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Title: Aqueous-phase chemistry of glyoxal with multifunctional reduced nitrogen compound: A potential missing route of secondary brown carbon

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Dear Anonymous Referee #2,

Thank you for the helpful and valuable review and comment. We have made careful revisions on the original manuscript according to your kind and helpful comments. The changed sentences have been marked as red color in the revised manuscript. Below is our point-by-point response to your comments:

Major Comments:

Question 1. The manuscript discussed about the effects of pH on the reaction, which seems to be contradictory. First of all, lines 140-154, the experimental data show that higher pH will lead to higher MAC values and more SBrC formation.

However, Figure 2 shows that the pH drop for MEA-GL mixture is faster and MEA-GL showed lower pH values than the other two mixtures. The author also stated in lines 160-162 that lower pH will lead to more SBrC formation.

These two statements in the manuscript are self-contradictory and should be addressed and reconciled.

Response: Thank you for the referee's comment. There is no contradiction between the results presented in lines 140 - 154 and 160 - 162 because the pH values utilized belong to distinct categories. The results of "higher pH will lead to higher MAC values and more SBrC formation" from lines 140 - 154 are obtained by using the initial pH values. That is, the chromophore formation rates and MAC values of the RNCs-GL reaction mixtures are increased when the initial pH values are increased. As the reaction goes on, the ambient pH values are decreased due to the formation of formic acid as a byproduct, which has been discussed and obtained in Sections 3.2 and 3.3. Hence, the results of "lower pH will lead to more SBrC formation" are deduced. We are very sorry for the confusion caused by our unclear expression. According to the referee's comments, some discussions are revised and added to the revised manuscript: "**In order to explore the influence of the initial pH values on the MAC values, a comparison of MAC values at initial pH 3 and 4 is performed for all three mixtures (Fig. 1a).**" (Please see lines 140 - 141) and

“Note that the trend of GRs shows a decrease from MEA-AS-GL, MEA-GL, to AS-GL mixtures at the beginning of the reaction time, while the MAC values of MEA-GL mixture are larger than those of two mixtures accompanied by the more rapid decrease of pH values in solution after the reaction is equilibrium (Figs. 1b and 2), suggesting that chromophore formation of three mixtures depends on the ambient pH value.” (Please see lines 161 - 164)

Question 2. Lines 189-240, the quantum calculations show that the ΔG values for the reaction of all three mixtures to generate DI_{MEA} are: MEA-GL<AS-GL, MEA-AS-GL>AS-GL on day 15. It is strange that the ΔG value shows AS-GL<MEA-AS-GL, while the MAC value shows the opposite trend where MEA-AS-GL>AS-GL.

The authors should explain further why these is this contradiction between the experimental value and quantum modeling results.

Response: We thank the referee for this constructive comment. The theoretical predictions are coincident with the experiment results because of the following reasons: (i) as discussed in section 3.2, we focus on the feasibility of the formation of intermediates rather than the order of the difficulty. Therefore, we utilized the reaction energies (ΔG_r) rather than the activation energies (ΔG^\ddagger) because the ΔG_r values are good at predicting the possibility of the formation of intermediates; (ii) the ΔG_r values mentioned by the referee are only ΔG_r values for the formation of the intermediates, i.e., DI_{MEA}, DI_{AS}, and DI_{MAG}. It only indicates that the formation of DI_{AS} from HA_{AS} is thermodynamically more feasible than the formation of DI_{MAG} from HA_{MAG1}, rather than specifying the formation of chromophores is easier. The total ΔG_r value of AS + GL → DI_{AS} is -7.8 kcal mol⁻¹, which is 5.1 and 10.9 kcal mol⁻¹ higher than the ΔG_r value of MEA + AS + GL → DI_{MAG} (-12.9 kcal mol⁻¹) and MEA + GL → DI_{MEA} (-18.7 kcal mol⁻¹), respectively, indicating that the formation of DI is thermodynamically most feasible in the MEA-GL mixture, in agreement with the highest MAC value in MEA-GL mixture measured in the experiment; (iii) in section 3.3, we focus on the mechanisms for the formation of chromophores in three mixtures, a detailed potential energy surface of the key elementary reactions predicted in section 3.2 was calculated and established using the activation energies (ΔG^\ddagger). Through the discussion of reaction barriers combined with geometries and natural charges, we found that the nucleophilic

addition (NA) reactions are regulated by both electrostatic attraction and steric hindrance effect. The additional branched chain on the N atom in MEA affected the natural charge and steric hindrance of the reaction intermediate, thus promoting the intramolecular interaction between N and C atoms to form SBrC chromophore, thus causing the MEA-AS-GL mixture to have a higher MAC value than AS-GL mixture.

