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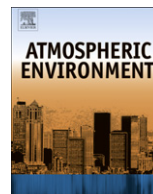


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# Mechanism of carboxylic acid photooxidation in atmospheric aqueous phase: Formation, fate and reactivity

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## ABSTRACT

In the first part of the work, we investigated the reactivity toward photogenerated hydroxyl radicals ( $\cdot\text{OH}$ ) of seven monocarboxylic acids and six dicarboxylic acids found in natural cloud water. This leads to the proposition of a schematic degradation pathway linking glutaric acid ( $\text{C}_5$ ) to complete mineralization into  $\text{CO}_2$ . We report a detailed mechanism on the succinic acid reactivity toward  $\cdot\text{OH}$  leading to the formation of malonic, glyoxylic and consequently oxalic acids and a comparison with reported pathways proposed by the CAPRAM (Chemical Aqueous Phase Radical Mechanism) is discussed. We also investigated the photooxidation of formic acid under atmospherically relevant conditions leading to the possible formation of oxalic acid *via* radical mediated recombination.

The second part focuses on the polychromatic irradiation (closed to solar irradiation) of a collected cloud aqueous phase showing that irradiation of cloud water leads to the formation of both formic and acetic acids. Carboxylic acid formation increases in the presence of photogenerated hydroxyl radicals from hydrogen peroxide, showing that photooxidation could play a key role in the formation of carboxylic acids under atmospherically relevant conditions.

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## 1. Introduction

Carboxylic acids are found in relatively high amounts in all of the environmental compartments (atmosphere, aquatic media and soil) (Chebbi and Carlier, 1996; Khare et al., 1999; Legrand et al., 2007; Löflund et al., 2002; Marinoni et al., 2004). In this paper, we will focus on the reactivity of carboxylic acids in the atmospheric aqueous phase, still subject to significant uncertainties.

Measurements of carboxylic acid concentrations in cloud waters have been performed in several studies (Hegg et al., 2002; Keene et al., 1995; Löflund et al., 2002). These studies suggested that these compounds represent up to 10% of the Dissolved Organic

Carbon (DOC) in clouds that is expected to be a very complex mixture (Khawaja et al., 1995; Löflund et al., 2002). Among the different results showing the important role of these compounds in nonurban environments, carboxylic acids can significantly contribute to the acidity of atmospheric precipitations, up to 64% (Keene et al., 1983).

The hydroxyl radical ( $\cdot\text{OH}$ ) is considered as the main oxidative species present in the atmospheric aqueous phase. As a function of photochemical conditions, its maximal concentration (at noon) in natural water is evaluated by cloud chemistry models between  $10^{-14}$  and  $10^{-12}$   $\text{mol L}^{-1}$  (Herrmann et al., 2000). It can be an important sink or source for organic compounds in the atmosphere. Indeed, most organic compounds react with  $\cdot\text{OH}$  at near diffusion-controlled rates in the aqueous phase. Therefore, the reactivity of organic species in aqueous phase during daytime is mainly due to the reaction with  $\cdot\text{OH}$  and numerous rate constants of  $\cdot\text{OH}$  on organic compounds and more particularly on organic acids have been experimentally evaluated and are reported in the literature (Buxton et al., 1998; Ervens et al., 2003; Herrmann, 2003).

In spite of their ubiquity in the environment and their high reactivity, only a few research groups have performed experimental

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work focussing on the degradation mechanisms of carboxylic acids induced by  $\cdot\text{OH}$  (Karpel Vel Leitner and Doré, 1996; Karpel Vel Leitner and Doré, 1997; Warneck, 2003). Moreover, these works were mainly limited to  $\text{C}_2$  carboxylic acids and degradation pathways and by-products were not always identified. In terms of mechanism, Karpel Vel Leitner and Doré (1996) photogenerated  $\cdot\text{OH}$  with photolysis of  $\text{H}_2\text{O}_2$  at 254 nm. The oxidation of different carboxylic acids induced by  $\cdot\text{OH}$  was performed in oxygenated and deoxygenated aqueous solutions. A mechanism of degradation is proposed for formic, oxalic and succinic acids. The authors conclude that oxidation of the carboxylic group is slow and the main way of oxidation goes through the hydrogen atom abstraction following by a C–C bond cleavage. This bond cleavage is also mentioned in the paper by Kawamura et al. (1996). Photochemical oxidation of succinic acid gives rise to the successive reduction of the carbonate chain length leading to the transformation of succinic acid to malonic acid and then oxalic acid. The possible mechanisms are recapped in the papers by Ervens et al. (2004) and more recently, Tilgner and Herrmann (2010). In these studies, they proposed a modelling work of gas and aqueous production and transformation of dicarboxylic acids from  $\text{C}_2$  to  $\text{C}_6$ . Moreover, laboratory experiments suggest that the hydroxyl radical reactivity toward carboxylic acids could be a relevant source of oligomers (e.g. HULIS (Humic Like Substances)) and Secondary Organic Aerosols (SOA) (Carlton et al., 2007; Tan et al., 2011).

In this work we first investigated the different ways of carboxylic acid degradation induced by hydroxyl radicals  $\cdot\text{OH}$  in synthetic and real cloud water collected at the top of puy de Dôme mountain. The carboxylic acids were chosen according to their natural abundance in the cloud aqueous phase (Charbouillot, 2011) and their value in the different schemes of degradation. The degradation and formation pathways of seven monocarboxylic acids and six dicarboxylic acids were studied in depth.  $\text{H}_2\text{O}_2$  was used as a photochemical source of  $\cdot\text{OH}$  radical via its photolysis. In the natural cloud waters main sources of  $\cdot\text{OH}$  include gas to drop partitioning and in situ formation via photolysis on the surface or in the bulk phases constituents present such as  $\text{H}_2\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-/\text{HNO}_2$  and  $\text{Fe(III)}$  aquacomplexes or organic complexes (Chameides, 1984; Jacob, 1986; Pandis and Seinfeld, 1989; Thompson and Stewart, 1991).

