiles for
152 succinic (C₄), pimelic (C₇) and suberic (C₈) acids are presented in the Supplement Material (left side of Figure
153 S2). It is remarkable that some products easily reached steady state, such as C₄H₇⁺ for adipic acid (C₆) and
154 C₃H₇O⁺ for suberic acid (C₈), whereas others exhibited almost linear increasing during one-hour irradiation i.e.,
155 C₄H₉O₂⁺ for glutaric acid (C₅) and C₅H₁₃O₂⁺ for pimelic acid (C₇). Interestingly, some of them dropped-off quite
156 fast after switching off lights (C₄H₇O₂⁺ for adipic acid and C₅H₉⁺ for pimelic acid), while others decayed very
157 slowly (C₃H₇⁺ for glutaric acid and C₂H₅O⁺ for adipic acid). Moreover, during the same experiment, when the
158 lights were switched on for the second time, the same products were observed, but with different time profiles.
159 Overall, about 50 different *m/z* ions were identified and the complete list of all detected VOCs is given in Table
160 S2.

161 Although the PTR-ToF-MS has a high mass resolution (more than 4000 *m/Δm*), allowing to differentiate
162 compounds with very close *m/z* e.g., ethanol (C₂H₇O⁺, *m/z* 47.049) and formic acid (CH₃O₂⁺, *m/z* 47.013), small
163 ions such as C₃H₅⁺ (*m/z* 41.039), C₂H₃O⁺ (*m/z* 43.018), C₃H₇⁺ (*m/z* 43.054), C₄H₉⁺ (*m/z* 57.069), will have
164 contributions from different fragments in a complex mixture. Fragmentation patterns for atmospherically
165 relevant OVOCs have already been studied and recently reviewed (Yuan et al., 2017), but it may be altered
166 depending on the actual experimental conditions (for example, humidity) and instrument settings (de Gouw and
167 Warneke, 2007). In an attempt to improve product identification, we measured pure standards for some
168 monocarboxylic acids (butanoic, pentanoic, heptanoic and octanoic) and aldehydes (Ponczek and George,
169 2018). We found out that under our operational conditions, the parent molecule MH⁺ is approximately, 77% of
170 the relative intensity. Fragments related to the loss of one molecule of water ([MH⁺] - H₂O) and, one molecule
171 of water and one group CO ([MH⁺] - H₂O - CO) were also found, whereas these two alternative fragmentation
172 channels were more variable, between 5-10% for ([MH⁺] - H₂O) and between 5 and 20% for ([MH⁺] - H₂O -
173 CO) depending on the acid.

174 Control experiments were performed to verify that the OVOCs detected were emitted solely from the photo-
175 induced process and not as a result of i) evaporation from the dicarboxylic acid or; ii) due to the presence of
176 impurities on the dust. For this, acid/dust coated inserts were subject to the same experimental conditions and
177 left overnight in the dark while the concentration of VOC was monitored. Also, dust films without any acid
178 were submitted to the same irradiation procedure. In both cases, no significant difference in OVOCs
179 concentrations was detected.

180 The net product formation was quantified by considering the first hour of irradiation and subtracting the baseline
181 values as measured before irradiation. This net product formation is presented in Figure 3 for glutaric (C₅) and
182 adipic (C₆) acids, and in Figure S2 (right side) for succinic (C₄), pimelic (C₇) and suberic (C₈) acids. In both

183 figures, error bars were calculated from three replicates. The mass variability of dust films was not an issue for
 184 the reproducibility of the results as it can be observed in Figure S3. Therefore, the relative abundance (RA_{VOC})
 185 of each VOC was calculated with respect to the total of VOCs emitted ΔC_{Total} , Eq. 1:

$$186 \quad RA_{VOC_A} (\%) = \frac{\Delta C_A}{\Delta C_{Total}} \times 100, \quad (1)$$

187 where ΔC_A is the mixing ratio of the respective VOC emitted (subtracting the values of the baseline signal), and
 188 ΔC_{Total} is the sum of all VOC emitted ($\sum \Delta C_A$ for all products).
 189

