

## Reply to the comment of Referee 1

We appreciate the editor and reviewers for providing useful comments on revising our manuscript. In the following, the original reviewer comments are shown in black, our responses to the comments are shown in blue, and corresponding updates on the manuscript are represented by *italic* fonts.

This is the review of the manuscript entitled “Suppressed atmospheric chemical aging of cooking organic aerosol particles in wintertime conditions” by Liu et al. This study investigates the chemical lifetime of cooking organic aerosol (COA) of three typical sources including canola oil, hot pot soup, and lard upon exposure to ozone. The second order reaction rate constants of ozone reacting with COA particles were determined as a function of temperature between -20 to 35 C. The reaction kinetics were derived by monitoring the degradation of the condensed phase organic by means of mass spectrometry and gas chromatography. It is observed that the reaction rate decreases by orders of magnitude as the temperature decreases. The temperature dependence of the reaction rate was fitted using a Vogel–Fulcher–Tammann (VFT) equation. This in turn was applied to predict the chemical lifetimes of COA across the globe for the months June and December. During northern hemispheric winter the chemical lifetimes of COA increased significantly.

This work is in the tradition of previous laboratory heterogeneous chemical reaction studies and thus fits the scope and audience of Atmospheric Chemistry and Physics. The experimental approach appears to be sound and the results present novel data. I have a few suggested minor revisions the authors should address before publication of this manuscript. Those points revolve around providing a few more details on the experimental approach and on data interpretation.

We appreciate the reviewer for the recognition of the worth of our research and helpful comments. The concerns raised by the reviewer are addressed in the revised manuscript, as detailed below.

### Minor comments:

1. Line 16: In heterogeneous reaction kinetics experiments typically the pseudo-first order decay is monitored. From this the second order rate constant could be derived. Do you imply a pseudo-second-order model that considers chemisorption as the rate-limiting mechanism of the process? Please elaborate.

We thank the reviewer for this comment. As the reviewer mentioned, pseudo-first-order reaction rate constants could be estimated by fitting experimental results using an exponential function. The pseudo-second-order constants were calculated by dividing the first-order rate constant by the ozone concentration during the experiment. As the excess amount of ozone was employed for the experiment, changes in ozone concentration due to the chemical reactions with COA particles were ignorable, meaning that COA particles were exposed to a constant concentration of ozone during an experiment. *We clarified this idea in the revised manuscript.*

*Line 15: The pseudo-second order chemical reaction rate constants ( $k_2$ ) were estimated from the experimental data by assuming a constant ozone concentration in the flow tube.*

*Line 207: Ozone concentration was assumed to be a constant value, as an excess amount of ozone was injected to the flow tube. As a result, the process was fit by the following equation by assuming the pseudo-second order reaction with ozone:*

2. Line 17: I am not sure if the statement of diffusion limitation is correct in this instance. If a reaction is diffusion-limited then the observed degradation does not reflect the actual reaction kinetics. However, changes in the reaction kinetics with temperature are observed. The authors likely meant to express that the second order rate constant is controlled by diffusion? As outlined further below, I would argue that a fit using a similar equation as the VFT description of viscosity is not a sufficient proof that only diffusion governed the observed temperature dependency of the reactivity.

We appreciate the reviewer for this comment. We agree with the reviewer that the influence of viscosity on reaction kinetics is only inferred, rather than being evidenced by directly monitoring the diffusion process of ozone. We think that future viscosity measurements of COA particles will be needed for experimentally verifying how oxidation kinetics is regulated. We revised this sentence in a more accurate way.

*Line 18: The result suggests that increased viscosity was likely the key factor to account for the decrease in chemical reactivity at the reduced temperature range, though the idea will still need to be verified by temperature-dependent viscosity data in the future.*

3. Line 66: "However,...". I do not understand this statement. If experiments are done correctly, reactive uptake measurements using aerosol particles or films result in the same reaction kinetics (Ammann et al., 2013). There are advantages and disadvantages for both approaches, e.g., gas-phase diffusion limitations. If the aim is to indicate that OA can remain in a metastable liquid phase, i.e., being supercooled (see, e.g., (Hearn and Smith, 2005)), which is less likely to occur using a film, then this has to be more clearly stated. Furthermore, I think it would be fair to acknowledge the study by (De Gouw and Lovejoy, 1998).

We thank the reviewer for this comment. As the reviewer mentioned, experimental approaches that employ substrates were highly prone to induce artifacts especially when the investigated chemical system was supercooled. We clarified it in the main text. In addition, we thank the reviewer for these references.