In the last part we focused on the aqueous photooxidation mechanism of formic acid leading to dimer formation (i.e. oxalic acid). The pathways of the different carboxylic acid transformations were identified and a general mechanism of the degradation of carboxylic acids present in the cloud aqueous phase is suggested and compared to the existing mechanisms found in the literature. In this study, we mainly focused our attention on the direct connection between carboxylic acid through photooxidation pathways. The possible formation of intermediates such as aldehydes and ketones, despite its importance in cloud aqueous phase chemistry, was not the central issue of this paper. A brief discussion about the possible atmospheric implications is reported in the final section on the basis of results obtained after irradiation of real cloud water sampled at the puy de Dôme station (France).

## 2. Materials and methods

### 2.1. Chemicals and aqueous solutions

The chemicals used in this work were obtained from Sigma-Aldrich: hydrogen peroxide not stabilized (35% in water), peroxidase from horseradish (POD) (solid containing 150–200 units per mg); *N,N*-diethyl-*p*-phenylenediamine Sulfate ( $(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{NH}_2 - \text{H}_2\text{SO}_4$ ) (DPD) (97%). All the carboxylic acids were also obtained from Sigma-Aldrich. Their purity was always greater than 97%, except for the formic ( $\geq 96\%$ ) and lactic ( $\geq 85\text{--}90\%$ ) acids.

All the solutions were prepared with deionized ultra pure aerated milli-q water from Millipore (resistivity =  $18.2\text{ M}\Omega\text{ cm}$ ) under laminar flux hood. Moreover, all the glass containers and injection material for ionic chromatography were washed three times with ultra pure water before use. If necessary, the pH values were adjusted with perchloric acid (1 N) and NaOH (1 N) by a JENWAY 3310 pH-meter to  $\pm 0.01$  pH unit. All the solutions were kept in dark conditions and the final preparations were performed in a room equipped with a sodium lamp (589 nm).

### 2.2. Chemical analysis

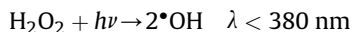
#### 2.2.1. Ionic chromatography

Ionic chromatography (IC) analyses were performed employing a DIONEX DX-320 equipped with an IonPac AG11 (guard-column  $4 \times 50\text{ mm}$ ) and an IonPac AS11 (analytical column  $5 \times 250\text{ mm}$ ) for anions and a DIONEX ICS-1500 equipped with an IonPac CG16 (guard-column  $4 \times 50\text{ mm}$ ) and an IonPac CS16 (analytical column  $5 \times 250\text{ mm}$ ) for cations. Working conditions were similar to those detailed by Jaffrezo et al. (1998) and Ricard et al. (2002). The use of an injection loop of  $750\text{ }\mu\text{L}$  gave detection limits for carboxylic acids of a few tenths of nM. The starting concentrations of carboxylic acids in water used during this work were between 5 and  $20\text{ }\mu\text{M}$  corresponding to typical range values measured in real cloud water (BEAM database; Löflund et al., 2002).

#### 2.2.2. $\cdot\text{OH}$ radical formation

The photochemical source of hydroxyl radical in this work was the photolysis of hydrogen peroxide.  $\text{H}_2\text{O}_2$  was chosen for its low reactivity with carboxylic acids in aqueous solution and its presence in cloud aqueous phase as a major photochemical source of  $\cdot\text{OH}$  radical formation (Marinoni et al., 2011).

$\cdot\text{OH}$  radical was directly produced by continuous photolysis of  $\text{H}_2\text{O}_2$ :



Hydrogen peroxide concentration was determined by spectrophotometric absorbance detection of a solution in which *N,N*-diethyl-*p*-phenylenediamine (DPD) was involved in a reaction catalysed by a peroxidase (POD). In the presence of POD,  $\text{H}_2\text{O}_2$  oxidizes two molecules of DPD to cationic radicals  $\text{DPD}^{+\cdot}$  (Bader et al., 1988), that are stable and absorb light at 551 nm ( $\epsilon = 21\,000\text{ M}^{-1}\text{ cm}^{-1}$ ). With a 10 cm optical pathway cell, the detection limit was  $0.1\text{ }\mu\text{M}$  calculated as 3 times the standard deviation of field blanks. Each measurement took less than 5 min.

### 2.3. Irradiation experiments

Organic acid solutions were irradiated in a photochemical reactor. The irradiation device was composed of a xenon lamp, a water filter to avoid the increase of solution temperature due to the Infrared radiations, a mirror to reflect the light vertically and a Pyrex reactor. A Pyrex plate, located at the top of the reactor, allowed for filtering of light at wavelengths higher than  $\sim 290\text{ nm}$ , corresponding to the solar emission. The reactor was a 500 mL cylindrical Pyrex container cooled by water circulation at a temperature of  $15 \pm 2\text{ }^\circ\text{C}$  in order to limit thermal reactions (see figure SM1). Samples were continuously stirred with a magnetic stirrer and a Teflon bar to ensure homogeneity.

The starting solution (350 mL) contained one carboxylic acid at  $1\text{ mg L}^{-1}$  and  $\text{H}_2\text{O}_2$  at 11.5 mM. The concentration of carboxylic acid corresponds to the  $\mu\text{M}$  level representing their typical amount found in cloud waters. The concentration of hydrogen peroxide used during this work, in agreement with experimental conditions used by

Altieri et al. (2008), was chosen in order to keep the hydroxyl radical formation rate ( $R_{\cdot\text{OH}}$ ) constant throughout the irradiation time.

