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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).

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 NHx and in ammonium sulfate (AS) solutions. Products and rates were monitored with 1H HMR. 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"?

We have changed the terminology from "kinetic mechanism" to "model kinetic mechanism" throughout the text. Any mention of "model kinetic mechanism" explicitly refers to the set of differential equations that govern the kinetics of the chemistry. To distinguish between the chemical speciation and kinetics, three mentions of "chemical mechanism" have been removed and replaced with "chemical scheme" and "model kinetic mechanism."

Can the authors provide more information into how products such as pyrrolinone were assigned? More discussion is need 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.

Thank you for this comment. The suggestions have strengthened our paper. As we did not have standards for proposed products against which to compare NMR and MS spectra, the proposed products were identified in situ with a combination of NMR and MS. TOF-MS with unit mass precision and LC-MS with <5 ppm mass precision were used to identify unambiguous molecular formula of reactant and reaction products. We recognize that unambiguous assignment of NMR shifts to specific molecules in a complex mixture can be tentative at best, and the language throughout the text now reflects this. However, as we describe below, the proposed products of reaction are consistent with the exact chemical formulae determined by MS, the expected NMR assignment as well as well-established understanding of organic chemistry of this type of chemical systems (e.g., glyoxal/NH_X).

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As is discussed in Section 2.2.2 of the main text, the species identification methodology was as follows: (1) determine molecular formula with MS measurement, (2) group NMR-identified protons based on integer signal, maintained through time, that are temporally consistent with speices measured with MS, (3) derive proposed proton assignment in NMR measurements to determine structures of proposed products.

1. The two proposed major products of butenedial/NH_X reaction, C_4H_5NO and $C_8H_7NO_2$, were identified with the observed m/z channels of formed products in butenedial/AS solutions. With new LC-MS measurements of both butenedial/NH_X and butenedial/OH^- reaction mixtures at high mass precision, these molecular formulae were unambiguous (Figure S12-S13, reproduced below, which also includes an accretion product of three butenedial units). Based on the molecular formulae, the reactant products have the same degree of saturation as their parent compounds.

Figure S12.

