

Potential Photooxidation Pathways of Dicarboxylic Acids in Atmospheric Droplets

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Abstract: Low molecular weight (LMW) dicarboxylic acids (DCAs) have received increasing attention because of their hygroscopic properties and capability of acting as cloud condensation nuclei (CCN). Based on the concentration profiles of intermediates identified during laboratory photooxidation of C₇–C₉ DCAs in a liquid-phase reaction system, chemometric analyses were conducted to examine the degradation pathways of DCAs for the formation of secondary DCAs. Among all secondary DCAs formed during the reaction, C₄ and C₅ DCAs showed the largest stoichiometric coefficients, indicating that sequential decarboxylation suggested in literature is unlikely the dominant pathway; other reaction routes e.g. preferential abstraction of hydrogen from carbon located at the central position of the DCA molecules by ·OH, followed by subsequent decomposition through the breakage of C-C bond, could play an important role.

Key words: Dicarboxylic acid, reaction pathway, intermediates, photooxidation

INTRODUCTION

Water-soluble organic species (WSOS) have recently received more attention because they have been assumed to be partially responsible for the water uptake of airborne particulates. Low molecular weight dicarboxylic acids (DCAs, C₂–C₉ DCAs), one of major classes of WSOS, contribute up to 50% of the organic aerosol mass^[1], can play an important role in both direct and indirect aerosol forcing^[2, 3, 4, 5]. Researchers have indicated that secondary formation through atmospheric oxidation could contribute to airborne DCAs^[6, 7, 8], while limited effort has been devoted to understand atmospheric photooxidation processes involving these acids. Previous studies have postulated that long-chain DCAs can be the precursors of smaller DCAs^[9, 10]; the hypothesized mechanisms were subsequently employed by Ervens *et al.*^[11] to show that C₂–C₆ DCAs can be formed in cloud droplets through OH radical oxidation. However, specific oxidation pathways and detail mechanism remain to be explored.

To better understand photooxidation mechanisms of atmospheric DCAs, azelaic acid was selected as the target compound because it can be one of important oxidation products of unsaturated acids, such as oleic acid and linoleic acid^[8, 12], which can be abundantly present from oceanic origins^[13], cooking, traffic and

biogenic emissions^[14, 15]. In addition, azelaic acid (C₉ DCA) has been postulated to be a precursor of smaller atmospheric DCAs^[10, 16]. Experiments were conducted to identify intermediates resulting from photooxidation of azelaic acid in a homogeneous (liquid) reaction system, simulating the reaction environments of cloud or fog droplets. Based on experimental concentration profiles of the intermediates identified in our earlier work, chemometric analyses was conducted in this work to examine the degradation pathway of azelaic acid and the subsequent formation of secondary DCA intermediates.

MATERIALS AND METHODS

Liquid-phase photooxidation system: Photooxidation of azelaic acid was carried out in a semi-batch fashion in a liquid-phase photooxidation system, consisting of an annular cylindrical reactor with a quartz sleeve at the center of the reactor to house the UV light source (15 W, Ster-L-RayTM, Atlantic Ultraviolet Corp., USA). The UV light source provided a principal output at 254 nm and a small amount of radiation at 185 nm, which would induce the formation of ozone from dissolved oxygen followed by the generation of H₂O₂. In turn, H₂O₂ would undergo photolysis (at 254 nm) as one of the ·OH sources. In addition, 185 nm radiation was

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mostly absorbed by water to subsequently produce ·OH. This also minimized the photolysis of other compounds in the reaction system. Our laboratory tests showed that C₂–C₉ DCAs have negligible absorbance at 254 nm and exhibited minimal photolysis.

In the semi-batch reactor, 150 mL solution (in ultrapure DI water) was circulated at a flow rate of 0.15 L min⁻¹, with a residence time outside the reactor for less than half a minute. About 0.5 mL aliquot was sampled every 45 min; depending on degradation rate at individual reaction conditions; the total volume of the withdrawn aliquot was less than 5% (by volume) of the circulated solution.