Minor comments

Question 1. Line 79: when altering the pH of the solution with addition of sulfuric acid or sodium hydroxide solution, will this also dilute the solution and cause the concentration of each solution to be different and diverge from 1M?

Response: Thank you for the questions raised by the referee. It will not affect the concentration of the mixture because the strongly alkaline MEA was pre-acidified before the mixing process and is followed by precise dilutions using a volumetric flask. In the process of preparing the mixture, the strongly alkaline MEA was pre-acidified by sulfuric acid first to ensure that the pH value of the mixture after mixing is between 3 and 4, which is our target pH value. After mixing and diluting, each mixture was fine-tuned with sulfuric acid or sodium hydroxide to reach a pH of 3 or 4. In this pH adjustment process, the sulfuric acid or sodium hydroxide solution we add is less than 1mL, and the concentration change is less than 2%. In summary, the use of sulfuric acid or sodium hydroxide solution to adjust the pH value has little effect on the concentration of each mixture.

Question 2. The word “spectrums” should be changed “spectra” throughout the text and also in the SI. For instance, Figures S4-S8 used spectrums.

Response: According to the referee’s suggestion, we have changed all “spectrums” to “spectra” in the text and SI.

Question 3. For all MS spectra (Figures 3, S4-S8), I suggest the authors should also show chromatographs as well.

Response: Thank you for the referee’s comment. We have added extracted ion chromatograms of all reaction products of into Figures S4 - S6 in the SI.