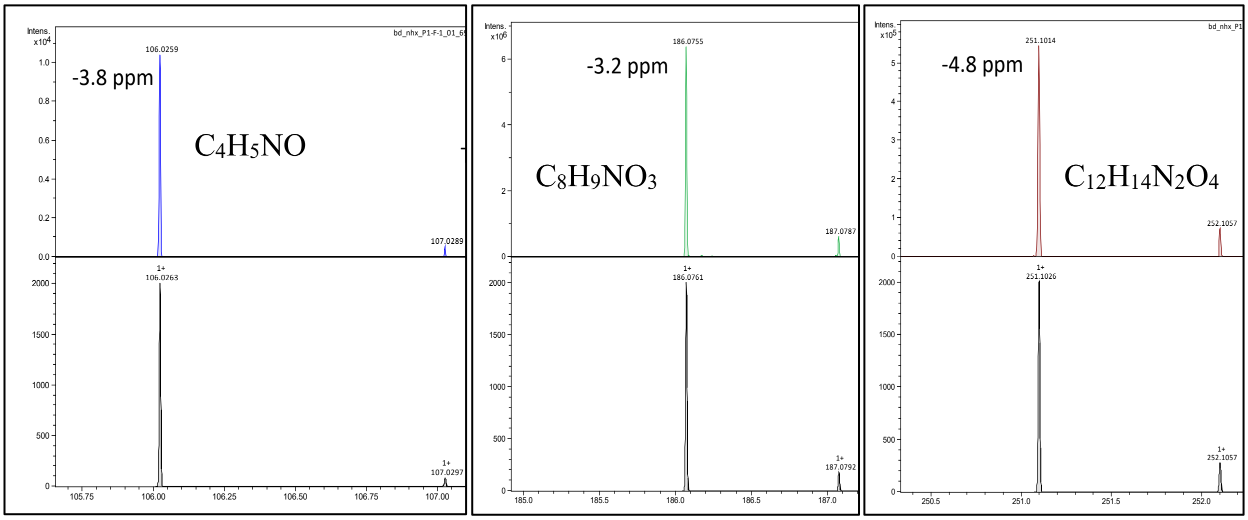
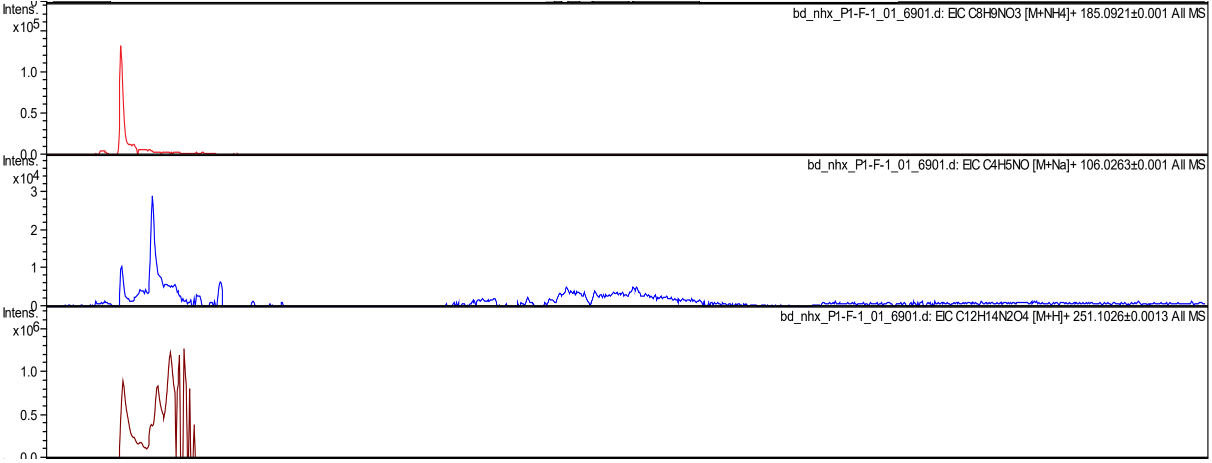
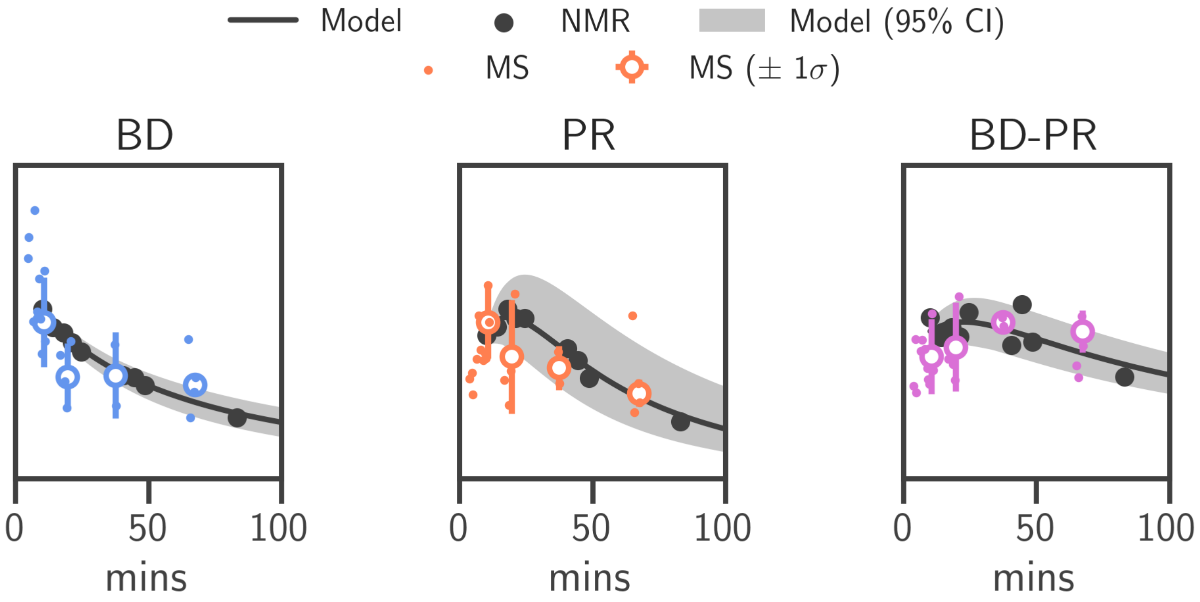


Figure S13.