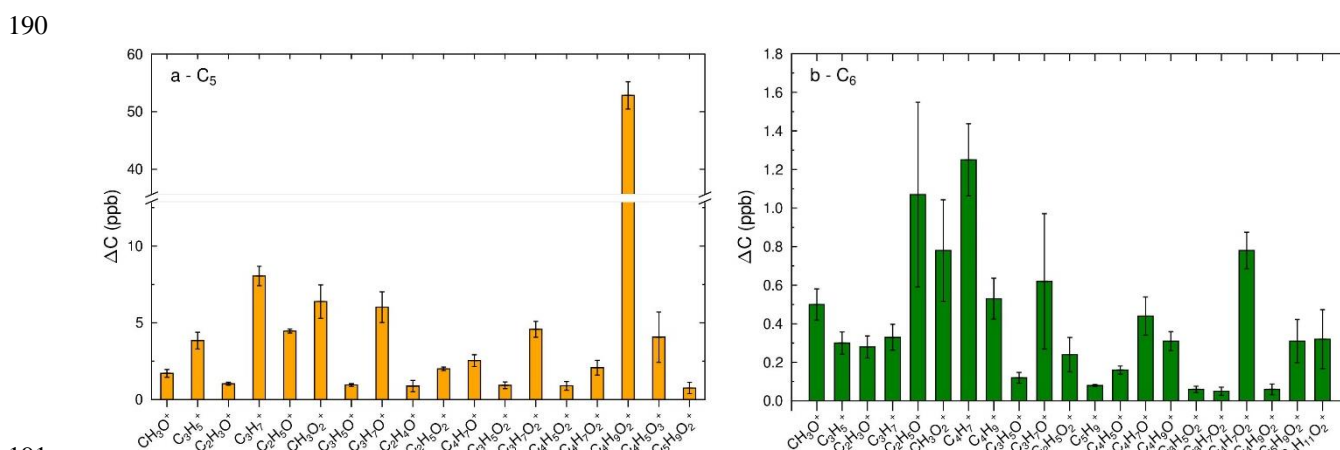


Figure 3: Net product formation for (a) Glutaric acid (C₅) and (b) Adipic acid (C₆) after 1h irradiation. The error bars represent the standard deviation of three replicates, evidencing the reproducibility of the results.

194 The relative abundance, as well as the formula assignment and identification of the three foremost gas-phase
 195 products for each dicarboxylic acid, is shown in Table 1. It can be observed that monocarboxylic acids and
 196 aldehydes are the most common products of diacids photooxidation. Formic acid, the simplest (monocarboxylic
 197 acid) MCA appeared for succinic (C₄), glutaric (C₅) and pimelic (C₇) acids with similar relative abundances,
 198 while acetaldehyde appeared as a major product for succinic (C₄), adipic (C₆) and suberic (C₈) acids although
 199 its relative abundance for succinic acid was much higher than for the other two diacids.
 200

201 It is worth pointing out that the detection of gaseous products depends not only on their formation reaction rates
 202 but also on their adsorption/desorption properties at the surface; besides, OVOCs interact differently with oxides
 203 components of ATD (Carlos-Cuellar et al., 2003; Li et al., 2001). For instance, more volatile compounds, such
 204 as small aldehydes will preferentially desorb, and molecules liable to hydrogen bonds may become more
 205 strongly bounded to dust surface hydroxyl groups (Chen et al., 2012; Styler et al., 2013). Therefore, some
 206 products may desorb more easily than others, while some of them must remain adsorbed to further oxidation.
 207 This point is further discussed in the discussion of the mechanism (Sec. 3.5).

208

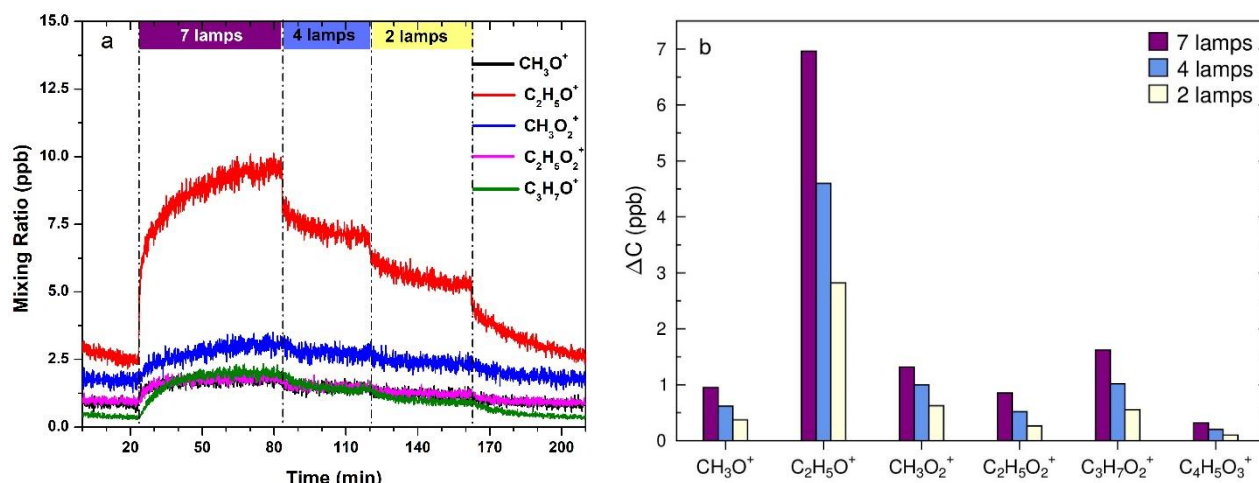
209 **Table 1: Main gas-phase products for each dicarboxylic acid, where ΔC is the net product formation on mixing**
 210 **ratio units (ppb) of the respective VOC emitted and RA is the respective relative abundance (Eq. 1). The standard**
 211 **deviation (Std Dev) was calculated for three replicates.**