In order to study the formation of dimer from the formic acid photooxidation, the most abundant carboxylic acid of cloud water (BEAM database) under atmospherically relevant aqueous water, irradiations of 20  $\mu\text{M}$  of formic acid were conducted in the presence of different amounts of  $\text{H}_2\text{O}_2$ .

If necessary, the pH was adjusted between 5.0 and 6.0 corresponding to the environmental pH range measured in the cloud aqueous phase (Marinoni et al., 2004). During the irradiation experiments, the concentrations of the different carboxylic acids and their degradation products were monitored by ionic chromatography. Samples (5 mL) were collected at fixed irradiation times. 50 mL of the starting solution kept in the dark at the same temperature was monitored throughout the experiment. No degradations or contaminations were observed under dark conditions. It is interesting to note that pyruvic and oxalic acid absorption spectra show an overlap with adopted irradiation sources (see Fig. 1). For the pyruvic and oxalic acids, the half-life time due to direct photolysis was estimated to be 16 and 95 h respectively under adopted irradiation conditions.

Fig. 1 displays the measured spectral irradiance of the xenon lamp, measured with an Ocean Optics SD 2000 CCD spectrophotometer (calibrated using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp) as well as a molar absorption coefficient of  $\text{H}_2\text{O}_2$ , oxalic, pyruvic and succinic acids in water solution at pH 5.5 (obtained with a Varian Cary 100 Scan UV–Vis double beam spectrophotometer). The wavelength-dependent light flux reaching the solution was calculated to be  $1.87 \times 10^{19}$  photons  $\text{m}^{-2} \text{s}^{-1}$  in the 290–370 nm range. This value was found to be close to those reported by Madronich and Flocke (1998) for actinic flux values at the Earth's surface in the same wavelength interval.

#### 2.4. Cloud water sampling

Sampling of cloud water was carried out at the puy de Dôme (pdD) station (48°N, 2°E; 1465 m a.s.l.), in the Massif Central Region (France). A large fraction of the time, the station is in the free troposphere and air masses from various origins are therefore exempt from the influence of local pollution.

The cloud droplet sampling was carried out by a one stage cloud droplet impactor equipped with a protection screen for the wind. With the air flux used ( $\sim 80 \text{ m}^3 \text{h}^{-1}$ ), the lower limit of the

aerodynamic diameter was approximately 7  $\mu\text{M}$  (Brantner et al., 1994), which ensured 80% collection efficiency. The impactor used for this study was made of stainless steel and aluminium. Cloud water samples were sterilized by filtration (0.22  $\mu\text{m}$  porosity, nylon filter) immediately after sampling to eliminate all the microorganisms. Irradiation experiments were performed after 12 hours on sampled cloud water, while, for analysis by ion chromatography (IC) carboxylic acid concentrations were determined no more than 24 hours after sampling. At every stage, sampling and analyses were carried out with the greatest precaution to minimize all possible external contamination and solutions were stored at 4 °C under dark conditions.

### 3. Results and discussion

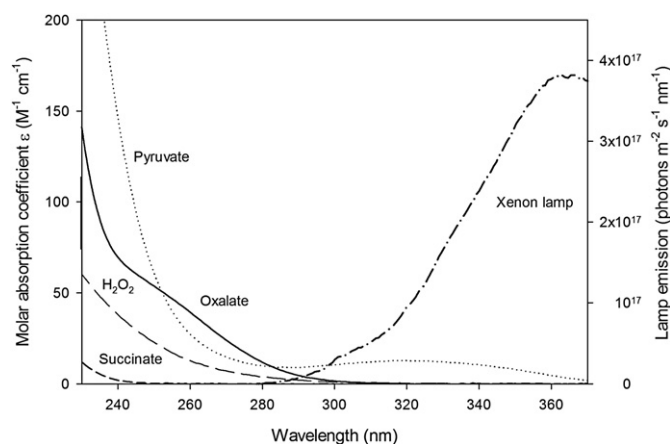
#### 3.1. Degradation of carboxylic acids photoinduced by $\text{H}_2\text{O}_2$ in aqueous solution

##### 3.1.1. Succinic acid photodegradation

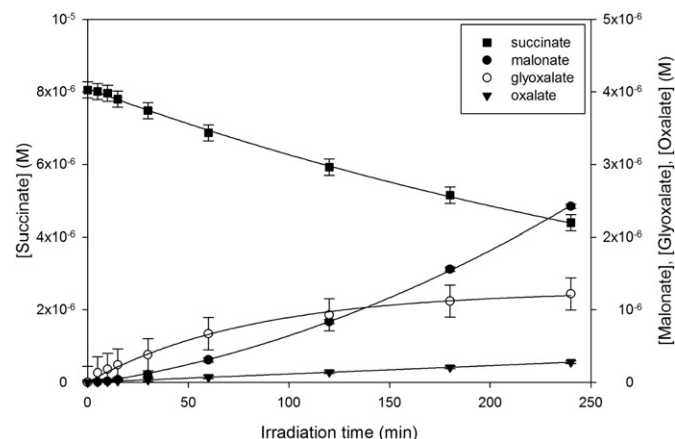
In cloud droplets, succinic acid originates from the dissolution of the soluble fraction of the particulate phase. This compound is found at significant concentrations in cloud water ranging from 0.6 up to 4.0  $\mu\text{M}$  (Löflund et al., 2002; Marinoni et al., 2004). In the atmosphere, succinic acid results from primary emissions from fossil fuel combustion and biomass burning, as well as from photochemical oxidation of organic precursors of both anthropogenic and biogenic origin (Chebbi and Carlier, 1996). In this section, the degradation mechanism of succinic acid in the presence of  $\cdot\text{OH}$  radicals is described in detail, while only the main results concerning the degradation product identification carried out for the other twelve carboxylic acids are reported. We focused on succinic acid oxidation pathways because its photoreactivity is still not fully understood. Moreover, succinic acid could be a potential source of smaller carboxylic acids via photooxidation.

