Response to Reviewer #4

We gratefully thank you for your constructive comments and thorough review. Below are our point-by-point responses to your comments.

(Q=Question, A=Answer, C=Change in the revised manuscript)

General Comments:

The article by Hu et al. titled "Reversible and irreversible gas-particle partitioning of dicarbonyl compounds observed in the real atmosphere" discusses the importance of reversable and irreversible gas-to-particle partitioning of glyoxal and methyl glyoxal. The authors present experimental and modeling results showing how irreversible gas-to-particle partitioning dominates the two partitioning pathways and also highlighted the other reaction processes that were not taken into account in the analysis of this study. The study is relevant for the atmospheric community and can be accepted to ACP after the comments have been addressed.

A: We highly appreciate your comments and suggestions. The questions you mentioned are answered as follows.

Major Comments:

Q1: Page 5, line 134: What are the other carbonyls that were measured in the gas and particle phases?

A1: We measured ten carbonyls in gas phase, including formaldehyde, acetaldehyde, acetone, propionaldehyde, methacrolein, butyraldehyde, methyl vinyl ketone, benzaldehyde, glyoxal, and methylglyoxal. And we also measure six carbonyls in particle phase, including formaldehyde, acetaldehyde, acetone, propionaldehyde, glyoxal, and methylglyoxal. We have specified it in our revised manuscript.

C1: Lines 208-211 in Sect. 3.1.1:

Ten carbonyls were measured in the gas phase, including formaldehyde, acetaldehyde, acetone, propionaldehyde, methacrolein, butyraldehyde, methyl vinyl ketone, benzaldehyde, glyoxal, and methylglyoxal; and six carbonyls were measured in the particle phase, including formaldehyde, acetaldehyde, acetone, propionaldehyde, glyoxal, and methylglyoxal.

Q2: Based on what's written at the end of page 7 and later, the measured dicarbonyls in the particle phase are only ones that have formed products of the reversible pathways. It wasn't clear earlier when you talk about experimental partitioning coefficients that they only include reversible partitioning, point it our somewhere earlier to avoid confusion.

A2: Thanks for your suggestion. Previous studies have pointed out that both glyoxal and methylglyoxal are always in hydrate forms or oligomer forms under atmospheric conditions (Barsanti and Pankow, 2005; Liggio et al., 2005; Elrod et al., 2021; Michailoudi et al., 2021). And dicarbonyls in monomer forms only accounts for ~1% in our study with lower physical solubility of dicarbonyls (e.g., K_H=5 M·atm^{-1} for glyoxal) (Schweitzer et al., 1998). Most of dissolved dicarbonyl monomers could participate into chemical reactions, forming hydrates and oligomers. We have pointed it in our revised manuscript to avoid confusion as follows.

C2: Lines 170-172 in Sect. 2.3

C_p (μg·m^{-3}) is the concentrations of dicarbonyls in the particle phase which is derived from the analysis of extracts, including monomers and their reversibly formed products (the product distribution is discussed in Section 3.2).

Q3: Page 8, line 210: How exactly are the proportions of hydrates and oligomers at different RH calculated? Table S2 gives the hydration rate constants as (pseudo) first order rate constants, so the amount of water should have no effect on the equilibrium, right? Or are the experiments used in these calculations somehow? Please specify in the text.

A3: Thanks for your suggestion. The proportions of hydrates and oligomers are calculated on the basis of the kinetic mechanisms listed in Table S2 using a 0-D box model with a steady-state approach. And the amount of water would have no effet on the equilibrium. We have specified the calculation in our revised manuscript.

C3: Lines 298-300 in Sect. 3.2

To roughly estimate the product distribution of the reversible pathway in the real atmosphere, we simplified reaction mechanisms and calculated the product distribution on the basis of on the basis of the kinetic mechanisms listed in Table S3 using a 0-D box model with a steady-state approach.

Minor and Technical Comments:

Q1: In the abstract "These two pathways of dicarbonyls jointly contributed to more than 25% of SOAs in the real atmosphere"

A1: Thanks for your suggestion. We have rephrased the sentences as follow.

C1: Lines 21-22 in the Abstract:

The partitioning processes of dicarbonyls in reversible and irreversible pathways jointly contributed to more than 25% of SOA formation in the real atmosphere.

Q2: Page 1, line 27-28: "The α-dicarbonyl functionality increases their water solubility and reactivity more than expected" would be better if you say something like "The α-dicarbonyl functionality leads to higher water solubility and reactivity than expected." Otherwise, specify how the solubility and reactivity have increased (from what).