Starting DCA	Products						
	<i>m/z</i>	Formula	Suggested product	ΔC (ppb)	Std Dev (ppb)	RA (%)	Std Dev RA(%)
Succinic C ₄	45.033	C ₂ H ₅ O ⁺	Acetaldehyde	9.44	1.99	59.5%	8.4%
	75.042	C ₃ H ₇ O ₂ ⁺	Propanoic acid	1.60	1.00	10.0%	5.7%
	47.011	CH ₃ O ₂ ⁺	Formic acid	1.12	0.35	7.1%	2.3%
Glutaric C ₅	89.059	C ₄ H ₉ O ₂ ⁺	Butanoic Acid	52.82	2.37	50.1%	0.7%
	47.011	CH ₃ O ₂ ⁺	Formic acid	6.39	1.09	6.1%	1.0%
	59.049	C ₃ H ₇ O ⁺	Propanal	6.02	1.00	5.7%	1.0%
Adipic C ₆	55.054	C ₄ H ₇ ⁺	Butyraldehyde	1.25	0.19	14.7%	0.7%
	45.033	C ₂ H ₅ O ⁺	Acetaldehyde	1.07	0.48	12.3%	4.1%
	87.042	C ₄ H ₇ O ₂ ⁺	Crotonic Ac/ Succialdehyde	0.78	0.09	9.2%	1.4%
Pimelic C ₇	69.069	C ₅ H ₉ ⁺	Pentanal	3.74	0.65	16.6%	0.4%
	117.091	C ₆ H ₁₃ O ₂ ⁺	Hexanoic Acid	3.37	1.26	14.6%	3.3%
	47.011	CH ₃ O ₂ ⁺	Formic Acid	1.68	0.30	7.5%	1.0%
Suberic C ₈	83.084	C ₆ H ₁₁ ⁺	Hexanal	1.58	0.59	20.6%	4.7%
	45.033	C ₂ H ₅ O ⁺	Acetaldehyde	0.85	0.12	11.4%	2.3%
	55.053	C ₄ H ₇ ⁺	Butyraldehyde	0.84	0.27	10.9%	1.9%

212

213 3.1 Light Intensity Dependence

214 The influence of light intensity on the product formation and yield was investigated by varying the number of
 215 lamps switched on, decreasing the radiant flux (300-400 nm) from 1.4 to 0.40 mW cm⁻². Figure 4 illustrates the
 216 concentration profiles and the quantification of products of a succinic acid/ATD coated film at different light
 217 intensities.



219

220

221

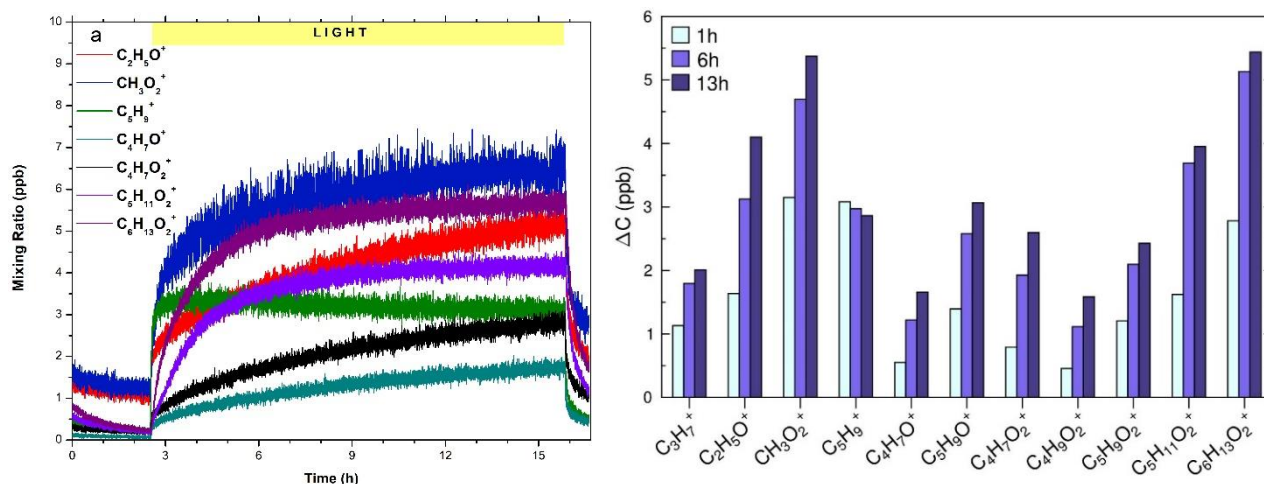
Figure 4: Light influence on product mixing ratios for succinic acid (C₄): (a) temporal profile and (b) net product quantification. The number of lamps switched on (2, 4 or 7) is indicated by the colors in the legend.

222

223 As the light intensity decreased, the concentration of products decreased visibly; the same behavior was
 224 observed for all the other DCA experiments. This observation highlights the photo-induced nature of the
 225 reaction occurring on ATDs surface since photocatalytic reaction rates are usually proportional to the radiant
 226 flux for low/moderate illumination intensities (Herrmann, 2010). For the region where the reaction rate is
 227 linearly proportional to the radiant flux, the formation of photogenerated holes (h^+) could be the limiting step
 228 (Herrmann, 2001; Ohtani, 2010), and once formed, they must react with an electron donor.