*Line 70: Most of previous temperature-dependent oxidation experiments of COA were conducted using organic films or droplets on substrates (Hung and Tang, 2010; Li et al., 2020; Liu et al., 2023). However, the existence of substrates may influence physicochemical processes such as phase transition, impacting chemical reactivity (Hearn and Smith, 2005; Liu et al., 2023; De Gouw and Lovejoy, 1998). Low temperature oxidation experiments for suspending COA particles are still needed.*

4. Line 109: I would not call those concentrations "normal" and "high". Both are unrealistically high. Please rephrase. You might want to express those concentrations also as a typically background and urban polluted ozone exposure time.

We thank the reviewer for pointing it out. We revised it as 'kinetics and products investigation experiments' in the revised manuscript.

*Line 116: Ozone concentration was adjusted to be 450 ppb and 7 ppm for kinetics and*

products investigation experiments, respectively.

5. Line 113 and following: When determining the heterogeneous oxidation kinetics using aerosol particles, one has to pay attention to how reactivity scales with particle size (surface/volume). See e.g., studies by (Lim et al., 2017; Slade and Knopf, 2014). Have those experiments been conducted? How does the size distribution change prior to and after ozone exposure?

We appreciate the reviewer for this comment. We did not conduct experiments to investigate size dependence in reaction rates. As shown in Figure S6 of the revised manuscript, the mode diameter of particle number size distribution was stable within the range of  $300 \pm 50$  nm, except for a few exceptional cases. The uncertainty in size would induce less than 10 % of errors in  $k_2$  according to previous oleic acid ozonolysis researches (Morris et al. 2002, Smith et al. 2002). No obvious change was found in size distribution after oxidation except for the 7 ppm experiment.

We added the following paragraph to describe the size distribution of particles and the potential influences on reaction rate constants.

*Line 240: There were some variabilities in particle number size distributions among the experiments. The mode diameters for the COA particles were 300-400 nm (Fig. S6), while the corresponding values for oleic acid particles were at around 400 nm. The size ranges were comparable to the ambient COA particles in Beijing (Ma et al., 2023). The differences in reactive uptake coefficients for oleic acid particles would change by less than 5 % for 200 and 400 nm particles, leading to negligibly small changes in  $k_2$  values (approximately 10 %) (Morris et al., 2002; Smith et al., 2002). The variabilities in particle sizes among the experiments did not likely affect the experimental results of the present study.*

*Line 107: Mode diameter for the number size distribution in the tank maximumly shifted 10 % during a set of experiment (Fig. S2).*

6. Somewhere in the introduction, to elevate the discussion, recent modeling studies that account for viscosity changes in multiphase chemical kinetics, could be briefly mentioned. E.g., (Berkemeier et al., 2021).

We appreciate this suggestion from the reviewer. We added the following sentence to address the point.

*Line 53: The laboratory data for ozonolysis of oleic acid were recently compiled and analyzed using the kinetic multilayer model (Berkemeier et al., 2021).*

7. Section 3.3 and Table 1: I struggle to understand Table 1 and suggest elaborating this discussion more. When just quickly looking at the table, its meaning is not very clear. In the second column  $k_2$  is derived for only the oleic acid component in the types of particles given in column 1? Whereas column three reflects the reaction kinetics using a wider range of the mass spectrum. Maybe change the table or its description to make this clearer. Except for the value of the previous study, the data is derived from the same experiments?

We thank the reviewer for pointing out this unclear expression. The values in column 2 were obtained from SV-TAG, while these in column 3 obtained from ACSM. Measurements by SV-TAG (column 2) and ACSM (column 3) were done in independent experiments under the same condition. We have updated it in

the revised version.

Line 230:

*Table 1. Comparison of obtained values of  $k_2$  (ppb $^{-1}$  h $^{-1}$ ) for oleic acid (OL) in particles by the SV-TAG and whole particles by the ACSM at 25 °C.*

Type	$k_2$ for OL in particles (by SV-TAG)	$k_2$ for whole particles (by ACSM)
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8. Does the difference in particle size distribution among the different aerosol source types matter when comparing their kinetics (Fig. S1)? See also comment above.

We appreciate the reviewer for this comment. We agree particle size distribution is one important factor which influence chemical reaction rates for aerosol particles. As we mentioned in the response to comment #5, difference of 100 nm in particle diameter would not change  $k_2$  value by more than 10 %. Therefore, chemical composition and viscosity change of particles were more important in our experiments. We add more description about the influence of particle size of  $k_2$  in the revised version.