Intermediates identification: Each time 50 µL of reactant solution was withdrawn for chemical identification and quantification during the experiment. The aliquot was dried using mild nitrogen, before 50 µL of tetrahydrofuran (THF, Merck, Germany) was added to re-dissolve the compounds. About 20–30 min after the addition of 20-µL of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, Sigma, USA), a derivatization reagent, 1 µL of derivatized sample was immediately injected into a gas chromatograph coupled with a mass spectrum detector (GC-MS, Hewlett Packard 6890, Hewlett Packard 5973, USA) equipped with an HP-5MS capillary column (5% phenyl methyl siloxane, 30.0 m × 250 µm × 0.25 µm, Agilent, USA). The injected sample underwent a temperature program for separation beginning at 60°C for 3 min followed by temperature ramping of 8°C/min up to 280°C and constant at 280°C for 3 min. 1-phenyldodecane (1-PD, Aldrich, USA) was employed as the co-injection standard to monitor the injection loss and instrumental performance. Four repeated analyses of a standard mixture consisting of C₂–C₉ DCAs (C₂ and C₆ DCAs, Merck, Germany; C₃–C₅, C₇ and C₉ DCAs, Aldrich, USA; C₈ DCA, Fluka, Switzerland) showed satisfactory recoveries of the tested procedure between 99 ± 1% and 103 ± 2%.

RESULTS AND DISCUSSION

As illustrated in Fig. 1, azelaic acid decayed exponentially as a first-order reaction, which can be described as,

$$\frac{d[C_{9-DCA}]}{dt} = -k_{1,obs} [C_{9-DCA}] \quad (1)$$

Where t is the reaction time; $[C_{9-DCA}]$ represents the concentration of azelaic acid and $k_{1,obs}$ is the observed first-order rate constant. Although, a number of active

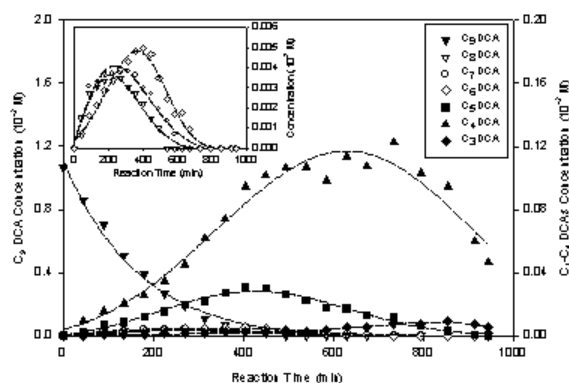


Fig. 1: Concentration profiles of secondary C₃–C₉ dicarboxylic acids during the photooxidation of azelaic acid. The inset shows the enlarged concentration profiles of the secondary C₆–C₈ dicarboxylic acids

Table 1: The second-order rate constants of C₄–C₉ DCAs with hydroxyl radical

DCA	Rate Constant (M ⁻¹ s ⁻¹)
C ₉ DCA	5.4 × 10 ⁹
C ₈ DCA	4.8 × 10 ⁹
C ₇ DCA	3.5 × 10 ⁹
C ₆ DCA	2.0 × 10 ⁹
C ₅ DCA	8.3 × 10 ⁸
C ₄ DCA ^a	3.1 × 10 ⁸

^aExcept for C₄ DCA (from Cabelli *et al.* [18]), all listed rate constants are taken from Scholes and Willson [19]

species are formed along with ·OH radical, effects of HO₂· and O₃, on azelaic acid degradation are negligible [17] and ·OH is the key oxidant in the reaction system. Thus, the degradation rate of azelaic acid can be expressed as,

$$\frac{d[C_{9-DCA}]}{dt} = k_{2,C_{9-DCA}} [\cdot OH][C_{9-DCA}] \quad (2)$$

Here, $k_{2,C_{9-DCA}}$ is the second-order rate constant of azelaic acid with ·OH and $[\cdot OH]$ is the concentration of ·OH radical. However, the apparent observed first-order degradation kinetics of azelaic acid indicates that ·OH concentration is at steady state during the decomposition of azelaic acid. Hence, comparing Equation (1) and Equation (2), the steady state concentration of ·OH can be estimated based on the following relationship,

$$k_{1,obs} = k_{2,C_{9-DCA}} \cdot [OH]_{ss} \quad (3)$$

Where $[OH]_{ss}$ is the steady state concentration of ·OH.

