

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2021-137

Anonymous Referee #3

Referee comment on "Revisiting the reaction of dicarbonyls in aerosol proxy solutions containing ammonia: the case of butenedial" by Jack C. Hensley et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-137-RC3>, 2021

Hensley and coworkers studied the reaction of butenedial, which has been observed in lab studies and ambient air, with OH- and water in the absence of NH_x and in ammonium sulfate (AS) solutions. Products and rates were monitored with 1H NMR. The butenedial was synthesized. LC-TOF-MS data were also taken to analyze products. This is a solid study. Generally I found the discussion of the chemistry, or analytical assignments, could have been more specific and clear. I have the following comments that should be addressed prior to publication.

Can "kinetic mechanism" be changed into something more clear like "kinetic modeling mechanism"?

Can the authors provide more information into how products such as pyrrolinone were assigned? More discussion is needed to support major reaction route and products in Figure 1. How were products confirmed or ruled out based on NMR shifts? I see that the SI has some assignments, but the text should refer to the SI when these assignments are called on, and it's not clear how these assignments were made and no citations to analogous compounds in the literature. It's a good idea to also discuss any limitations when it comes to unambiguously assigning structure from NMR shifts in a complex mixture and/or from m/z.

Some of the figures/tables in the SI are not referred to in the main text. For example, when the authors mention the solutions turn brown they should probably refer to the figures they provided in the SI, otherwise the reader does not know to look.

92 What is the concentration of butenedial in ambient air? Is it observed in the gas or condensed phase? How do these concentrations compare with the initial concentrations the authors chose for this work, and if they are very different, please discuss how this work can extrapolate to the ambient environment.

99 "react with OH-" is stated multiple times, without discussion about how. Please summarize what is known about how OH- reacts with the moieties of interest, and please discuss the specific mechanism. Same thing with NHx.

149 The mass spectra show a number of odd peaks. Did the authors rule out 2N products and how did they confirm 0N products? It would be good to specifically address whether this system is anticipated to form 2N cyclic compounds like in other dialdehyde systems. What is the mass precision after calibration in order to differentiate between 0-2N? (the assigned mass and peak shown in S4 are roughly 5 ppm off)

193-200 Can the authors provide citations for any of these reactions that they are suggesting, such as OH- reacting with BD to form a hydroxyacid (and by which pathway, i.e., addition/abstraction and where) and then ultimately leads to oligomeric light absorbing products (again, by which pathways). And what do the oligomeric light absorbing products look like?

236 Reaction R3 is an example of an accretion product given in this work. Its assignment was shown in Figure S6/S8 and associated discussion. The text should reference the carbon/proton assignments in S6, and discuss how those assignments were made (including any NMR reference tables used and for which proxy molecules). Also instead of "produces" it should say "proposed to produce" because these are only tentative assignments after all. Please insert a few sentences to discuss the specific mechanism by which this product can form, via reaction R3 with OH⁻.

Even though the solutions look visibly brown, the authors did use a lot of carbon material initially. What is the mass absorption coefficient (MAC) of these reactions and how do they compare to other brown carbon (e.g., from Updyke 2012)?

320 clarify "favorable separation"

345 I see that the authors considered the wet deposition lifetime of aerosols (~ 1 week) from Seinfeld and Pandis. I'd also suggest to calculate the wet deposition lifetime of the molecule based on equation 12 in this work (<https://acp.copernicus.org/preprints/acp-2021-137/>) to better motivate the importance of aqueous partitioning for this compound compared to its gas phase photolysis.

330 the lifetimes decrease with increasing pH. Can the authors discuss relevance of this reaction to aerosol water, which tends to be acidic (such that BD would have lifetimes of > 4 h, and would photolyze before that) but would be the locations where one would find higher NH₄⁺. Comparatively pH 6 might be cloud droplet range, but then ionic strengths are low.

