

Atmos. Chem. Phys. Discuss., referee comment RC1
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Referee comment on acp-2021-137

Anonymous Referee #1

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-RC1>, 2021

This paper summarizes aqueous-phase reaction studies of butenedial as it reacts with OH^- (at high pH) and $\text{NH}_3 / \text{NH}_4^+$ (" NH_x ," at neutral and acidic pH). In both cases, brown carbon is produced. Rates are compared with wet deposition as sinks for butenedial, and it is concluded that reaction with NH_x can compete with wet deposition at mildly acidic pH or high aerosol-phase NH_x concentrations. The atmospheric significance of butenedial should be better established at the beginning of the article, but in general, the work is extremely thorough and the conclusions are convincing.

Specific comments:

Line 41: The introduction contains many chemical justifications for studying aqueous-phase chemistry of butenedial, but this sentence is the only atmospheric justification given: "Larger, complex dicarbonyls are also thought to be important products of biomass burning and fossil fuel combustion (Arey et al., 2009; Aschmann et al., 2011, 2014; Gómez Alvarez et al., 2007, 2009; Volkamer et al., 2001; Yuan et al., 2017), but they have rarely been studied or quantified in the atmosphere. " It would be helpful if the authors could here address the question of whether butenedial has ever been reported in an aerosol field study or a chamber oxidation study. If not, why was it specifically selected? It would seem odd to study the chemistry of a reactant that has not yet been identified in the atmosphere or in a chamber study.

Line 51: The ease of using bulk-phase methods to study aerosol-phase chemistry is described here, but the drawbacks of using only these methods should also be described. These include lack of sites for surface chemistry to take place.

Line 21, 61-64, 317 and 320: According to Noziere et al., 2009, and Sedehi et al., 2013, the quadratic dependence of the rate on glyoxal concentrations is only observed at high concentrations, and switches to 1st order at concentrations below the molar range. The argument (made three times in the manuscript and referenced as a key difference from glyoxal in the abstract) that the quadratic rate law contributes to the reaction shutting off at low concentrations is therefore not sound. The paragraph in the discussion should be rewritten to avoid a reliance on this idea. But I agree with the rest of the statement at line 62.

Line 108: The manuscript states that no overlapping products were observed between OH⁻ and NH_x experiments. However, the OH⁻ reaction products were detected using negative ion mode, and the NH_x reaction products were detected using positive ion mode on a different mass spectrometer. Were the two reactions tested using the other mass spectrometric methods to screen for these overlapping products? I did not find a clear answer to this question in the manuscript or supplement.

Technical Corrections:

Line 148: The manuscript states that 0.5 M sodium carbonate (Na₂CO₃) – sodium bicarbonate (NaHCO₃) buffer was added to every reaction solution with ammonium. Table 1 states that a pH range of 3 to 9 was studied, but the carbonate buffer could only be used at the upper end of this range. How was pH experimentally set to values less than 8?

Line 182: This sentence refers to a fitting procedure described in section 2.3.1, but the sentence is part of section 2.3.1. A typo?

References Cited

Noziere, B., P. Dziedzic and A. Cordova (2009). "Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH_4^+)." *Journal of Physical Chemistry A* **113** (1): 231-237.

Sedehi, N., H. Takano, V. A. Blasic, K. A. Sullivan and D. O. De Haan (2013). "Temperature- and pH-dependent aqueous-phase kinetics of the reactions of glyoxal and methylglyoxal with atmospheric amines and ammonium sulfate." *Atmospheric Environment* **77**: 656-663.