2. As is shown in Table S5, excluding butenedial, we observe two groups of protons with integer signal that is maintained through the progress of reaction. They are, in δ (ppm) [number of protons], Group 1: 6.55 [1], 5.92 [1], 3.37 [2] and Group 2: 6.29 [1], 6.03 [1], 5.97 [1], 5.65 [1], 5.43 [1], 3.41 [2]. In a new figure, Figure S15, reproduced below, temporal agreement between NMR and MS measurements indicate that "Group 1" corresponds to C_4H_5NO and "Group 2" corresponds to $C_8H_7NO_2$.

Figure S15.



3. Pyrrolinone: the specific structure of C_4H_5NO is proposed through analogous reactions and consistency with expected NMR protons. Following work on glyoxal/NH_X reactions (Yu, Kampf), butenedial reaction with NH_X converts an aldehyde into an imine. The proposed imine has molecular formula C_4H_5NO. However, this molecular structure cannot explain the observed upfield protons (two at 3.37 ppm). We suggest that ring closure through the Paul Knorr mechanism results in a pyrrole. Subsequent rearrangement, which has been observed for hydroxypyrroles, leads to the proposed pyrrolinone product. We suggest the two upfield protons at 3.37 ppm belong to the methylene group, while the downfield protons at 6.55 and 5.92 ppm are vinylic. The proton with signal at 6.55 ppm is assumed to be attached to the carbon adjacent to the NH group, while the proton with signal at 5.92 is assumed to be attached to the other vinyl carbon. Agreement was verified with NMR prediction software (https://www.nmrdb.org/new_predictor/index.shtml?v=v2.121.0, last accessed: 2021 April 11) (Banfi and Patiny, 2008).

   Butenedial-pyrrolinone "dimer": To the best of our knowledge, butenedial-pyrrolinone (BD-PR) "dimer" has not be studied and is assigned tentatively in this work. Given that (1) pyrrolinone is a likely product of reaction, (2) aldehyde-pyrrole condensation reactions are well-established to take place (source), (3) the proposed butenedial-pyrrolinone "dimer" has molecular formula $C_8H_7NO_2$ (therefore agrees with observed

> product at m/z 150 consisting of two butenedial building blocks and one NH_X), and (4) glyoxal forms similar "dimers" with imidazole, the product of its reaction with NH_X, we propose that BD-PR "dimer" the second observed species in NMR. The molecule is assigned the "Group 2" protons. Tentative assignments are based off of assignments for butenedial and pyrrolinone. Downfield protons (6.29, 6.03, and 5.97 ppm) are assigned according to the carbon skeleton derived from the butenedial part of the "dimer," furthest from the linkage. The methylene protons are assigned to 3.41 ppm. According to prediction software, the vinylic proton on the ring should be slightly downfield (5.65 ppm) and the proton of the carbon with a single hydroxyl group should be slightly upfield (5.43 ppm) (Banfi and Patiny, 2008). Agreement was verified with NMR prediction software (Banfi and Patiny, 2008).

There may be other minor products, such as the diazepine, produced from the reaction, although they are not expected to be significant enough to warrant inclusion in the mechanism. Any major species that could be undetectable with one technique (due to e.g., low proton affinity in the case of MS and spectral interference in the case of NMR) should be observed with the other. Our new LC-MS-UV/Vis studies of the products also show clear evidence for an accretion product consisting of three butenedial and two NH_X, providing further evidence that this accretion process is active.

Section 2.2.2 has been rewritten to be more explicit about how products of BD/NH_X reactions were determined, as is shown here.