A solution of 8  $\mu\text{M}$  of succinic acid and 11.5 mM of  $\text{H}_2\text{O}_2$  was prepared and the pH was adjusted to 5.0. The sampling times of 5 mL were the following:  $t_0$  (before the addition of  $\text{H}_2\text{O}_2$ ),  $t'_0$  (after addition of a few  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$  from a stock solution), 5, 10, 15, 30, 60, 120, 180, and 240 min. The evolution of the starting sample kept in the dark was monitored for the same time. No evolution was observed in the sample under dark conditions.

The kinetics of succinic acid disappearance as well as the formation of the main by-products such as oxalic, glyoxylic and malonic acids in the presence of hydroxyl radical are presented in Fig. 2. From the experimental data the following mechanism (Fig. 3)



**Fig. 1.** Molar absorption coefficients in aqueous solution (pH = 5.5) (left-axis) of  $\text{H}_2\text{O}_2$  (long-dashed line) and carboxylic acids used during this work: oxalate (solid line), pyruvate (dotted line) and succinate (dashed line). The dashed-dotted line with the right-hand axis shows the emission spectrum of the adopted xenon lamp reaching solution in the range 280–370 nm (total flux intensity =  $1.87 \times 10^{19}$  photons  $\text{m}^{-2} \text{s}^{-1}$ ).



**Fig. 2.** Time dependence of succinate, malonate, glyoxylate and oxalate concentrations during the irradiation of an aqueous solution of succinate (8  $\mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  (11.5 mM) at pH = 5.0. Error bars represent three times detection limit estimated from IC analysis for each compound.

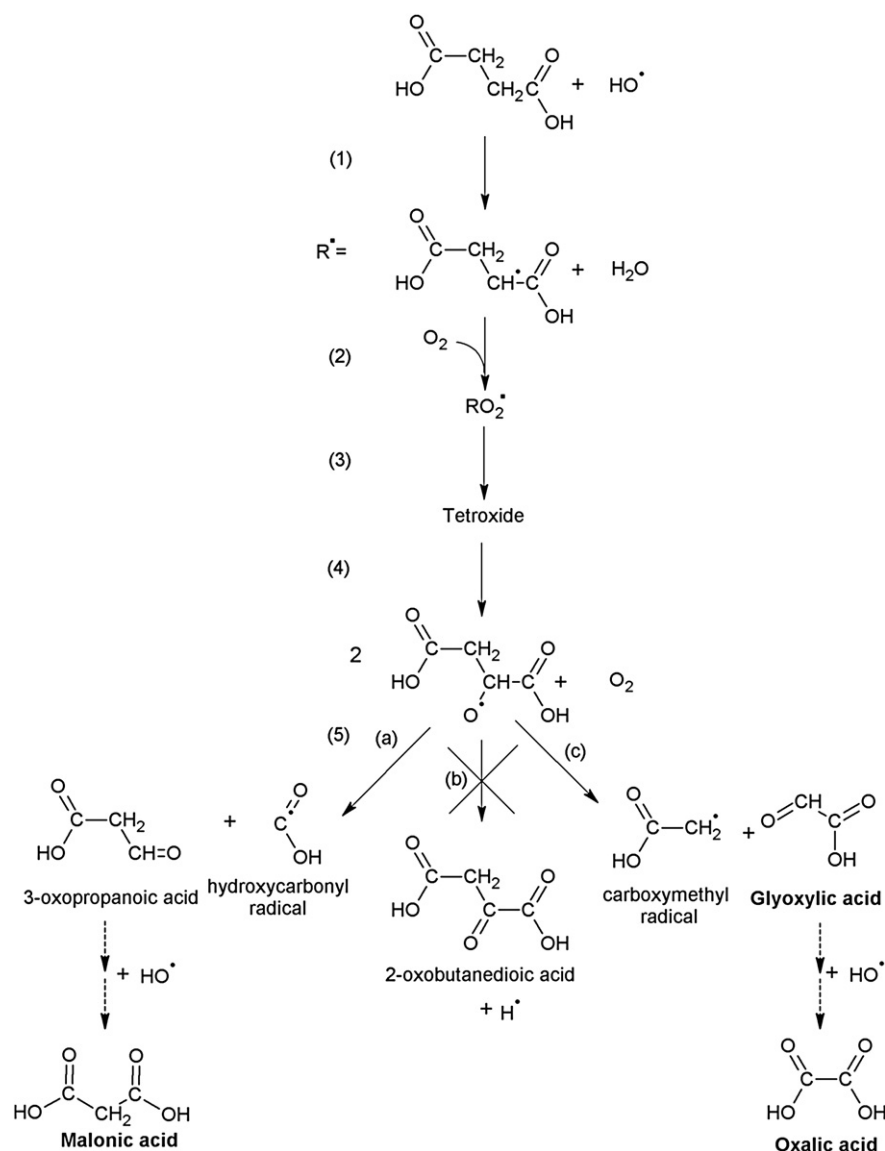


Fig. 3. Mechanism of succinic acid transformation in the presence of hydroxyl radical produced by hydrogen peroxide photolysis.