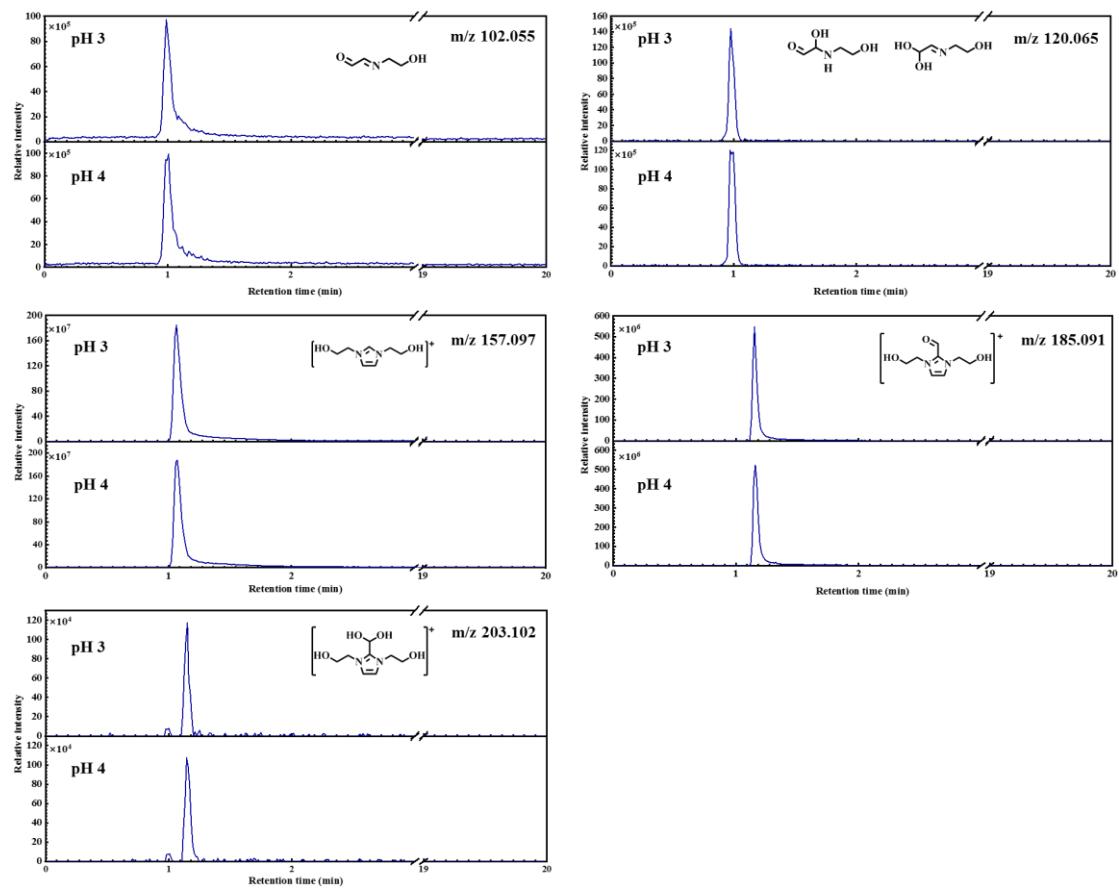


Figure S4. The extracted ion chromatograms of all reaction products for MEA-GL mixture at the initial pH of 3 and 4.

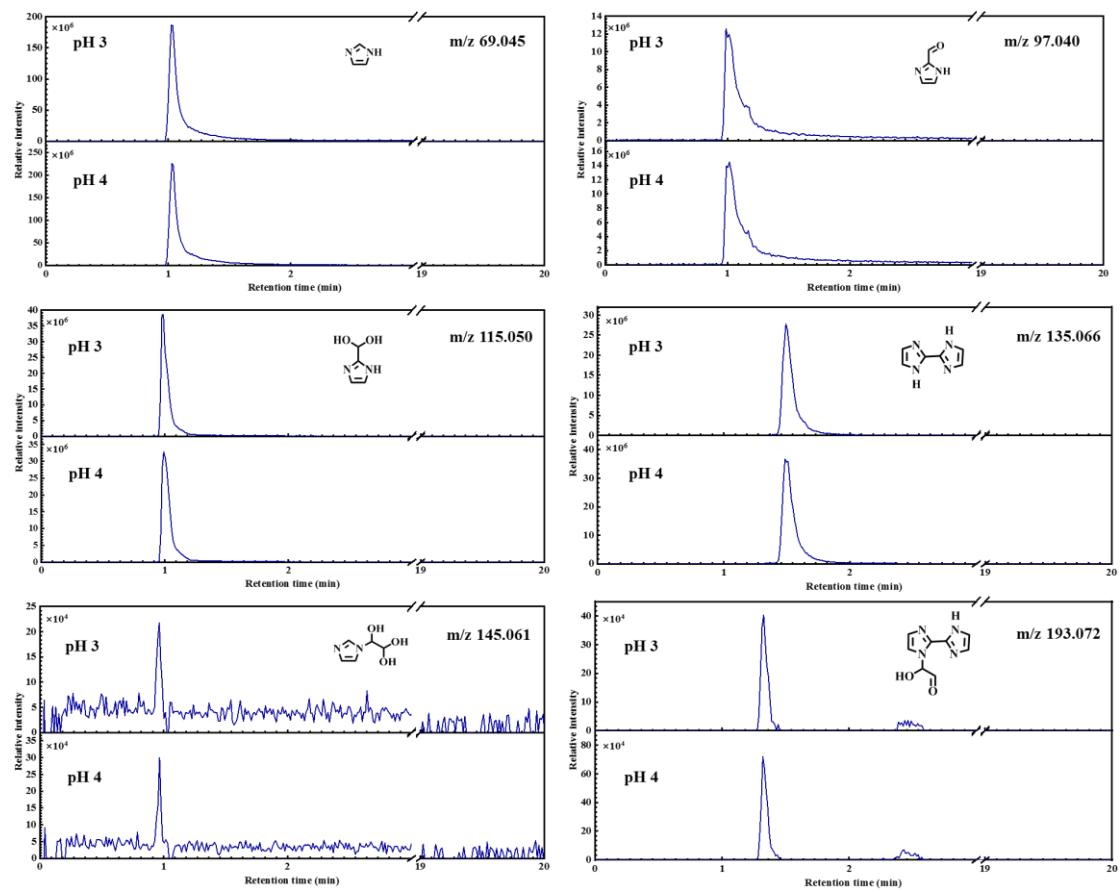


Figure S5. The extracted ion chromatograms of all reaction products for AS-GL mixture at the initial pH of 3 and 4.