All the identified secondary DCAs had a bell-shape concentration profile (shown in Fig. 1) with a maximum concentration (c_{max}) at corresponding time of t_{max} . Succinic acid (C₄ DCA) and glutaric acid (C₅ DCA)

Table 2: The calculated stoichiometric coefficients of secondary DCAs and corresponding correlation coefficient (r^2) during the photon-induced $\cdot\text{OH}$ oxidation of C_9 - C_7 DCA

Initial DCA	Stoichiometric Coefficients of Secondary DCA (r^2)					
	C_9 DCA	C_8 DCA	C_7 DCA	C_6 DCA	C_5 DCA	C_4 DCA
C_9 DCA	-(0.99)	7.9×10^{-3} (0.99)	7.8×10^{-3} (0.98)	4.6×10^{-3} (0.95)	1.7×10^{-2} (0.93)	3.8×10^{-2} (1.00)
C_8 DCA	-	-(0.99)	2.0×10^{-2} (0.94)	2.1×10^{-2} (0.92)	4.7×10^{-2} (0.85)	0.11 (0.87)
C_7 DCA	-	-	-(0.98)	3.5×10^{-2} (0.84)	5.5×10^{-2} (0.83)	0.31 (0.89)

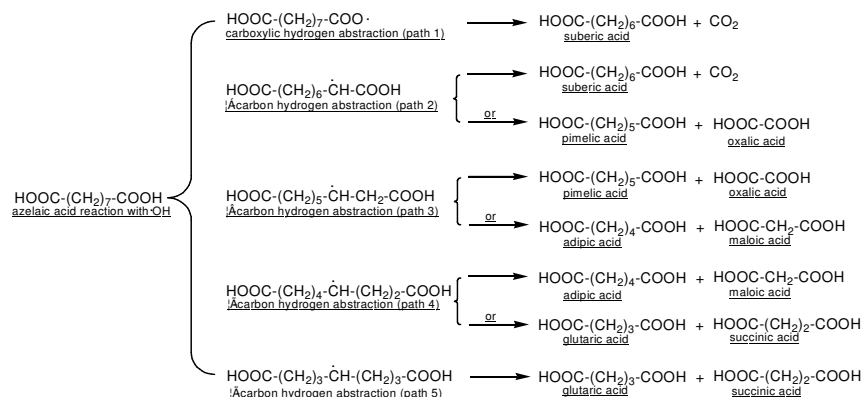
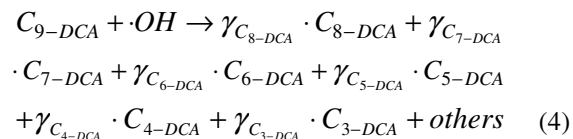


Fig. 2: Proposed reaction pathway for identified secondary dicarboxylic acids during photooxidation of azelaic acid

were most abundant among the secondary C_3 - C_8 DCAs. C_2 DCA (oxalic acid) was not identified during the degradation of azelaic acid, which is due to its high degradation rate observed in our experiments conducted with only oxalic acid (not shown here). The formation of C_8 DCA (suberic acid) supports the postulation of Kawamura and Sakaguchi^[10] that larger DCAs can undergo sequential decarboxylation to form smaller DCAs. Figure 2 presents the potential formation pathway of secondary dicarboxylic acids, where photooxidation of azelaic acid can be initiated through H-abstraction by $\cdot\text{OH}$ at 5 different locations (paths 1-5, Fig. 2), forming corresponding DCA radicals prior to further oxidation to generate secondary DCAs. The formation pathway of secondary DCAs from $\cdot\text{OH}$ oxidation of the parent azelaic acid can be qualitatively expressed as,