> 0.9 M butenedial/0.45 M AS (VWR, > 99%) mixtures were prepared in water and D_2O with the internal standards PEG-6 or DMS and 0.5 M sodium carbonate (Na_2CO_3) – sodium bicarbonate ($NaHCO_3$) buffer. The solution immediately turned orange brown *(Figure S16)*. After 20 min of reaction, mass spectra of the mixtures indicated nitrogen-containing products with signals at m/z 84, 149, 150, and 168, assumed to be adducts with H^+ *(Figure S11)*. The most reasonable chemical formulas of these products were C_4H_5NO (83 Da), $C_8H_8N_2O$ (148 Da), $C_8H_7NO_2$ (149 Da), and $C_8H_9NO_3$ (167 Da). $C_8H_9NO_3$ was the parent molecule for the $C_8H_7NO_2$ fragment. *C_4H_5NO (83 Da), $C_8H_9NO_3$ (167 Da), and $C_8H_9NO_3$ (251 Da) were observed unambiguously with high-resolution LC-MS measurement of an equivalent solution (Figure S12).*
>
> The 1H-NMR spectra (Figure S14) showed *two* distinct groups of quantitative related signals that had similar temporal behavior (Table S5). Each group of peaks whose quantitative signal strength behaved as integers and had the same temporal behavior was presumed to arise from a single compound. *One group was assigned to C_4H_5NO and the other to $C_8H_9NO_3$ according to agreement in chemical evolution between MS and NMR measurements (Figure S15).* A molecular structure was proposed for each cluster of peaks and the molecular formulas mentioned above, *according to NMR peak assignments and analogous reactions (see SI Section 2.4, including Figures S9-S10)*. The inferred products were as follows: 2-pyrrolinone (pyrrolinone, PR, C_4H_5NO), and a butenedial-pyrrolinone "dimer" (BD-PR, $C_8H_9NO_3$). We propose that 2-butenal-1,3-diazepine (diazepine, DZ, $C_8H_8N_2O$) is a minor product that is observable with MS but was not detected with the less sensitive NMR. The growth of broad peaks embedded in the baseline suggested substantial formation of accretion products *(Figure S14). Additionally, high-resolution LC-MS-UV/Vis measurements suggested evidence of pyrrolinone, butenedial-pyrrolinone "dimer," and a "trimer" formed from addition of butenedial and NH_X to the "dimer" (Figures S12-S13). In particular, the proposed "dimer" and "trimer" are strongly π-conjugated and light-absorbing (Figures S12-S13). As such, accretion products composed of butenedial, NHx, and pyrrolinone* could explain the dark color of the solution *(Figure S17)*.

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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.

We have included several references to the SI throughout the main text to guide the reader to important figures.

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.

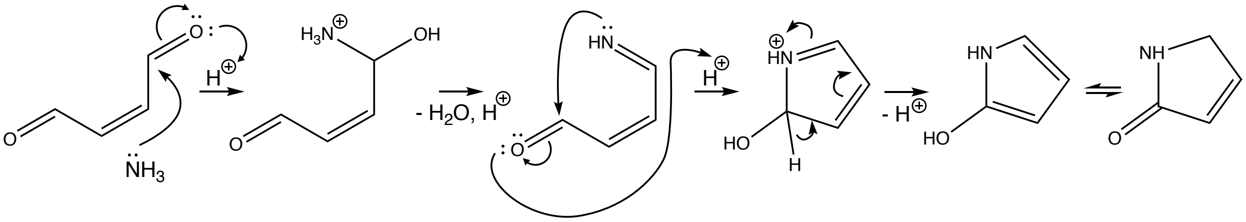
See response to first comment of Reviewer 1. Butenedial has not been measured quantitatively in ambient air, to the best of our knowledge.

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.

<u>Reaction with NH_X.</u>

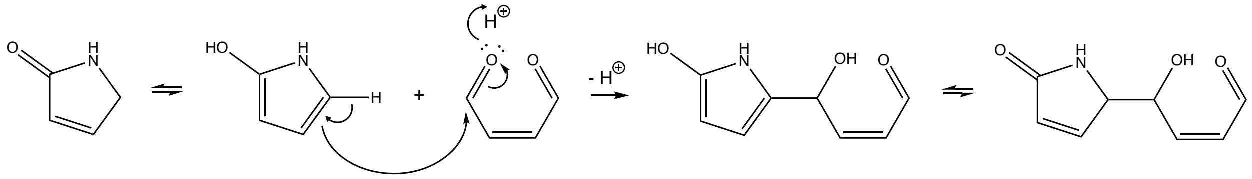
Thank you for this suggestion. As is discussed in Section 2.4 of the SI, carbonyl/NH_3 reactions is proposed to occur through well-established Paul Knorr synthesis. We have included new figures with movement of electrons for butenedial/NH_3 reactions (Figures S9-S10, shown below). A new reference to this description is on Line 175 of the main text.

Figure S9.