A2: Thanks for your suggestion. The α-dicarbonyl functionality is hydrophilic and contributes to hydrate formation. The EPA's chemical and physical property calculator, EPISUITE, predicts that the hydrated form of carbonyls is less volatile and more water-soluble than the un-hydrated form (EPA., 2012), owing to the strong effect of the two hydrogen-bonding groups in the hydrated form (Elrod et al., 2021). And hydrate form of carbonyls can easily participate in continuous radical reactions with higher activity by H-abstraction to form higher-molecular-weight oligomers (Michailoudi et al., 2021). We have revised the sentences in the revised manuscript.

C2: Lines 28-33 in Sect. 1:

The α-dicarbonyl functionality leads to higher water solubility and reactivity of dicarbonyls than expected, as the α-dicarbonyl functionality is hydrophilic and contributes to hydrate formation. The hydrate form of carbonyls is less volatile and more water-soluble than the un-hydrated form (EPA., 2012), owing to the strong effect of the two hydrogen-bonding groups in the hydrated form (Elrod et al., 2021). Moreover, hydrates can easily participate in radical reactions with higher activity by H-abstraction to form higher-molecular-weight oligomers (Michailoudi et al., 2021).

Q3: page 2, line 36-37: "however, there is still a missing sink for the two dicarbonyls" Do you mean that the known sinks listed before are not large enough to explain the loss of the dicarbonyls from the gas phase? Or that there is a specific sink mentioned by Volkamer et al. that wasn't listed here? Please specify.

A3: Thanks for your suggestion and we regret for the unclear expression. We mean that there is a specific sink mentioned by Volkamer et al. (2007) that wasn't listed before. And the missing sink stated here refers to the gas-particle partitioning process of dicarbonyls. We have specified this sentence in the revised manuscript.

C3: Lines 42-43 in Sect.1:

however, there is still a missing sink for the two dicarbonyls (Volkamer et al., 2007), that's the gas-particle partitioning process, which would be fully discussed in this study.

Q4: page 3, line 72: "among key regions with relatively higher PM2.5 concentrations" Do you mean that the key regions have relatively higher PM2.5? Or Beijing has relative higher PM2.5 concentrations than the other key regions? Please specify.

A4: Thanks for your suggestion and we regret for the unclear expression. We mean that the key regions (including Beijing) have relatively higher $PM_{2.5}$. We have specified this sentence in the revised manuscript.

C4: Lines 82-83 in Sect.1:

Chen et al. (2021) found that the average concentration of dicarbonyls in Beijing is lowest among the key regions that have relatively higher $PM_{2.5}$ concentrations, indicating there is a more efficient partitioning process of dicarbonyls.

Q5: Page 5, line 145: define GL and MG

A5: Thanks for your suggestion. GL and MG are the abbreviation of glyoxal and methylglyoxal. And we have defined GL and MG in our revised manuscript.

Q6: Page 6, line 164: "lower temperature promoted the partitioning processes" do you mean gas-to-particle partitioning, or also particle-to-gas? It isn't clear by saying "partitioning processes".

A6: Thanks for your suggestion and we regret for the unclear expression. We mean that lower temperature promoted the gas-to-particle partitioning processes. We have specified this sentence in the revised manuscript.

C6: Line 241 in Section 3.21.2:

lower temperature promoted the gas-to-particle partitioning processes.

Q7: Page 7, line 197: "which are more reactive than their counterparts" how do you determine "more reactive"? Aren't glyoxal and methylglyoxal also reactive, because they quickly react with water to become hydrates? Or are the reactions of the hydrates even faster than the non-hydrated glyoxal?

A7: Thanks for your suggestion and we regret for the incorrect expression. The hydrated form of carbonyls is more water-soluble than the un-hydrated form (EPA. 2012). Moreover, carbonyls are always in hydrate forms in aqueous reactions under atmospheric conditions (Liggio et al., 2005; Elrod et al., 2021; Michailoudi et al., 2021) . But we think it's incorrect to directly compare the reactivity between dicarbonyls in monomer and in hydrate forms. We have deleted this sentence in our manuscript.

Q8: Page 7, line 199: "the most thermodynamically favored oligomer reactions for glyoxal and methylglyoxal" Specify that the reactions are for the hydrates, not (only) non-hydrated glyoxal and methylglyoxal.

A8: Thanks for your suggestion. We have specified that the reactions are for hydrates in our revised manuscript.

Q9: Page 8, line 208-209: "The product distribution of the reversible formation could well explain this phenomenon." How?

A9: We regret for the unclear expression of this sentences. We have rephrased the sentences in our revised manuscript.