229 3.2 Long-term Irradiation Experiments

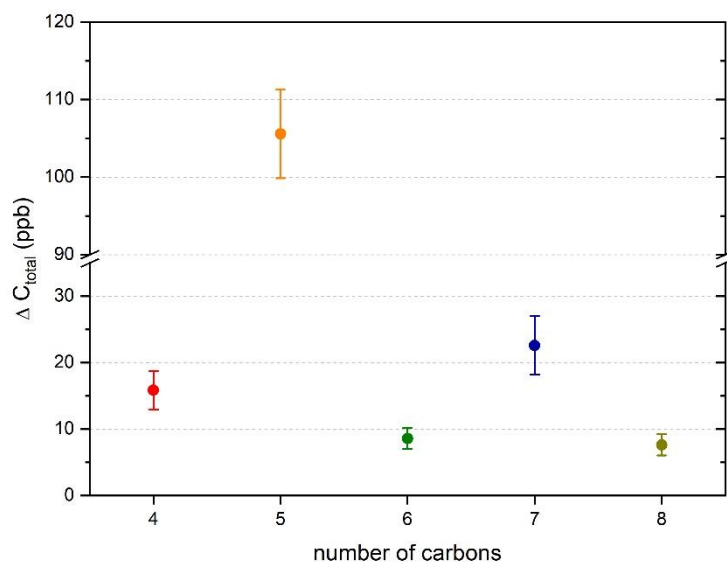
230 As shown in Figure 5, the emission of several VOCs is sustained up to 14 hours of continuous illumination for
 231 a film of ATD and pimelic acid (C₇). When the lights were turned off, the flow of all VOCs decayed, instantly.
 232 In addition, it is possible to follow the time evolution of products: while some of them such as $\text{C}_6\text{H}_{13}\text{O}_2^+$ (m/z
 233 117.090) and $\text{C}_5\text{H}_{11}\text{O}_2^+$ (m/z 103.073) proceed towards steady state after some hours, others such as $\text{C}_2\text{H}_5\text{O}^+$
 234 (m/z 45.033), $\text{C}_4\text{H}_7\text{O}^+$ (m/z 71.048) and $\text{C}_4\text{H}_7\text{O}_2^+$ (m/z 87.044) increase continuously throughout the irradiation
 235 period. C_5H_9^+ (m/z 69.069) reaches a maximum after 1 h and then, slowly decreases. The same tendency for
 236 different products was observed in the experiments with other dicarboxylic acids. According to the different
 237 time evolution of the detected products we observed, for instance, that for pimelic acid (C₇) $\text{C}_6\text{H}_{13}\text{O}_2^+$ and
 238 $\text{C}_5\text{H}_{11}\text{O}_2^+$ that correspond to monocarboxylic acids reached steady state, whereas $\text{C}_2\text{H}_5\text{O}^+$, $\text{C}_4\text{H}_7\text{O}^+$ and $\text{C}_4\text{H}_7\text{O}_2^+$
 239 which correspond to aldehydes continue to increase their concentrations. This observation shed light in the
 240 elucidation of the mechanism where the C_{n-1} monoacidcarboxylic acids are produced first, while the aldehydes
 241 are produced in steps later.



242
243 **Figure 5: Gas-phase products – Long-term Irradiation for Pimelic Acid (C₇).** (a) Mixing ratio temporal profile and
244 (b) net product distribution for 1h, 6 h and 13h of illumination.

245 3.3 Even-Odd alternation of diacids reactivity

246
247 Figure 6 **Erreur ! Source du renvoi introuvable.** presents the total gas-phase product mixing ratio i.e., the sum
248 of all VOCs emitted ($\sum \Delta C_A$ all products) for 1 hour of irradiation for each dicarboxylic acid studied as a
249 function of the number of carbons, showing a clear alternation of reactivity between even and odd compounds.
250 Odd-carbon DCA exhibit higher reactivity than the even-carbon analogous ones.



252
253 **Figure 6: Total gas-phase products mixing ratio after 1h of irradiation for all five dicarboxylic acids studied, as a**
254 **function of carbons number in DCA molecules. Error bars represent the standard deviation for three replicates.**

255 Several studies report odd-even alternation of solid-state physical properties of diacids, namely, saturation vapor
256 pressure (Bilde et al., 2015), melting point (Thalladi et al., 2000), solubility in water (Zhang et al., 2013) and in
257 organic solvents (Zhang et al., 2014). Odd-carbon DCAs are more soluble, have higher vapor pressure, lower
258 melting point and sublimation enthalpy. Recently, the odd/even alternation behavior on chemical reactivity was

259 reported by Fairhurst and coworkers (Fairhurst et al., 2017) and, Zhao et al (2017) (Zhao et al., 2017)
260 respectively, in the reactive uptake on solid C₃–C₈ diacids films and chemical reactivity of submicron C₃–C₇
261 dicarboxylic acid particles with gas-phase amines.