was proposed starting from the hydrogen abstraction from the  $\text{CH}_2$  groups on the succinic acid molecule (step 1). The generated succinic radical ( $\text{R}^\bullet$ ) reacts with molecular oxygen to form the corresponding peroxy radical  $\text{RO}_2^\bullet$  (step 2). In the particular case of the peroxy radical from succinic acid, the bimolecular reaction is strongly favoured leading to the tetroxide compound (step 3). The decomposition of unstable tetroxide into molecular oxygen and two alkoxy radicals is a well-known reaction (von Sonntag and Schuchmann, 1991) leading to the formation of an alkoxy radical (step 4) that can undergo three  $\beta$ -fragmentations (step 5). The first one (a) is the scission of the  $\text{CH-COOH}$  bond rising to the hydroxycarbonyl radical and an aldehyde derivative (3-oxopropanoic acid) that could react once again with the hydroxyl radical giving the malonic acid. The second possibility is the  $\text{CH-CH}_2$  (c) breaking, leading to the formation of the carboxymethyl radical and glyoxylic acid. It is interesting to note in Fig. 2 the plateau reached at around 120 min of irradiation for the glyoxylic acid formation (corresponding to  $1.2 \mu\text{M}$ ). Taking into account that at pH 5.0 the glyoxylic acid is 98% under its anionic form (i.e. glyoxylate) and the second order rate constant with

hydroxyl radical  $k_{\text{OH, Glyoxalate}} = (2.6 \pm 0.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Ervens et al., 2003), we can explain this trend with a competitive hydroxyl radical reactivity between glyoxylate and unreacted succinic acid ( $\sim 6 \mu\text{M}$  at 120 min). Moreover, glyoxylate/glyoxylic acid reactivity with hydroxyl radical produces oxalic acid via  $^\bullet\text{OH}$  mediated oxidation (confirmed also during irradiation of glyoxylic acid in the presence of hydroxyl radical).

Finally the third possible  $\beta$ -fragmentation could be the  $\text{C-H}$  bond (b) giving to the undetected 2-oxobutanedioic acid. A general description concerning reactivity of carboxylic acids toward hydroxyl radicals is given in a supplementary material section (schemes 1 and 2 in SM).

The molar concentrations of malonic, glyoxylic and oxalic acids represent 62, 31 and 7% of the disappeared succinic acid after 1 hour respectively. The identification of different carboxylic acids corresponds to approximately 100% of the succinic acid degraded in the first two hours of irradiation showing that transformation of succinic acid into these three products is a quantitative transformation. From the quantitative analysis of the degradation products, the  $\beta$ -fragmentations from the pathways (a) and (c) represent respectively



62 and 38% of the succinic acid disappeared so the  $\beta$ -fragmentation from way (b) should be negligible. Moreover from a thermodynamic point of view, the energy required to break a C–H bond ( $410 \text{ kJ mol}^{-1}$ ) (b) is stronger than the energy of the C–C bond ( $339 \text{ kJ mol}^{-1}$ ) and so more difficult to break (Hornback, 2006).

The difference observed between the formation of the carboxylic acids toward ways (a) and (c) seems to be supported by the stability of the generated carbon-centered radical because the tertiary radical obtained in way (a) is more stable and as a consequence, pathway (a) should be favoured compared to (c). The half-life time of the succinic acid, in our experimental condition, was estimated to be approximately 4.6 hours.

The reactivity of succinic acid toward photogenerated hydroxyl radicals has been previously investigated by Karpel Vel Leitner and Doré (1996). They reported that reactivity of hydroxyl radicals using monochromatic radiation at 253.7 nm, led to the fast formation of malonic acid followed by a plateau and the slow, but linear, formation of oxalic acid. Undetected glyoxylic acid could be due to its fast degradation attributed to its absorption at  $\lambda = 253.7 \text{ nm}$ . Other studies from Deguillaume et al. (2009), Herrmann et al. (2005) and Tilgner and Herrmann (2010) based on the CAPRAM aqueous phase mechanism suggested that the oxidation of succinic acid leads to the formation of 3-oxo propanoic acid (decarbonylation) and then to malonic acid. This mechanism also leads to the formation of glyoxylic acid through several intermediates (for details, see the CAPRAM website: [http://projects.tropos.de/capram/capram\\_30.html](http://projects.tropos.de/capram/capram_30.html)).

### 3.1.2. Phodegradation of other carboxylic acids

The same experiments were carried out for all the carboxylic acids (glutaric, tartaric, malic, lactic, malonic, propionic, pyruvic, glycolic, glyoxylic, acetic, oxalic and formic) and two aldehydes (acetaldehyde and formaldehyde) commonly found in atmospheric aqueous phase (Li et al., 2008; Munger et al., 1995). The main primary by-products observed due to the reaction with hydroxyl radicals in our experimental conditions are summarized in Fig. 4.

In our experimental conditions, longer half-life times are observed for malonic, oxalic and acetic acids (24, 15.5 and 8.0 h respectively) (see table SM1 for all the half-life times). These

carboxylic acids have also the special feature of being the degradation products of other carboxylic acids. Degradation by  $\cdot\text{OH}$  of (i) glutaric, succinic, malic, propionic acids leads to the formation of malonic acid; (ii) propionic, pyruvic, lactic acids or acetaldehyde leads to the formation of acetic acid and (iii) glyoxylic, tartaric, lactic, propionic and glycolic acids lead to the formation of oxalic acid (Fig. 4). Such mechanisms leading to the “accumulation” of oxalic acid via photooxidation of higher carboxylic acids could be responsible for the relatively high concentration found in cloud water (Marinoni et al., 2004) and in aerosol particles (Kundu et al., 2011; Legrand et al., 2007).

