Reply on RC2:

General:

The authors presented experimental results of (1) phase transition behaviors and (2) photochemical degradation of mixed particles with glycine (GC) and ammonium nitrate (AN) or sodium nitrate (SN). Experiments were conducted in a custom-built flow cell reactor with deposited particles, aided by in-situ Raman characterization and off-line chemical analysis. As relative humidity (RH) varied, the mixed particles underwent phase transitions in line with observations in literature. The photochemical behaviors (300-nm light illumination) of AN + GC particles and SN + GC particles, however, are distinctly different, with the latter being much more reactive than the former. The authors proposed that the availability of more abundant "free" nitrate ions in the SN + GC system (where nitrate is not strongly bonded with GC, and binding between carboxylic group of GC and sodium ion "frees up" the nitrate ions) might be the reason behind, as nitrate photolysis can generate an array of oxidants to oxidize GC. This statement was supported by Raman observation that SN + GC particles showed higher signal intensity of "free" nitrate ions. It was implied from this observation that GC, or more generally free amino acids, might decay faster in Na-rich particles (e.g., coarse sea spray aerosols) than in ammonium-rich particles (e.g., urban aerosols). The experiments were well designed and conducted, and arguments in the manuscript are also well articulated. I therefore recommend Minor Revision before publication.

Authors' Response: Thank you so much for your valuable comments. Kindly please find our responses accordingly below.

Specific:

P7, reason(s) for faster photo-degradation of SN + GC particles. The authors presented at least three possible reasons to explain the observed faster decay of GC in the SN + GC particles than in the AN + GC particles: (1) more abundant "free" nitrate ions (the first paragraph in P7), (2) ionic form of GC (anion, zwitterion, or cation) (the second paragraph in P7), and (3) water-to-glycine molar ratio (the third paragraph in P7). It is not clear how these potential reasons are related to each other. That is, are they in parallel, being all possible, with the first one the most important (as the authors stated), and they might even be competing? Or are they intertwining to result in the observed result, i.e., the zwitterion ion (reason 2) form promotes the formation of "free" nitrate ions (reason 1)? Clarification of this might be helpful in understanding what other inorganic cations (e.g., potassium, magnesium etc.) and other free amino acids (what ion form is prevailing in relevant pH range) will behave in similar photochemical processes. In addition, the last sentence in L222 reads ambiguous. Not sure whether it is referring to SN + GC particles or AN + GC particles. If the former, it is contradictory to previous statements; if the latter, please specify.

Authors' Response: Thank you for the insightful comments. The "free nitrate" affords nitrate photolysis to generate oxidants for glycine, while the ionic form of glycine and its availability may modulate the reactivity of glycine. They are all possible consequences of the molecular

configuration in the concentrated AN+GC and SN+GC systems. However, the strong linear relationship between nitrate photolysis rate constant and percentage glycine decay implies that the efficiency of nitrate photolysis is more important than the reactivity of glycine in determining the overall decay rate of glycine. We have expanded our discussion on this point as follows.

Line 216-235: The apparent nitrate photolysis rate constant J shows a good correlation with the percentage GC decay ($R^2 = 0.99$, Figure 4b), which suggests that nitrate photolysis is the key driver for the glycine decay.

The different reactivity of glycine between SN+GC and AN+GC particles may also contribute to the distinct photochemistry. For instance, glycine can be ionized into different forms according to the local conditions, including cationic, zwitterionic, and anionic of different reactivities (Aikens et al., 2006). Zwitterionic denotes the charge-separated form amino acids in aqueous solutions and in crystalline states (e.g., NH_3^+–CH_2–COO^-). Several possible zwitterionic conformers of glycine have been proposed with the addition of 1-3 water molecules (Krauklis et al., 2020). The rate of anionic glycine reacting with OH radicals is 2-orders of magnitude higher than that of zwitterionic glycine (Berger et al., 1999; Buxton et al., 1988), while that of zwitterionic glycine is several times higher than cationic glycine. These differences were due to the increased energy barriers for oxidation upon protonation (Wen et al., 2022). However, the protonation constants of glycine in concentrated solution were difficult to define. Qualitatively, a possible lower degree of glycine protonation in SN+GC particles than AN+GC particles might enhance the reactivity of glycine.