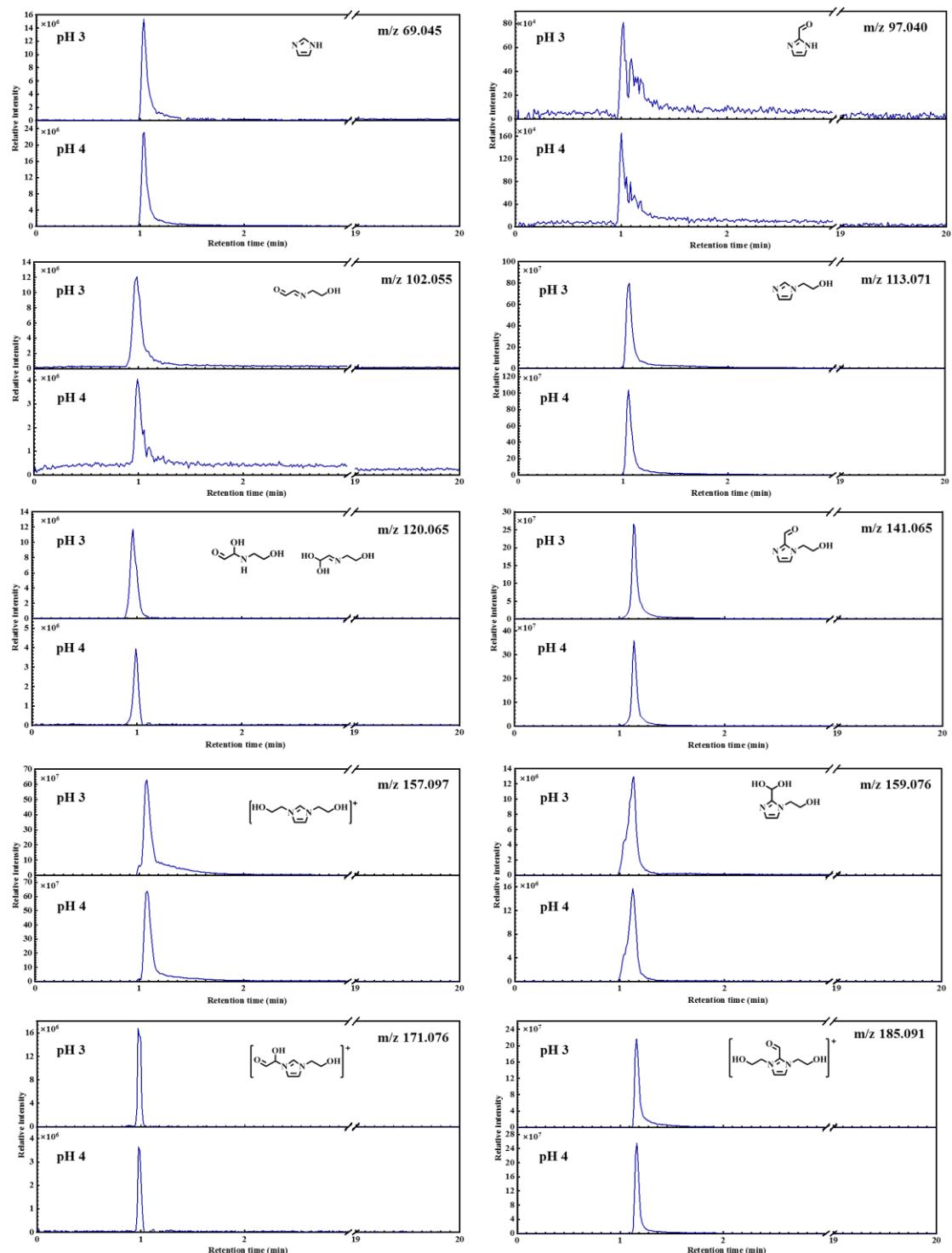


Figure S6. The extracted ion chromatograms of all reaction products for AS-MEA-GL mixture at the initial pH of 3 and 4.