Line 240: *There were some variabilities in particle number size distributions among the experiments. The mode diameters for the COA particles were 300-400 nm (Fig. S6), while the corresponding values for oleic acid particles were at around 400 nm. The size ranges were comparable to the ambient COA particles in Beijing (Ma et al., 2023). The differences in reactive uptake coefficients for oleic acid particles would change by less than 5 % for 200 and 400 nm particles, leading to negligibly small changes in  $k_2$  values (approximately 10 %) (Morris et al., 2002; Smith et al., 2002). The variabilities in particle sizes among the experiments did not likely affect the experimental results of the present study.*

9. It may be worthwhile to mention that you are likely not gas-phase diffusion limited in the case of ozone uptake? I assume the uptake is sufficiently slow. Citing previous studies using canola oil or oleic acid might be helpful in this regard.

We thank the reviewer for this suggestion. We mentioned it and added corresponding references in the revised version.

Line 279: *Li et al (2020) reported that the reaction of ozone and canola oil liquid film was not gas diffusion limited, meaning that the determining factor for  $k_2$  should be identified in particle phase.*

10. Line 197-198: Looking at Fig. S5 it seems the ratio was greater one for lowest temperature measurements. Could it be that surface-dominated oxidation resulted in more products that did not volatilize due to lower temperatures?

We thank the reviewer for this question. We agree with the reviewer that surface chemical reactions might be the dominant under low temperature because of enhanced viscosity. However, due to the technical limitation of the ME-2 approach, we are unable to tell relatively small changes in chemical compositions that could be induced by surface reactions. Both the ME-2 and ACSM analysis are mass-based. Thus, the approach is sensitive to chemical reactions in the bulk phase, rather than a surface layer. The following statement was provided in the revised manuscript to address the issue.

Line 214: *It should be noted that  $f_{fresh}$  was occasionally larger than  $f_{fresh\_0}$  when the chemical reaction was extremely slow/negligible at low temperatures. As the ACSM is*

*a mass-based instrument, detecting changes in chemical composition due to ozonolysis is challenging when the reacted mass fraction is small. The output of the ME-2 analysis would have relatively large uncertainties when the change in chemical composition is comparable to or less than fluctuations in experimental data. In these cases,  $k_2$  was forced to be zero in the following analysis.*

11. Line 244: Which transition (phase?) do you mean here?

We thank the reviewer for this comment. We provided the definition of 'transition temperature' in the revised version.

*Line 258: The transition temperature was defined as the point at which  $k_2$  became an order of magnitude smaller than that at room temperature.*

12. Line 256-260: Condensed-phase diffusion is related to viscosity. However, I doubt, just because you can fit observations reasonably well with a VFT equation, though fit parameters are arbitrary and have no physical meaning, you can infer that only diffusion controls the entire oxidation process. This comes back to my comment in the abstract. There could be several processes going on in series or parallel which you are not resolving. See, e.g., (Pöschl et al., 2007; Berkemeier et al., 2021; Li and Knopf, 2021; Willis and Wilson, 2022). Clearly, your results demonstrate the importance of bulk diffusion but as long we cannot resolve all the intermediate steps, I suggest stating this observation more conservatively.

We appreciate the reviewer for this suggestion. We agree that many processes controlled the reaction at the same time, while diffusion was the key factor in our experiments. We thank the reviewer for providing the useful references. We updated this point in the revised version.

*Line 270: Previous studies demonstrated that numerous processes such as gas and bulk phase diffusion, adsorption and desorption, surface and bulk reaction are involved in determining oxidation rate of aerosol particles (Berkemeier et al., 2021; Pöschl et al., 2007; Li and Knopf, 2021; Willis and Wilson, 2022). Especially, accurate estimation of viscosity is important.*

*Line 293: VFT equation fit the experimental data well, demonstrating that the bulk diffusion was likely the key factor in controlling the reaction rate of COA particles.*

#### Technical corrections:

13. Line 121: Omit "also" since you already used "In addition,..." .

We have revised it as suggested.

14. Figure 3: Typo in legend "Palmitic".

We are sorry for the typo. We have revised it.

15. Line 154: "species" should be "spices"?

We are sorry for the typo. We have revised it.

16. Line 205: Missing "respectively"?

We are sorry for the missing. We have added it.

#### References

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