On the contrary, shorter half-life times are observed for formic, pyruvic and glyoxylic acids (0.4, 0.5 and 0.7 h respectively). In fact, pyruvic acid is very instable in the presence of  $\text{H}_2\text{O}_2$  (half-life time  $\sim 30 \text{ min}$  in the presence of  $11.5 \text{ mM H}_2\text{O}_2$ ) (Stefan and Bolton, 1999) and probably in the presence of other oxidant species. At pH 5.5, glyoxylic acid is under its anionic form (glyoxylate) and the second order rate constant with hydroxyl radical  $k_{\cdot\text{OH}, \text{Glyoxylate}} = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Ervens et al., 2003) is high enough to justify its fast degradation in the presence of hydroxyl radicals. Moreover, according to the different experiments carried out in the laboratory, two compounds, lactic and pyruvic acids, are present in very low concentrations and not observed during the degradation of other carboxylic acids studied. This is confirmed by the measurements in cloud aqueous phase where they are not systematically present and when they are present, their concentrations are very low (Marinoni et al., 2004).

The case of formic acid is particular due to its high abundance in the cloud aqueous phase (Marinoni et al., 2004) and its very short half-life time in the presence of  $\cdot\text{OH}$  radicals and under our experimental conditions (0.4 h). The high abundance of formic acid is certainly due to the fact that it is the last carboxylic acid, before  $\text{CO}_2$ , in the oxidation chain of the large majority of organic compounds present in the atmosphere. However, this compound is easily oxidizable with one of the highest rate constants toward photogenerated hydroxyl radicals ( $k_{\cdot\text{OH}, \text{formate}} = 3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Chin and Wine, 1994).

From our experimental results, a mechanism of carboxylic acid degradation in the presence of  $\cdot\text{OH}$  radicals and in aqueous solution

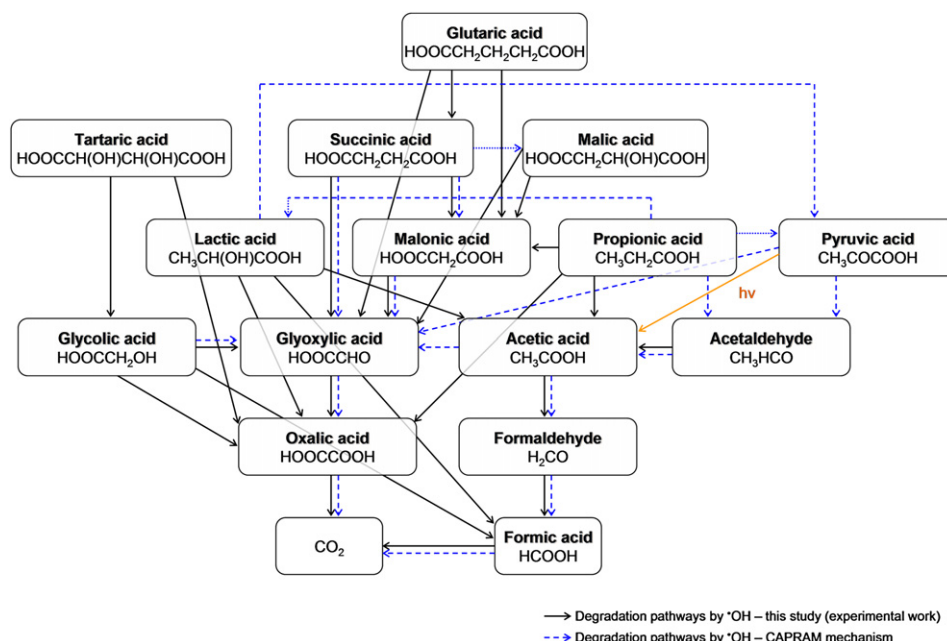


Fig. 4. General scheme of carboxylic acids degradation from glutaric acid to  $\text{CO}_2$ .

is proposed (Fig. 4). The main intermediates (carboxylic acids) are identified from the glutaric acid (dicarboxylic acid with 5 carbon atoms) to the complete mineralization into  $\text{CO}_2$ . In this figure, we have also added (blue dotted line) the conversions between the carboxylic acids that are implemented in the current most explicit cloud chemistry model. Most of the oxidation pathways we observed in this study are taken into account in the model but some significant connections between carboxylic acids are missing. For example, the model mechanism does not consider the production of oxalic and formic acids by the oxidation of lactic acid but it considers the oxidation of lactic acid into pyruvic acid and the production of lactic acid by propionic acid oxidation. This shows that there are still some uncertainties associated to the transformation of carboxylic acids in the atmospheric aqueous phase and that more investigations are needed.

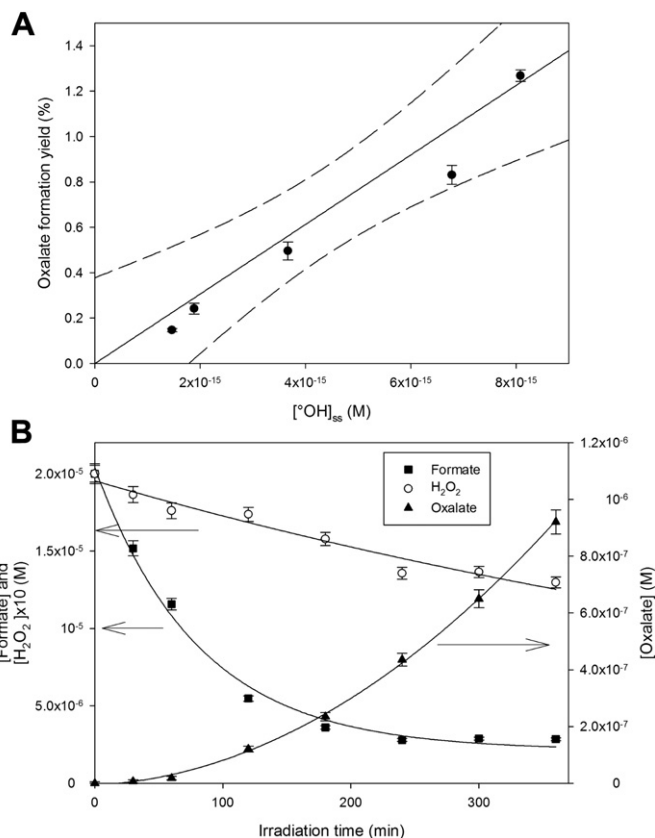
### 3.1.3. Formic acid photooxidation and oxalic acid formation