As shown, reaction is proposed to begin with NH_3 nucleophilic attack of a protonated carbonyl, which dehydrates, deprotonates, and forms an imine intermediate, as has been shown for, e.g., glyoxal (Nozière et al., 2009; Yu et al., 2011; Laskin et al., 2015). We propose that the imine undergoes ring closure in the case of butenedial, which would form a reactive hydroxypyrrole, and under acidic to slightly acidic conditions, is expected to tautomerize to the stable pyrrolinone form.

Figure S10.



As is discussed in Section 2.4 of the SI, pyrroles are known to tautomerize depending on pH (Capon, 1989). We propose that the OH^- dependence of reaction R3 arises from this pH-dependent tautomerization. Aldehyde-pyrrole condensation is well known through, for example, extensive study on the synthesis of polyphorins (Koelsch and Richter, 1935). As shown in Figure, hydroxypyrrole is proposed to undergo electrophilic substitution reaction with butenedial, which typically for heterocycles occurs at the second position (adjacent to NH group). The ring may tautomerize again. The reaction is analogous to glyoxal-imidazole accretion reactions that are also known to occur (Yu et al., 2011; Kampf et al., 2012).

Reaction with OH^-.

Carbonyl/OH^- reactions tend to produce disproportionation products through the well-established Cannizzaro mechanism (source). Disproportionation reactions have been shown for many other dicarbonyls, including glyoxal, methylglyoxal, and phenolglyoxal (Fratzke and Reilly, 1986). Such reactions begin with OH^- nucleophilic attack of a carbonyl, and through subsequent hydride ion transfer to an adjacent carbonyl, the hydride donor carbonyl is oxidized to a carboxylate and the other carbonyl is reduced to an alcohol. As mentioned in the text, in the case of glyoxal, disproportionation produces the hydroxy acid, glycolic acid (Fratzke and Reilly, 1986).

The corresponding hydroxy acid for butenedial/OH^- reaction is γ-hydroxycrotonic acid. The molecular formula of γ-hydroxycrotonic acid and several of its oligomer products (up to the 11-mer) were observed with new LC-MS-UV/Vis measurements, as shown in Figures S5-S6, reproduced below. This suggests that disproportionation reactions take place for butenedial/OH^-. We have included new figures with movement of electrons for butenedial/OH^- reactions (Figures S4, shown below). This information now has a reference in Section 2.1 of the main text.

Figure S5.

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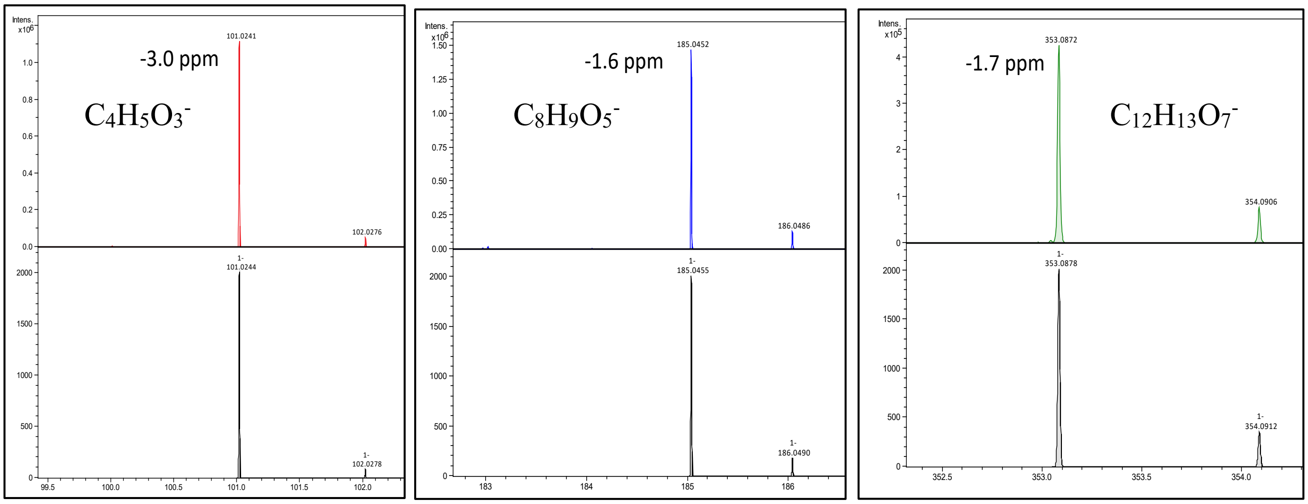


Figure S6.