Here $\gamma_{\text{C}_{n-DCA}}$ is stoichiometric coefficient of individual secondary DCAs (C_n DCA). To determine the corresponding stoichiometric coefficients $\gamma_{\text{C}_{n-DCA}}$ in Equation (4), following equations are established using simple chemometric approach:

$$\frac{d[\text{C}_{8-DCA}]}{dt} = \gamma_{\text{C}_{8-DCA}} k_{2, \text{C}_{9-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{9-DCA}] - k_{2, \text{C}_{8-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{8-DCA}] \quad (5)$$

$$\frac{d[\text{C}_{7-DCA}]}{dt} = \gamma_{\text{C}_{7-DCA}} k_{2, \text{C}_{9-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{9-DCA}] - k_{2, \text{C}_{7-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{7-DCA}] \quad (6)$$

$$\frac{d[\text{C}_{6-DCA}]}{dt} = \gamma_{\text{C}_{6-DCA}} k_{2, \text{C}_{9-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{9-DCA}] - k_{2, \text{C}_{6-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{6-DCA}] \quad (7)$$

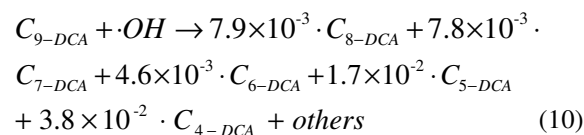
$$\frac{d[\text{C}_{5-DCA}]}{dt} = \gamma_{\text{C}_{5-DCA}} k_{2, \text{C}_{9-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{9-DCA}] - k_{2, \text{C}_{5-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{5-DCA}] \quad (8)$$

$$\frac{d[\text{C}_{4-DCA}]}{dt} = \gamma_{\text{C}_{4-DCA}} k_{2, \text{C}_{9-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{9-DCA}] - k_{2, \text{C}_{4-DCA}} [\cdot\text{OH}]_{ss} [\text{C}_{4-DCA}] \quad (9)$$

Where $k_{2, \text{C}_{n-DCA}}$ is the second-order rate constant of corresponding C_n DCA reaction with $\cdot\text{OH}$; and $[\text{C}_{n-DCA}]$ is the concentration of corresponding secondary C_n DCA. It should be noted that, other potential intermediates may subsequently proceed with additional reactions to contribute to the corresponding DCAs in Equations (5-9). However, it can be seen from Fig. 1 that the maximum concentrations of C_8 and C_7 DCAs occur around 180 min whereas most identified intermediates such as 4-hydroxy-butanoic acid (one of potential C_4 DCA precursors, $t_{\text{max}} = 315$ min) showed a t_{max} later than 180 min and by this time 60% azelaic acid has degraded. Thus the corresponding contribution to DCAs from these intermediates can be neglected in this period when formation of these intermediates dominates over their degradation in the reaction system. In addition, here C_3 DCA (malonic acid) were not included in the calculation because in addition to $\cdot\text{OH}$

oxidation, this compound can undergo self-degradation through a six-centered cyclic transition state^[17]; the corresponding experimentally obtained concentrations are excluded in this modeling.

Based on the available secondary order rate constant, k_{2,C_n-DCA} , of DCAs shown in Table 1, we solve ordinary differential equations (ODEs) (Equations (1-3) along with Equations (5-9)) using MATLAB and summarize the solved stoichiometric coefficients in Table 2. So the above Equation (4) can be rewritten as,



Likewise, the experiments were also conducted using individual C₈ DCA (suberic acid) and C₇ DCA (pimelic acid) as initial reactants (Fig. 3 and 4). Following the same approach of formulating secondary DCAs resulting from azelaic acid oxidation with $\cdot OH$ shown above, stoichiometric equations of C₈ and C₇ DCAs are established as,

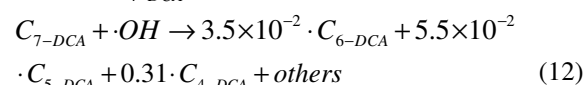
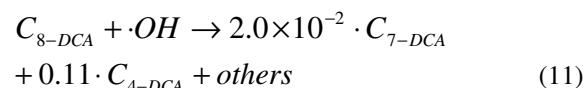


