10 May 2021

Author Response for “Revisiting the reaction of dicarbonyls in aerosol proxy solutions containing ammonia: the case of butenedial” by Jack C. Hensley et al.

We thank the anonymous referee for their thoughtful comments, which have helped improve the manuscript. Our replies are below (referee comment in bold face, response in normal face, manuscript indented with new content in italics, maintained content in normal face, and removed content in strike-through).

This paper summarizes aqueous-phase reaction studies of butenedial as it reacts with OH^- (at high pH) and NH_3 / 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; Gomez 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.

The history of butenedial measurement in ambient air and chamber oxidation studies is further described on Line 97. This account has been extended in the manuscript to better motivate studies of butenedial, as suggested by the reviewer:

> ~~Butenedial is an unsaturated 1,4-dialdehyde observed as a major product of aromatic and furan degradation in laboratory studies (Arey et al., 2009; Aschmann et al., 2014; Bierbach et al., 1994; Coggon et al., 2019; Stockwell et al., 2015; Strollo and Ziemann, 2013; Volkamer et al., 2001) and in ambient air (Obermeyer et al., 2009).~~ *Butenedial is an unsaturated 1,4-dialdehyde known to be a major oxidation product of atmospherically abundant aromatics and furans (Bierbach et al., 1994; Coggon et al., 2019; Stockwell et al., 2015; Strollo and Ziemann, 2013; Volkamer et al., 2001; Raoult et al., 2004; Müller et al., 2016). Laboratory studies of OH oxidation of precursor compounds have recorded butenedial yields of 10.3% (Berndt and Böge, 2006) and 16% (Gómez Alvarez et al., 2007) from benzene; 13% (Gómez Alvarez et al., 2007) and 11-32% (Arey et al., 2009) from toluene; 10-29% (Arey et al., 2009) from o-xylene; and 99% (Gómez Alvarez et al., 2009) and 75% from furan (Aschmann et al., 2014). Butenedial and other dicarbonyls were detected in ambient air samples with elevated loading of aromatic hydrocarbons (Obermeyer et al., 2009). To the best of our knowledge, butenedial has not yet been quantitatively measured in field studies, in part due to the aforementioned challenges of measuring dicarbonyls.*

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.

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In an upcoming manuscript, we contrast butenedial/NH_X reaction in bulk solutions and levitated particles, which considers the limitations of bulk solution studies when extrapolated to atmospheric aerosol. A sentence has been added in the manuscript to address the major limitations, starting on Line 51:

> Bulk solutions can mimic the aqueous phase of actual atmospheric particles, albeit at lower ionic strength *and reagent concentrations and without surface effects, which may influence particle phase chemistry (Yan et al., 2016; McNeill, 2015). The extrapolation of chemistry quantified in bulk solutions to atmospheric particles is evaluated in another study (Hensley et al., 2021, in prep). Bulk solutions have the additional* advantage […]

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.

Thank you for this point. The manuscript has been updated such that comparison of butenedial and glyoxal reaction with NH_X does not rely on a difference of reaction order at low concentrations:

Lines 63-69:

> Yu et al. (2011) and Kampf et al. (2012) demonstrate that imidazole formation from glyoxal/NH_X follows a rate law of the form $k[GL]^2[NH_4^+][NH_3]$, and is as such fastest at neutral to basic pH (Maxut, 2015). *Noziere et al. (2009) suggest that glyoxal/NH_X is second order at low reactant concentrations, where imine formation is the rate-limiting step (Sedehi et al., 2013).* Although imidazoles have also been detected in chamber experiments of deliquesced AS aerosol, the reaction is observed to be too slow at typical dicarbonyl concentrations and aerosol pH and NH_X to affect chemical composition~~, in part due to the quadratic dependence on glyoxal~~ (Galloway et al., 2009; Yu et al., 2011).

Lines 341-342:

> While imidazole production is second order in glyoxal and NH_3 and explicitly pH dependent~~, rendering it inefficient at low ambient concentrations~~ (Yu et al., 2011), pyrrolinone production is linearly dependent on butenedial and NH_3,

Lines 344-345:

> We suggest that dicarbonyls […] can form heterocycles with bimolecular rate laws~~, which means they can occur even if ambient concentrations are low.~~

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.

We find that butenedial/OH^- reaction is slow at pH < 9 (0.9 M butenedial/0.45 M AS has solution pH < 6) and butenedial/NH_X reaction is negligible in butenedial/OH^- experiments, which did not have a source of NH_X. This demonstrates that these reactions were studied in isolation of one another. We observed that product spectra in NMR measurements of butenedial/OH^- and butenedial/NH_X reaction mixtures are not the same, although this was a qualitative verification and is omitted from the manuscript. Additionally, we did not observe evidence of butenedial/NH_X reaction products in butenedial/OH^- reaction mixtures with LC-MS operated in positive mode.

The manuscript is updated to explicitly articulate the above on lines 117-119:

> As is ~~justified~~ *shown* later, reaction with OH^- was found to be negligible at the pH and NH_X conditions of the butenedial/NH_X reaction studies, and vice versa, *indicating that butenedial/OH^- and butenedial/NH_X reactions were studied in isolation of one another.*~~, as no overlapping products were observed.~~

Technical Corrections:

Line 148: The manuscript states that 0.5 M sodium carbonate (Na_2CO_3) – sodium bicarbonate ($NaHCO_3$) 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?

In butenedial aqueous solutions with NH_X, initial pH is determined by: (1) residual acetic acid from butenedial synthesis, (2) ammonium sulfate (AS), and (3) carbonate buffer system, if added. Without addition of carbonate buffer, the starting pH of solution is >3-4, as was the case for solutions with initial composition 0.4 M butenedial/0.2 M AS (Figure S22).

The reviewer refers to solutions with initial composition 0.9 M butenedial/0.45 M AS, with 0.5 M carbonate buffer added. The starting solution pH ~6 reflects the consumption of some acidity by the added buffer. As seen in Figure 3, pH decreases during reaction, presumably due to a reaction byproduct, as was demonstrated for glyoxal/AS reaction (Yu et al., 2011). The influence of the identified factors on solution pH for the 0.9 M butenedial/0.45 M AS experiments is now specified in Section 2.3.2 on lines 204-206:

> *pH was affected by residual acetic acid from butenedial synthesis, ammonium sulfate, addition of carbonate buffer, and production of acid during reaction.* pH was estimated with an empirical formulation that agreed closely with measurements (Figure S19).

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?

Section 2.3.2 has now been appropriately labeled on line 200.

~~2.3.1~~ *2.3.2* Butenedial/NH$_X$ reaction

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