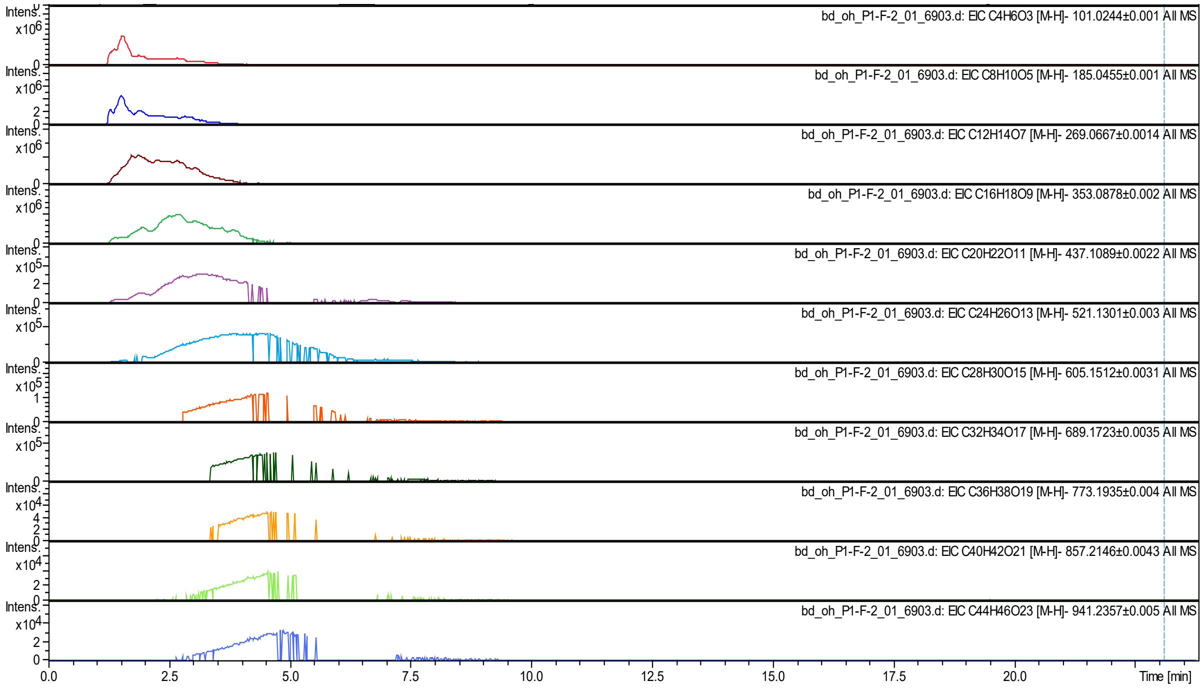
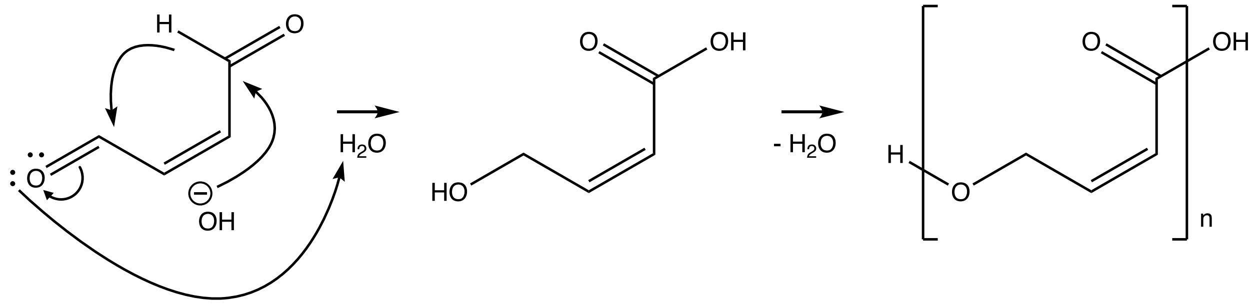


Figure S4.