Table 2 shows that the above calculated stoichiometric coefficients of Equations (10-12) for C₄ and C₅ DCAs are much higher than those of other secondary DCAs during the photooxidation of individual C₇-C₉ DCAs, suggesting that the sequential decarboxylation suggested by Kawamura and Sakaguchi^[10] can not be the dominant reaction pathway. A more direct decomposition, such as breakage of the center C-C bonds via $\cdot OH$ -hydrogen abstraction of carbon located at the middle position of parent C₇-C₉ DCAs (e.g., paths 4 and 5 for oxidation of C₉ DCA shown in Fig. 2) could substantially contribute to smaller DCAs. This observation can be indirectly supported by theoretical and experimental estimation of Serpone *et al.*^[20], who showed that non- α -positioned carbons of C₄ and C₅ monocarboxylic acids (MCAs) have a higher density of frontier electrons and thus are preferably attacked by $\cdot OH$. Using electron paramagnetic resonance (EPR), Dixon *et al.*^[21] observed free radical intermediates of aliphatic

carboxylic acid photodegradation (e.g. acetic acid, propanoic acid), also suggested that H abstraction occurs preferentially at carbon atom with the longest distance away from the carboxylic group.

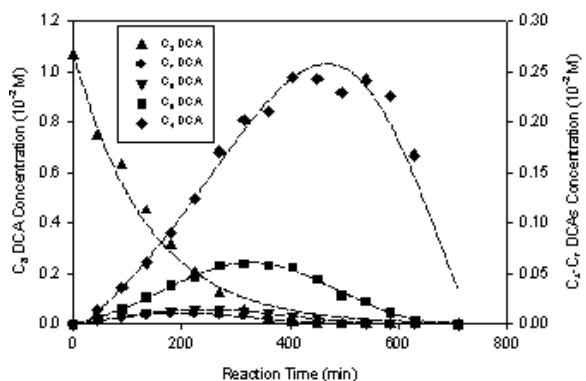


Fig. 3: Concentration profiles of secondary C₄-C₇ dicarboxylic acids during the photooxidation of C₈ dicarboxylic (suberic) acid

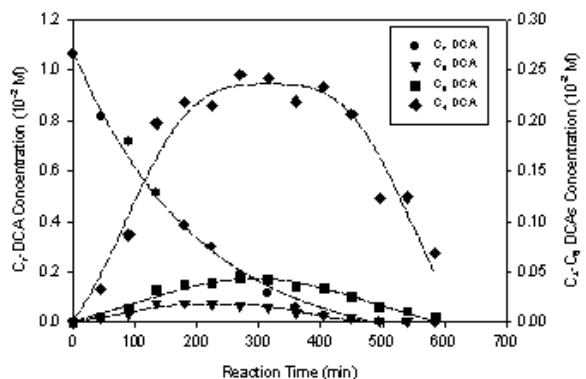


Fig. 4: Concentration profiles of secondary C₄-C₆ dicarboxylic acids during the photooxidation of C₇ dicarboxylic (pimelic) acid

Consistently, Taniguchi *et al.*^[22] found that the abstraction of H atom of monocarboxylic acid (MCA) by $\cdot OH$ more actively occurred at C-H bond of the methyl groups than at those adjacent to the carboxylic groups. This could be explained by electron density at individual locations of the MCA molecules; carboxylic groups tend to draw electron from immediate adjacent methyl groups, resulting methyl groups away from the carboxylic group become relatively richer in electron density. Hence, $\cdot OH$, which is electrophilic, would preferably abstract H from methyl groups farther away from carboxylic groups. However, the above reaction mechanism has been proposed based on simple experiments, fundamental quantum calculation and

experimental identification of the reactive radicals are needed to verify abovementioned reaction mechanisms of carboxylic acids.

CONCLUSION

Secondary DCAs identified during photooxidation of individual C₉-C₇ DCAs in a liquid-phase system confirmed the hypothesis that longer DCAs can be the precursors of shorter DCAs. Based on chemometric analyses using experimental data, the stoichiometric coefficients for C₄ and C₅ DCAs are determined, which are much larger than those of other secondary DCAs, suggesting that sequential decarboxylation mentioned in literature is unlikely the dominant pathway; other reaction routes such as preferential abstraction of hydrogen by ·OH from the central carbon of DCA molecules could play an important role. Fundamental quantum calculations and experimental identification of radicals are needed to verify the reaction mechanisms of DCAs derived based on resultant intermediates.

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