In order to better understand the behaviour of carboxylic acids in cloud water, the fate of formic acid, was investigated. 20  $\mu\text{M}$  of formic acid were irradiated in the presence of different concentrations of  $\text{H}_2\text{O}_2$  (from 100  $\mu\text{M}$  to 1 mM) at  $\text{pH} = 5.5$  under polychromatic wavelengths. Moreover, hydroxyl radical formation rates were measured for each amount of  $\text{H}_2\text{O}_2$  using a fluorescence technique based on the reactivity of terephthalic acid (TA) with hydroxyl radicals previously described (Charbouillot et al., 2011). The steady-state concentrations of hydroxyl radicals ( $[\cdot\text{OH}]_{\text{ss}}$ ) were then calculated using the following Eq. (1).

$$[\cdot\text{OH}]_{\text{ss}} = \frac{R_{\cdot\text{OH}}}{k_{\text{TA}\cdot\text{OH}}[\text{TA}]} \quad (1)$$

where  $R_{\cdot\text{OH}}$  is the hydroxyl radical formation rate ( $\text{M s}^{-1}$ ),  $k_{\text{TA}\cdot\text{OH}}$  the second order rate constant between terephthalic acid and hydroxyl radical ( $4.0 \pm 0.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Charbouillot et al., 2011) and  $[\text{TA}]$  the concentration of terephthalic acid used for the calculation of hydroxyl radical formation rate (1 mM).

We notice that the formation yield of oxalic acid, determined as the ratio between the initial formation rate of oxalic acid and the initial degradation rate of formic acid, ranges from 0.5 to 1.3% in the presence of 100  $\mu\text{M}$  (i.e.  $[\cdot\text{OH}]_{\text{ss}} = 1.5 \times 10^{-15} \text{ M}$ ) and 1 mM (i.e.  $[\cdot\text{OH}]_{\text{ss}} = 8.1 \times 10^{-15} \text{ M}$ ) of  $\text{H}_2\text{O}_2$  respectively (Fig. 5A). Hydroxyl radical steady-state concentration range has been chosen in agreement with reported values by Herrmann and coworkers (2010) for remote and urban cloud droplets case study: from  $2.9 \times 10^{-16}$  up to  $1.6 \times 10^{-15} \text{ M}$  and from  $4.8 \times 10^{-15}$  up to  $6.9 \times 10^{-14} \text{ M}$  respectively. Fig. 5B reports the time evolution of oxalic acid upon irradiation of 20  $\mu\text{M}$  of formic acid and 200  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$ . Under such conditions, the half-life time of formic acid is about 80 min and oxalic acid formation could be explained on the basis of the proposed mechanism presented in Fig. SM2). This mechanism was proposed to explain the formation of oxalic acid from the photooxidation of formic acid. The first step is the hydrogen abstraction on the formic acid molecule to form the hydroxycarbonyl radical ( $\cdot\text{COOH}$ ). Then, this radical can react following three different pathways. The first one (a) is the conversion degradation into  $\text{CO}_2$ . The second pathway (b) involves the recombination of two radicals leading to the formation of oxalic acid (dimerization). The third one (c) is the reaction between hydroxycarbonyl radicals and molecular oxygen to form the corresponding peroxy radical followed by the tetroxide formation. Tetroxide, as discussed in the SM, can be dissociated into two alkoxy radicals and molecular oxygen. The alkoxy radical can be degraded in  $\text{CO}_2$  and hydroxyl radicals or it can react with another alkoxy radical to form oxalic acid and molecular oxygen. We notice that the formation of oxalic acid from the degradation of formic