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)

Analysis of butenedial/NH_X mixtures was performed with TOF-MS, with unit mass precision. As shown in previous work with the same TOF-MS, the internal standard, hexaethylene glycol, has a parent ion at m/z 283 and with fragments at m/z 63 + 44 n and occasionally clustered with water molecules (Birdsall et al., 2019, 2018). The only 0N species that was confirmed was butenedial, which we have measured previously at the m/z 85 channel (Birdsall et al., 2019). The only 2N species that could be at the m/z 85 channel (with a four-carbon backbone) is $C_4H_8N_2$, which would require saturation of the carbon backbone, and is not likely. As mentioned on Line 157, a diazepine is a 2N product that was observable with MS although it was not detected with NMR. This suggests that production of pyrrolinone through ring-closure of the imine is favorable compared to the "dimerization" reaction that would produce the diazepine, which would be analogous to imidazole formation. Diazepine is therefore a minor product of reaction.

Additional high-resolution measurements were performed with LC-MS-UV/Vis of both butenedial/NH_X and butenedial/OH^- reaction mixtures to determine unambiguous molecular formula. As shown in Figure S5 and S11 (reproduced in comments above and below), mass precision was <5 ppm. As mentioned in previous comments, in butenedial/OH^- reaction mixtures, we observed evidence of a hydroxy acid (without N) and its oligomers. Additionally, LC-MS of butenedial/OH^- reaction mixtures in positive mode did not show evidence of butenedial/NH_X products.

With LC-MS-UV/Vis of butenedial/NH_X reaction mixtures, we additionally confirm the previously determined molecular formulae of butenedial/NH_X products.

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?

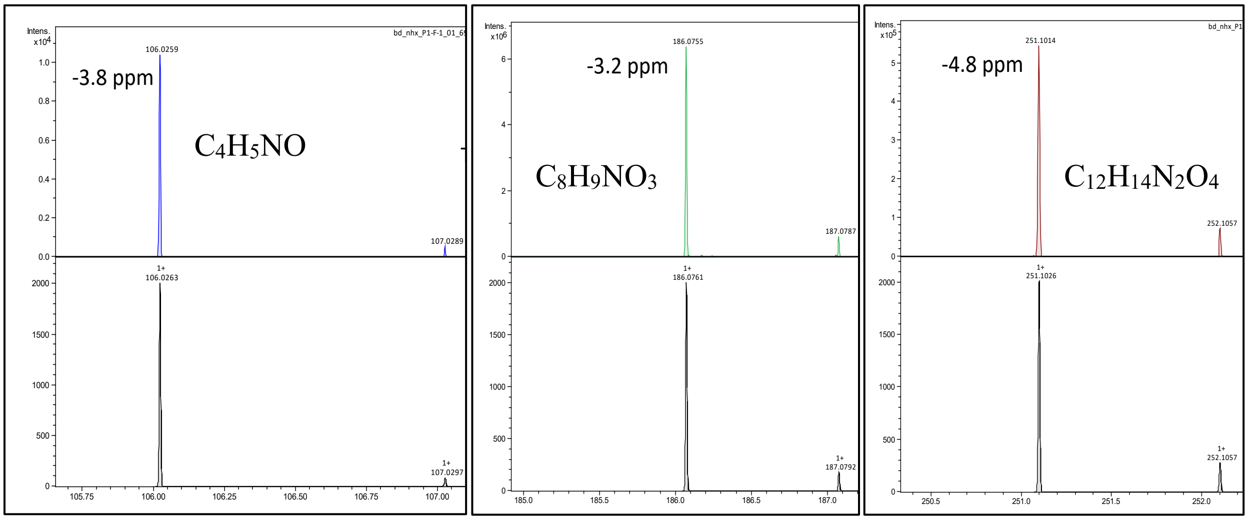
As mentioned in comment to Line 99 above and in the text, we reference the work of Fratzke & Reilly (1986), which has characterized glyoxal reaction with OH^- and forms the chemical basis for the proposed butenedial/OH^- reaction. Butenedial/OH^- reaction has not been studied previously, to the best of our knowledge. See response to the comment on Line 99 above for more information about the initial reaction pathway, as well as a proposed product of reaction, hydroxycrotonic acid. Hydroxy acids are known to oligomerize through condensation reactions (as is the case for lactic acid and glycolic acid).