We also note that the initial water-to-glycine mole ratios were higher for AN+GC particles (6) than SN+GC particles (2), and sodium has higher hydration number (6)(Medoš et al., 2019) than ammonium (4)(Guo et al., 2020). Therefore, the availability of free water in AN+GC particles is likely higher than in SN+GC particles. This could affect the configuration of glycine dimers or trimers, such as the possible complexation or charge interactions between the anionic carboxylate and the cationic -NH_3^+ groups. These factors could also modulate the photo-reactivity of glycine.

The pHs of the mixed GC nitrate particles at 80% RH were around 6 according to the pH paper (Craig et al., 2018), at which zwitterionic glycine is the most abundant form. Without any information of possible unknown molecular interactions that affect the protonation equilibrium, we assume that glycine is mostly in the zwitterionic form. As shown in Figure 3a, the complexation of glycine with the cation is crucial in allowing free nitrate for photolysis. Other atmospheric cations, such as potassium, magnesium and calcium, can also form complexes with the carboxylic group of amino acids (Case et al., 2020; Lester et al., 2010; Tang et al., 2016). The pH of global ambient aerosol can span from 0-6 (Weber et al., 2016; Liu et al., 2017), which means that amino acids can exist in both cationic (0<pH<2) and zwitterionic (2<pH<10) forms (Locke et al., 1983; Stroud et al., 1983). Previous studies have reported that cationic amino acids have enhanced complexation with metal cations due to the protonation (Moision et al., 2002). We have incorporated this information into the revised manuscript.

Line 266-271: As shown in Figure 3a, the complexation of glycine with the cation is crucial for allowing free nitrate for photolysis. Other atmospheric cations, such as potassium, magnesium and calcium, can also form complexes with the carboxylic group of amino acids (Case et al., 2020; Lester et al., 2010; Tang et al., 2016). The pH of global ambient aerosol can span from 0-6 (Weber et al., 2016; Liu et al., 2017), which means that amino acids can exist in both cationic ($0<pH<2$) and zwitterionic ($2<pH<10$) forms (Locke et al., 1983; Stroud et al., 1983). Previous studies have reported that complexation is enhanced for cationic amino acids due to the protonation (Moision et al., 2002).

P9, implications. What causes the stronger binding between sodium ion with the carboxylic group compared to that between ammonium ion with the carboxylic group. Is it because sodium is a stronger alkaline species than ammonium? Or due to some sort of indirect effect (e.g., how much solvated the carboxylic group is) from the low water-to-glycine ratio in the SN + GC system? In ambient aerosol particles, there might be other alkaline species too (potassium, magnesium, amines etc.). It would be good to comment on whether alkalinity of degree of solvation might lead to such increased photodegradation of free amino acids, if possible.

Authors' Response: Unlike metal cations, ammonium lacks vacant orbitals to coordinate with the amino acid functional groups. Hence ammonium cannot form stable complexes with amino acids, but only protonate them. We agree that the effect of alkalinity and solvation level on the fate of amino acids upon nitrate photolysis is an interesting topic for future research, and we have mentioned it in the revised manuscript.

Line 273-280: Overall, our work sheds light on the potential role of particulate nitrate photolysis in the sink of the atmospheric FAAs, which impacts the cycling of atmospheric organic nitrogen. The reaction rate constants between FAAs and different oxidants from nitrate photolysis can further help quantify the contribution of nitrate photolysis in FAA degradation and improve the prediction of the atmospheric lifetime of FAAs. The reactivity analysis in concentrated systems is complex, and our experimental results can provide valuable data to parameterize the complex thermodynamics in future studies. Systematic studies of the detailed molecular mechanism and the factors influencing nitrate photochemistry and FAA decay, such as molecular configuration, alkalinity, and solvation are recommended. Quantum chemical and molecular dynamic simulations with appropriate parameters would be useful tools for this purpose.

Technical:

P1/L13: add "of" before "glycine".

Authors' Response: We have added an "of" before "glycine".

P2/L49: remove "(Wen et al., 2022)" at the end of the sentence.

Authors' Response: We have removed "(Wen et al., 2022)" from the end of the sentence.

P2/L52: remove "behavior.".

Authors' Response: We have removed "behaviors".

P4/L109: revise citation format of "Matsumoto et al….".

Authors' Response: We have revised the format of "Matsumoto et al.".

P5/L135: I do not see Equation 9.

Authors' Response: Sorry for the confusion, we have corrected the equation number.

P6/L171: should NH3 be -NH2 or -NH3+? Are you referring to the amino group of GC?

Authors' Response: We have revised the NH_3 to $-NH_3^+$.

Reference

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