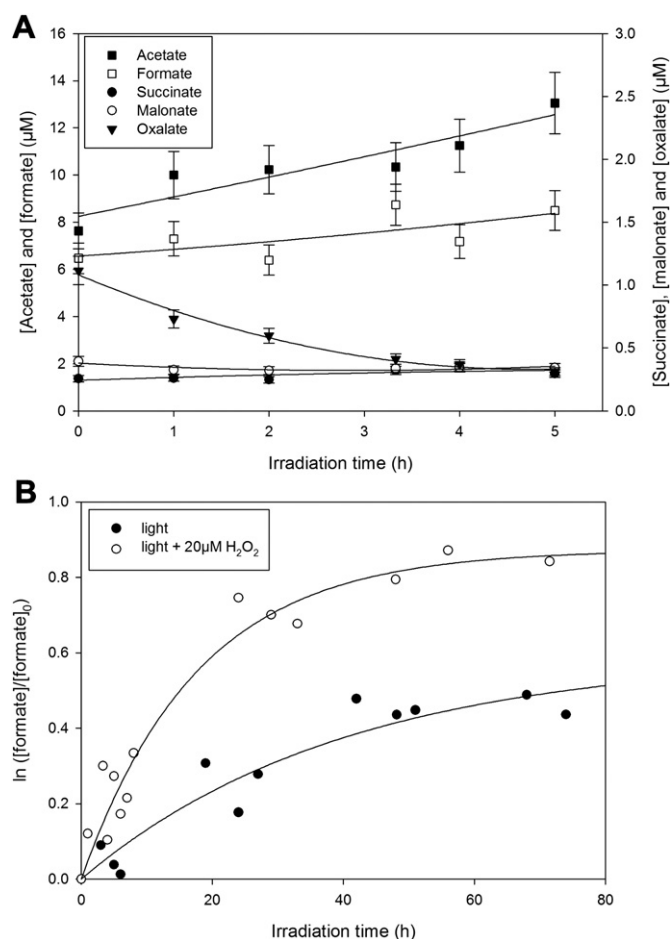


**Fig. 5.** A) Oxalic acid formation yield (%) from the photodegradation of 20  $\mu\text{M}$  of formic acid at  $\text{pH} = 5.0$  as function of hydroxyl radical steady-state at  $\text{pH} 5.0$  and  $15 \pm 2^\circ \text{C}$ . The solid line represents linear regression of averaged points and the dashed lines denote the 95% confidence interval of this fit. B) Time evolution of formate,  $\text{H}_2\text{O}_2$  and oxalate concentrations during the irradiation of 20  $\mu\text{M}$  formate in the presence (200  $\mu\text{M}$ ) of  $\text{H}_2\text{O}_2$  at  $\text{pH} = 5.0$  under polychromatic wavelengths. Note that  $\text{H}_2\text{O}_2$  concentration is divided by 10 in the figure (see y-label).

acid involves molecular oxygen for the pathway (c). In order to confirm the proposed mechanism, irradiations of formic acid (20  $\mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  (200  $\mu\text{M}$ ) were conducted with and without oxygen. These experiments showed that the formic acid degradation rate and the oxalic acid formation rate were respectively two times and four times higher in the presence of oxygen demonstrating the existence and partial competition of ways (b) and (c) proposed in Fig. SM2.

### 3.2. Irradiation of cloud aqueous phase

In order to evaluate the carboxylic acid fate in the presence of hydroxyl radicals under more realistic atmospheric conditions, we performed a series of irradiation experiments of cloud water collected at the top of the puy de Dôme without and after addition of 20  $\mu\text{M}$   $\text{H}_2\text{O}_2$ . In such experiments, concentrations of the different carboxylic acids (acetic, formic, succinic, malonic and oxalic acids) were monitored as a function of irradiation time. Time evolutions of carboxylic acid concentrations are reported in doped solutions (Fig. 6A). A small increase of the concentrations of acetic, formic, succinic and malonic acids is observed. On the contrary, a decrease of the concentration in oxalic acid is shown almost certainly due to the direct photolysis under the adopted irradiation conditions. In Fig. 6B we reported the normalized  $\ln(C/C_0)$  evolution of formic acid during irradiation of the sampled cloud water. It is interesting to note that production of formic acid is increased in the presence of



**Fig. 6.** Irradiation of a cloud water sample collected at puy de Dome station. A) Concentration of acetate, format, succinate, malonate and oxalate as a function of the irradiation time (sample + 20 μM H<sub>2</sub>O<sub>2</sub> added before irradiation). B)  $\ln([formate]/[formate]_0)$  evolution toward irradiation time of the formic acid concentration. Starting H<sub>2</sub>O<sub>2</sub> concentration in sampled cloud water was measured to be less than 1 μM.

added hydrogen peroxide as a photochemical source of hydroxyl radicals.

This irradiation experiment shows that i) photochemical processes impact the concentration of carboxylic acids in cloud aqueous phase; ii) the organic compounds, naturally present in the cloud aqueous phase, can be considered as a possible source of main carboxylic acids via oxidation-mediated processes.

#### 4. Conclusions

The two kinds of experiments carried out on the photooxidation of the main carboxylic acids in water show an important chemical reactivity more particularly towards photogenerated  $\cdot\text{OH}$  radicals. In the first part of the paper, the reactivity of  $\cdot\text{OH}$  on different carboxylic acids was established, showing that the degradation of carboxylic acids leads mainly to the degradation into other carboxylic acids of a smaller carbon chain length. The shortening of the carbon chain is particularly favoured for the dicarboxylic acids. Indeed, the degradation of glutaric acid leads to the formation of succinic acid, then to malonic and oxalic acids through glyoxylic acid formation. This mechanism of dicarboxylic acid degradation in aqueous phase was proposed in several modelling studies (Ervens et al., 2004; Herrmann et al., 2005; Tilgner and Herrmann, 2010). However, it is important to note that the experiments with formic acid mainly led to its transformation into CO<sub>2</sub>, but the formation of

oxalic acid (representing about 1% of the formic acid disappeared) was also observed. This result suggests the transformation in organic compounds of higher molecular weight and mechanism of radical condensation as highlighted in several recent papers (Carlton et al., 2007; Lim et al., 2010; Tan et al., 2011). The main goal of our future work will be to know which physico-chemical conditions favour the chain fragmentation processes (shortening by oxidation) or the organic radical recombination (increase of the molecular weight).

The irradiation of the cloud water samples in the laboratory photoreactor leads mainly to the global production of carboxylic acids. The increase in the concentration of the main carboxylic acids, systematically observed in the presence of higher hydrogen peroxide concentrations, shows that the hydroxyl radical is involved in the oxidation processes and could be considered as one of the main oxidant species responsible for the transformation of the organic matter present in atmospheric water. These experiments demonstrate that carboxylic acids can be produced in cloud aqueous phase by photochemical processes and mainly by the reactivity of  $\cdot\text{OH}$ .

In conclusion, the photochemical mechanisms described in this work will be very helpful to interpret experimental data obtained under laboratory as well as under *in situ* conditions. It will open new perspectives to investigate more complex situations. These results will be integrated into atmospheric cloud chemistry models in order to assess the multiphase chemistry that really takes place in cloud systems.

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#### Appendix A. Supplementary material

Supplementary material related to this article can be found online at [doi:10.1016/j.atmosenv.2012.03.079](https://doi.org/10.1016/j.atmosenv.2012.03.079).

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