With new LC-MS-UV/Vis measurements previously described, we observe evidence of hydroxycrotonic acid and its oligomers formed in butenedial/OH^- reaction mixtures (Figure S5, see comment 99 above). As shown in Figure S6 (reprinted in response to comment 99), hydroxycrotonic acid and its oligomers are capable of absorbing light in the 300-450 nm range, as is typical for brown carbon (e.g., Laskin, 2015). This strongly supports evidence for accretion products due to the build-up of material in the baseline of the NMR spectrum, which with conjugated π bonds, is known to enhance the absorptivity.

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-.

Thank you for these points regarding butenedial/NH_X accretion products. With new LC-MS-UV-Vis measurements of butenedial/NH_X reaction mixtures, we observe unambiguous evidence for this "dimer" as well as a "trimer," composed of three butenedial building blocks and two NH_X, formed in solution (Figure S11, reproduced below). The strong signal intensity of both "dimer" and "trimer" suggests that accretion products, composed of butenedial and pyrrolinone, are substantial. We now rely more strongly on this evidence in the methods section of the text and in the SI than on the tentative NMR assignments, which as Reviewer 3 mentions previously, are difficult in complex reaction mixtures. Specific discussion of the butenedial-pyrrolinone "dimer" formation is in the response to the comment of line 99, is also in Section 2.4 of the SI, and now referenced in the main text, following the comment of line 99. Discussion of the NMR assignments is in the author response to Reviewer 3's second comment.

Figure S11.



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)?

The mass absorption coefficients were not measured for butenedial/NH_X products in this study, although they would be important for accurate knowledge of the climate implications of the chemistry.

320 clarify "favorable separation"

Made more specific in the manuscript, see Line 344-345:

> We suggest that dicarbonyls with ~~a favorable separation of reactive aldehyde groups~~ *at least two carbons between carbonyl groups* can form heterocycles with bimolecular rate laws.

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.

As mentioned on Lines 369 of the text, butenedial has a very large Henry's law constant ($\sim 6\times10^7$ M atm^{-1}), indicating that it is highly soluble in water, much more so than methylglyoxal and glyoxal. Therefore, it is expected that atmospheric butenedial readily partitions to aqueous aerosol. We provide lifetimes of reactive loss for butenedial in particles, which as shown in the text, is 18 minutes for particles with pH 6 and 4 M NH_X. Thus, under high pH and NH_X conditions, aqueous reaction is capable of competing with fast gas-phase photolysis, which has a first-order lifetime of 15 min (Newland et al., 2019).

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The provided link is directed to this preprint. To determine time scales of mass transfer from gas to particle, following Maxwellian Flux (Seinfeld and Pandis, 2016), Zaveri et al. (2014) derive the following gas-particle partitioning flux for a species i:

$$\frac{dA_i}{dt} = \frac{3k_{g,i}}{r}\left(c_{g,i} - \frac{A_i}{\sum_j A_j}\ c_{g,i}^*\right) - k_r A_i$$

Where A_i is the particle concentration of species i in mol cm^{-3}, $\sum_j A_j$ is the total molar concentration of all species in the particle in mol cm^{-3}, r is the particle radius, $k_{g,i}$ is the gas mass-transfer coefficient of species i in s^{-1}, $c_{g,i}$ is the gas-phase concentration of species i in mol cm^{-3}, c_g^* is the effective saturation vapor concentration of species i in mol cm^{-3}, and k_r is the first order rate constant of bulk phase reaction. Calculation of mass transfer timescales requires knowledge of the gas-phase concentration of butenedial as well as surface uptake coefficients that control $k_{g,i}$, neither of which are measured.

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.

In Section 4.2, we discuss regions where high NH_3 and high pH coincide. Although aerosol pH is indeed typically acidic, certain locations, such as the North China Plain (NCP) or northern India, tend to have aerosol that contains alkaline components, high aerosol water content, and elevated NH_3. Recently, it was shown that near-surface aerosol pH was typically 4.4-5.7, and in some locations could consistently be > 6, in the NCP (Tao et al., 2020). As is mentioned in the reviewer comment, clouds have similarly high pH, but reactions in clouds may not be as relevant as reagent concentrations would be substantially reduced compared to aerosol. A sentence has been added to the manuscript to specify aerosol pH from this recent study at Lines 374-375:

> *For example, recent work suggests that near-surface particle pH is 4.4-5.7 in the NCP and in some locations, could be consistently > 6 (Tao et al., 2020).*

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