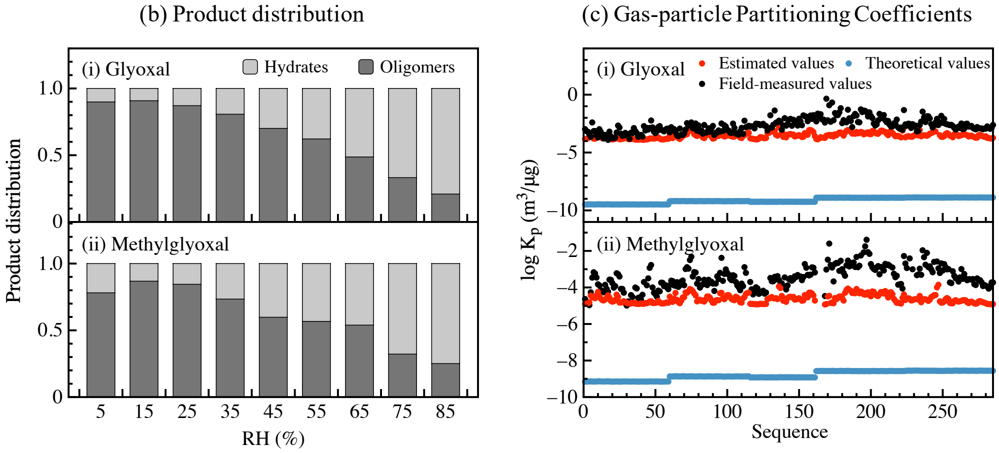
C9: Lines 286-290 in Section 3.2

It increased significantly when RH increased from <10% to 60%, as dicarbonyls were more favorable to dissolve into hygroscopic aerosols during their growth (Mitsuishi et al., 2018; Xu et al., 2020). However, from 60% to 80% RH, it exhibited the opposite trend and decreased with increasing RH, as higher water concentrations at elevated RH levels may dilute the monomer concentration in the particle phase and hinder oligomerization reactions (Healy et al., 2009), and the product distribution of the reversible formation could also well explain this phenomenon.

Q10: Figure 2c: The two gray colors (estimated and theoretical values) are very similar, how about using some colors for them? Also, correct "porduct" to "product" in the title and add y-axis label to Figure 2b.

A10: Thanks for your suggestion and we regret for the errors in Figure 2. We have changed the colors in Figure 2c, corrected "porduct" to "product" in the title and added y-axis label to Figure 2b. The revised Figure 2b and Figure 2c are presented as follow.

C10:



Q11: Page 8, line 223: "Combined with the vapor pressure of dominant products" where do you get the vapor pressures of the dominant products?

A11: We get the vapor pressures of dominant products from previous studies. As for glyoxal, the vapor pressures of the reversible products are 10^{-6} atm and 10^{-11} atm for hydrates and oligomers, respectively (Hastings et al., 2005). And as for methylglyoxal, the vapor pressures of the reversible products are 10^{-5} atm and 10^{-11} atm for hydrates and oligomers, respectively (Axson et al., 2010). We have noted it in our revised manuscript.

C11: Lines 314-316 in Sect. 3.2:

Combined with the vapor pressure of dominant products published in previous studies (Hastings et al., 2005; Axson et al., 2010), their gas-particle partitioning coefficient can be roughly estimated and can effectively fit the field-measured values.

Q12: Figure 3: What are the lines in 3b? Also model like in 3c? Also, there are typos in the caption "(i) galyoxal and (ii) methylglyxoal".

A12: Thanks for your suggestion and we regret for the typos in the caption of Figure 2. The lines in Figure 3b are the fitting lines of irreversible uptake coefficients γ of dicarbonyls and SNA concentrations in aerosol liquid water. And we have corrected the typos in the caption in our revised manuscript.

Q13: Page 10, line 287: There are 2 figures in the Supplement labelled S7. In the second Fig. S7, what is the concentration unit for SNA in the ratios? Mass/mole/volume ratio?

A13: Thanks for your suggestion. We have revised the label of figures in the Supplement. And the concentration unit for SNA in the ratios is molality (mol/L ALWC). We have noted the concentration unit in our revised Supplement.

Q14: Page 13, line 369: "Furthermore, we note that there may be other potential explanations for the increase in particulate concentrations and the uncertainty in the gas-particle partitioning process." Particulate concentrations of what? And which partitioning processes?

A14: We regret for the unclear expression. “increase in Particulate concentrations” in this sentence refers to the increase in particle mass caused by dicarbonyls. And “partitioning processes” refers to all partitioning pathways, including physical adsorption, reversible pathways and irreversible pathways. We have specified this sentence in our revised manuscript.

C14: Lines 455-457 in Sect. 4:

Furthermore, we note that there may be other potential explanations for the increase in particle mass caused by dicarbonyls and the uncertainty in the gas-particle partitioning process, including physical adsorption, reversible pathways and irreversible pathways.

Q15: Page 13, line 371-372: "Other reversible pathways, like adducts formed from glyoxal with inorganic species, like sulfate and ammonia, could also promote the gas-particle partitioning process." I think you mean "such as", not "like". You used the word "like" similarly also earlier in the manuscript so check those too.

A15: Thanks for your suggestion. We have checked the word and revised it in our revised manuscript.

Reference:

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