262 Concerning photooxidation reactions in the homogeneous liquid-phase, Yang and coworkers (Yang et al., 2008)
263 examining the oxidation kinetics and mechanisms of C₂–C₉ DCAs by OH-radical, observed the monotonic
264 increase of DCAs degradation rate constant as a function of carbon numbers (for a number of carbons > 4) and
265 no alternation was reported. On the other hand, Sun et al. (Sun et al., 2014) observed the same odd/even
266 fluctuation on reactivity as reported herein, for TiO₂-based heterogeneous liquid-phase photocatalytic
267 degradation of C₂-C₆ dicarboxylic acids. ATR-IR spectra indicated that malonic acid adsorbed on TiO₂ from an
268 aqueous solution in the dark exhibited two different carboxylate groups adsorption geometries (Dolamic and
269 Bürgi, 2006). Later, the same authors (Dolamic and Bürgi, 2007) compared ATR-IR vibration bands of malonic
270 (C₃) and succinic (C₄) and proposed different adsorption modes for each acid since for succinic acid both
271 carboxylic groups were equivalent. Sun and coworkers (Sun et al., 2014) confirmed different surface adsorption
272 geometry for glutaric (C₅) and succinic acids(C₄). For odd-DCAs, one carboxylic group adopt monodentate
273 coordination and the other, bidentate coordination with TiO₂ surface; whereas, for even-DCAs, the two
274 carboxylic groups exhibit the same bidentate bridging coordination. These observations can explain the
275 differences between homogeneous and heterogeneous photooxidation mechanisms of dicarboxylic acids.

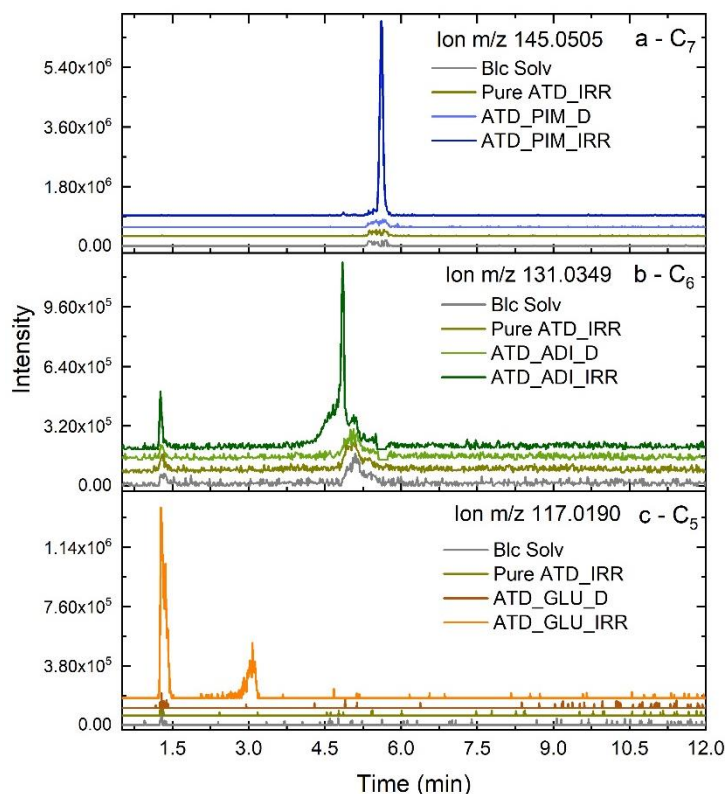
276 In Table 1, it can be seen that the odd-numbered diacids mostly produced the C_(n-1) monocarboxylic acid and
277 formic acid whereas even-DCAs mainly produced aldehydes. Succinic acid (C₄), however, even having as
278 primary product acetaldehyde, also produced propanoic and formic acids, whereas the other even-numbered-
279 DCAs did not produce MCA in detectable amounts in the gas phase. Another remarkable observation was the
280 fact that glutaric (C₅) and pimelic (C₇) acid samples showed a very strong odor after irradiation indicating the
281 production of odorous compounds (such as butanoic and hexanoic acids) in concentrations perceptible to the
282 human nose. The even-carbon DCAs tubes did not exhibit any strong odor.

283 3.4 Surface products

284 To better understand the mechanism and possible differences between the odd and even compounds, we
285 analyzed by UHPLC / (-) HESI-MS the extracts of products that remained adsorbed on the mineral surface. In
286 Figure 7 we compare the irradiated sample chromatogram of pimelic acid, adipic acid, and glutaric acid (C₇, C₆
287 and C₅, respectively) experiments to three respective blanks: the pure extraction solvent mixture [Blc Solv], a
288 pure ATD irradiated tube[Pure ATD_IRR], a sample from dust containing the same acid but kept in the dark
289 [ATD_DCA_D].

290 Succinic acid (C₄) (*m/z* 117.0190) was found as major surface-product from glutaric acid (C₅) reaction. Glutaric
291 acid (*m/z* = 131.0349) was found in the adipic acid (C₆) experiment sample, and the ion *m/z* = 145.0503
292 corresponding to adipic acid was observed in the pimelic acid (C₇) sample. Diacids identification was made by

293 comparison with standard solutions in concentrations equivalent to those found in the samples. As observed in
294 Figure 7, the mentioned products were only found in the irradiated sample containing the corresponding DCA.



