

Interactive comment on “Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls” by C. M. Pavuluri et al.

Anonymous Referee #1

Received and published: 9 February 2015

It is now well accepted that water soluble organic compounds undergo aqueous chemistry in atmospheric waters and form secondary organic aerosol (SOA). Moreover, aqueous chemistry could be a chemical aging process of hygroscopic wet aerosols at high RH, yet largely unexplored. The manuscript by Pavuluri et al. demonstrates this aging process through aqueous photochemistry. Pavuluri et al. sampled two types of ambient aerosols (i.e., biogenic aerosols (BA) and anthropogenic aerosols (AA)), conducted UV-photolysis after wetting BA and AA samples, presented real-time measurements of organic compounds (carbonyls and diacids) and discussed photochemi-

C129

cal degradation and formation of these organic compounds. Most of degradation and formation were due to OH radical formed from various sources (e.g., Fenton reactions, H₂O₂, and photosensitizers), whereas the degradation of C₂/C₃ diacids was due to Fe species, which form strong light absorbing Fe ligands. I think this manuscript is well written and suitable for the readership of Atmospheric Chemistry and Physics, so I recommend it for publication. Following comments are provided for authors' consideration.

[Page 1198, Line 14-16] Authors should mention the phase of ambient aerosol samples. Were they liquid and all the organic/inorganic constituents well distributed? And were they hygroscopic so they took up water evenly by wetting? Since authors conducted separate photochemical reaction vessel experiments, not only the reaction time but the phase, the hygroscopicity and the morphology of aerosols should matter.

[Page 1198, Line 28-Page 1200, Line 7] Pyruvic acid and methylglyoxal do absorb 254 nm UV, and radical reactions take place. But UV photolysis of these is minor when OH radical reactions of these occur. In addition to Fe-catalyzed UV photolysis and NO₃ photolysis, authors should discuss photochemical effects of sulfates. Although authors did not measure sulfate concentrations, in Table 1 substantial amounts of S were found. Noziere et al., Geophys. Res. Lett. (2009) measured organosulfates formed by the UV photolysis of organic compounds.

[Page 1205, Line 12-23] Authors claim that Fe-catalyzed photolysis is the main decomposition reaction of C₂ & C₃ diacids since these diacids form strong light absorbing Fe ligands. Is this still true for the photolysis of tropospheric UV (>300 nm)? Besides, C₂/C₃ diacids form stable and low volatile carboxylate salts with amines. Is still Fe the major sink when amines are present? By the way, photochemical reactions were conducted up to 120 hrs. I am not sure why reactions exceed daytime 12 hrs? There should occur other reactions (e.g., NO₃, O₃ reactions, acid catalysis) during the nighttime. Besides, using 254 nm UV should represent daytime photochemistry in less than 12 hrs.

C130

[Page 1207, Line 6-7] Shouldn't author mention rate constants of the OH radical reaction in the aqueous phase? What they have is the gas-phase rate constants. By the way, in the aqueous phase, the glyoxal rate constant is bigger. To me, methylglyoxal production in AA is just sufficient to maintain "the steady state."

[Page 1209, Line 22-23] Did authors find any evidence of photochemical oligomerization (i.e., organic radical-radical reaction) when the concentrations of organic precursors are high (mM or above)? Tartaric acid is the major dimer product of glyoxal + OH (Lim et al., Atmos. Chem. Phys., 2010) and C₆H₁₀O₆ (m/z-177) is the major dimer product of methylglyoxal + OH (Tan et al., Atmos. Chem. Phys., 2012).

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 1193, 2015.