295

296 **Figure 7: Chromatograms obtained for diacids surface products, following extracted ions as indicated, comparing**
297 **the irradiated samples [ATD_DCA_IRR] to the blanks (pure extraction solvent [Blc Solv], pure ATD irradiated**
298 **[Pure ATD_IRR] and the corresponding diacid/ATD sample kept in the dark [ATD_DCA_D]); for (a) pimelic acid**
299 **(C₇) sample, ion $m/z = 145.0503$; (b) adipic acid (C₆) sample, ion $m/z = 131.0349$; (c) glutaric acid (C₅) sample, ion**
300 **$m/z = 117.019$.**

301

302 The dicarboxylic acid C_(n-1) appeared as an adsorbed product for all four diacids analysed by LC-MS; in the case
303 of glutaric (C₅), adipic (C₆) and pimelic acids (C₇) (chromatograms shown in Figure 7), they were also the most
304 abundant surface product. Many other organic compounds, which are not sufficiently volatile to desorb from
305 the surface, have been detected in the sorbed phase. The integrated peak areas for some compounds identified
306 for adipic (C₆), pimelic (C₇) and suberic (C₈) acids experiments are shown in Figure S4 for the irradiated samples
307 compared to the dark ones in order to evidence the relative abundance of the products generated under
308 illumination.

309 These results indicate that the photooxidation mechanism of dicarboxylic acids results in the diacid C_(n-1)
310 suggesting their decarboxylation is an important step. Also, other highly oxygenated products such as (C_nH_{2n}-
311 ₂O₃), (C_mH_{2m}O₃), (C_mH_{2m}O₄), etc. were found, Table 2. It should be pointing out the appearance of molecules
312 of greater molecular weight than the original acid suggests dimerization or recombination of radicals throughout
313 photooxidation.

314

315 **Table 2: List of the main condensed phase compound classes of products when glutaric, adipic, pimelic or suberic**
 316 **acids ATD films were exposed to light. Most abundant products are highlighted in bold.**

General Formula	Proposed Function	Glutaric (C ₅)	Adipic (C ₆)	Pimelic (C ₇)	Suberic (C ₈)
C _m H _{2m-2} O ₂	dialdehyde			C ₆ H ₁₀ O ₂	C ₆ H ₁₀ O ₂
C_mH_{2m-2}O₃	Oxo or keto acid	C₄H₆O₃	C₅H₈O₃, C₄H₆O₃	C₆H₁₀O₃	C₇H₁₂O₃ C₆H₁₀O₃
C_mH_{2m-2}O₄	DCA	C₄H₆O₄	C₅H₈O₄	C₆H₁₀O₄, C₅H₈O₄	C₇H₁₂O₄
C _m H _{2m-2} O ₅	OH-DCA			C ₆ H ₁₀ O ₅	
C _m H _{2m-4} O ₆			C ₁₀ H ₁₆ O ₆	C ₁₂ H ₂₀ O ₆	
C_mH_{2m}O₃	OH-MCA	C₄H₈O₃	C₅H₁₀O₃	C₆H₁₂O₃	C₆H₁₂O₃
C_mH_{2m}O₄	Di-OH-MCA		C₅H₁₀O₄	C₆H₁₂O₄	C₇H₁₄O₄
C _m H _{2m-4} O ₄	unsat DCA	C ₅ H ₆ O ₄		C ₇ H ₁₀ O ₄	
C _m H _{2m-4} O ₅	oxo-DCA		C ₆ H ₈ O ₅	C ₁₁ H ₁₈ O ₄ C ₇ H ₁₀ O ₅ , C ₆ H ₈ O ₅ , C ₁₂ H ₂₀ O ₅	C ₈ H ₁₂ O ₅
C _m H _{2m-4} O ₆			C ₁₁ H ₁₈ O ₆ , C ₁₀ H ₁₆ O ₆		

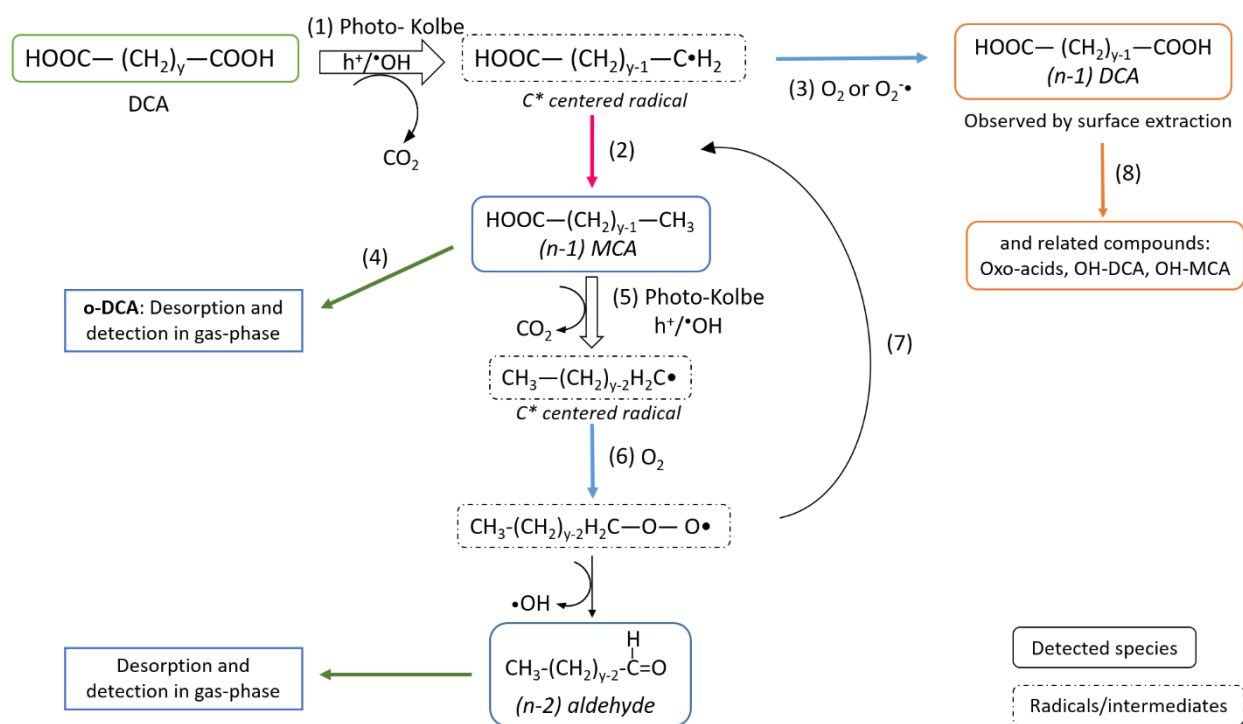
317

318

319 3.5 Mechanistic Insights

320 Taking into consideration the results presented previously for the products observed in the gas and sorbed phases
 321 and also their relative abundances, a general mechanism is proposed for dicarboxylic acids photo-oxidation
 322 (Figure 8). It is worthwhile to mention that the reactivity of mineral dust is attributed, and assumed for the
 323 mechanism presented herein, to the content of semiconductor materials generally present in variable amounts.
 324 ATD, specifically, contains 2.0 – 5.0 wt% Fe₂O₃ and 0.5 – 1 wt% TiO₂.

325



326

327 **Figure 8: Proposed mechanism for dicarboxylic acids photooxidation on ATD surface under UV-A radiation.**
 328 **Species in solid rectangles were observed by our analytical techniques.**

329

330 The photooxidation of dicarboxylic acids is suggested to start with the photo-Kolbe reaction (step 1) forming a
 331 C-centered alkyl radical and CO₂, with decarboxylation being the first and limiting step. The difference in the
 332 adsorption mode is suggested to explain the alternation in the reactivity of DCAs; the monodentate geometry of
 333 odd-carbon DCAs makes one carboxylic group weakly bounded and more susceptible to the attack of oxidizing
 334 agents such as h_ν⁺ and radicals (Sun et al., 2014). The bidentate bridging mode, on the other hand, should
 335 disfavor the cleavage of the α-carbon bond resulting in less reactivity for even-carbon diacids.

336 After decarboxylation, the alkyl radical can react either by abstracting an H atom from another organic molecule
 337 or surface species, or with O₂. The step 2 (H-abstraction by the alkyl radical) will lead to the C_(n-1) MCA observed
 338 mostly for the odd-DCA, and the reaction with oxygen (step 3) gives the C_(n-1) DCA (Dolamic and Bürgi, 2007).
 339 The adsorption/desorption equilibrium determines the partition of the product in the gas/surface phases. For
 340 odd-DCA, the decarboxylation is faster than for even-DCA, and the C_(n-1) MCA is abundant enough to be
 341 released and detected in the gas-phase (step 4). For the even-DCA, the C_(n-1) MCA is scarce, and once it is
 342 formed, it proceeds to next oxidation steps.

343 The monocarboxylic acid, in turn, continues the oxidation process, undergoing decarboxylation and, once again,
 344 forming alkyl radicals (step 5) which can react with O₂ resulting in peroxy radicals (step 6) that will lead to
 345 carbonylated compounds. The arrow in step 7 represents this pathway can occur successively with each of the
 346 intermediates leading to the formation of (n-1) products at each stage. The higher volatility of aldehydes and

347 formic acid favor their desorption from the surface and explains why they are overwhelmingly detected in the
348 gas-phase.

349 For a didactic question, the mechanism was depicted in Figure 8 by separating two reactional pathways, one
350 that leads to the gas-phase products (blue rectangles) and the other that results in surface-sorbed compounds
351 (orange rectangles). However, the $C_{(n-1)}$ DCAs observed on the dust surface are also liable to undergo the same
352 kind of reactions as the starting DCA contributing to the products detected on the gas-phase. Moreover, similar
353 to the reaction shown in step 6, after the first decarboxylation, and reaction with O_2 (step 3), the alkyl peroxy
354 radicals ($R-O-O\cdot$) can lead to oxo acids (step 8), as R, in this case, still has another carboxylic group, as shown
355 as follows on Reactions R1– R4).



360 If $R\cdot$ is formed from the DCA, RCHO is an oxo-acid: $HOOC-CH_2(n)-CHO$

361 If $R\cdot$ is formed from the MCA, RCHO is an aldehyde.

362
363 The diversity concerning dust particles components behavior punctuates the complexity of the process and
364 emphasizes the importance of the investigation of natural and complex samples where synergy effects among
365 constituent materials can modify the expected results for single components systems. Styler and Donaldson
366 discussed in their study of oxalic acid decomposition on different mineral proxies (Styler and Donaldson, 2012),
367 that the heterogeneous reactivity of realistic dust has contributions of both iron and titanium oxides
368 photochemistry. According to their observations, the reactivity of each semiconductor can be influenced by
369 environmental conditions, for instance, the presence of O_2 decreased the importance of iron-mediated process
370 whereas it enhanced the reactivity for pure TiO_2 .

371 The same comment holds when we compare our results with the studies by Sun et al. (2014), and by Dolamic
372 and Burgui, (2007) who have investigated the photocatalytic degradation of dicarboxylic acids aqueous
373 solutions on TiO_2 . Although these studies bring similar and useful mechanistic insights, regarding the products,
374 both reported only acids (mono and dicarboxylic); whereas, in this study, we observed a greater variety of
375 products, notably carbonyl compounds (aldehydes / ketones) in the gas-phase and oxygenated and hydroxylated
376 substituted products in the particulate phase.

377 From the atmospheric point of view, the emission of carbonyl compounds is relevant since they are photoactive
378 and contribute to the formation of radicals that will participate in the bulk gas-phase chemistry (Mellouki et al.,
379 2015). For instance, carbonyls are fundamental in the formation of HO_x species; additionally, reactions of

380 carbonyls with Br and Cl are also major sources of HBr and HCl in the upper troposphere and lower stratosphere
381 (Lary and Shallcross, 2000).

382

383 **3.6 Conclusions and Atmospheric Implications**

384 In this study, we have shown that photo-induced reactions can take place on realistic dust surfaces coated with
385 organic compounds. Our results show that when starting with a single dicarboxylic acid, the particles catalyzed
386 chemical reactions producing a complex mixture of organic compounds upon irradiation. We have characterized
387 the products of this photooxidation process presenting both the volatile compounds that are emitted in the gas-
388 phase and the low volatility ones which stay adsorbed on dust. Moreover, it was proposed a mechanism that
389 agrees and summarizes experimental observations. Surprisingly, the reactivity of the dicarboxylic acids
390 presented an alternation concerning the number of carbons of the chain, and the odd-DCA exhibited greater
391 reactivity than the even ones. Although unexpected, the alternation of properties (physical and also chemical)
392 has already been observed regarding to DCAs.

393 About the products detected adsorbed on the solid phase, it is emphasized the presence of highly oxygenated
394 and substituted products that is especially important because of their higher polarity and affinity with water.
395 Keskinen et al. (2014) measured the hygroscopicity of ATD seed particles exposed to SOA from the ozonolysis
396 of α -pinene and found an increase by a factor of four for 100-150 nm particles (Keskinen et al., 2014). Their
397 results highlight the effect of organic matter heterogeneous coating on solid particles hygroscopic properties
398 and cloud droplet activation. Sullivan and Pradher, by contrast, commented that the association of DCA acids
399 with mineral dust or sea salt could form insoluble complexes possibly diminishing cloud activation properties
400 of those particles (Sullivan and Prather, 2007).

401 In addition, studies of ice nucleation (IN) have shown that particle coatings decreased IN ability compared to
402 pure ATD (Niedermeier et al., 2010). Möhler and coworkers (Möhler et al., 2008) have investigated the ice
403 nucleation efficiency of ATD particles coated by condensation of semi-volatile products from the reaction of α -
404 pinene with ozone and found out that these SOA compounds lowered or even suppressed, in certain conditions,
405 the heterogeneous ice nucleation potential of dust. The influence of organic matter oxidation state on CCN and
406 IN activity is not yet a consensus in the scientific community, and more mechanistic understanding is needed.
407 However, it is broadly recognized that organic compounds coating insoluble dust cores affect their CCN and IN
408 potential.

409 Water is known to play an important role in photocatalytic reactions efficiently generating OH-radicals and
410 changing selectivity towards total oxidation (Herrmann, 2001) but also competing for reactive sites. We did not
411 investigate the direct influence of water or relative humidity, although in our procedure no effort was made to
412 eliminate all the water used in the coating process; and therefore, water molecules must have remained on the

413 surface, especially those strongly bonded (by hydrogen bonds). However, a systematic evaluation of the role of
414 relative humidity might be interesting and indeed, recommended for future studies.

415 Overall, the results obtained herein agree with other studies (Kawamura and Bikkina, 2016), (Helmi Rozaini,
416 2012), (Kawamura and Sakaguchi, 1999) suggesting that longer chain DCA are precursors of shorter diacids.
417 We could wonder that heterogeneous photochemical processing might be an important pathway for small DCA
418 formation.

419 In conclusion, this study revealed the role of irradiation in the aging of organic coated mineral surfaces. The
420 chemical and physical properties of mineral aerosols can be substantially influenced by the photochemical
421 production of small diacids and the evolution of their intermediates. Furthermore, the dust potential to induce
422 reactions that lead to the oxidation of organic acids and the release of oxygenated volatile organic compounds
423 to the gas-phase could alter atmospheric composition in the surroundings of a dust plume.

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429 **Supplement** related to this article is available.

430 **Competing interests.** The authors declare that they have no conflict of interest

431

432

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