We appreciate the careful consideration of our manuscript by the reviewers. We have carefully responded to all of the point-by-point comments and issues raised by the reviewer and have revised the manuscript accordingly. These revisions are described in detail below. We also agree to submit this manuscript as a technique note in Atmospheric Chemistry & Physics.

Reviewer

In my view this is a much improved paper; the authors addressed my major concerns, and the new manuscript now discusses when the PMF approach is valid/necessary. I do think this discussion (of the PMF approach vs the tracer approach) could still be more thorough; further, the PMF results raise some questions about the heterogeneous chemistry that are currently not discussed. These concerns, which need to be addressed prior to publication, are described below.

Response: Thank you for your positive comments. We have responded appropriately below.

1) Discussion of PMF vs the marker-ion approach:

- Given that the authors are no longer arguing that previous AMS-based heterogeneous oxidation experiments have severely underestimated uptake coefficients, the text should clearly state so; plus lines 475-478 should be deleted. It may also help to cite my previous comment as evidence that the tracer and PMF approaches can sometimes agree (and Smith et al. 2007 as evidence that the tracer approach and molecular-ion approaches can sometimes agree as well).

Response: In our revised manuscript, we have confined our discussion to the condition that a UMR-AMS is used to measure OA and when the structure of products is highly similar to the reactants. In such cases, tracer based kinetics may at times be underestimated. This has been emphasized throughout the paper. For example, in lines 496-501 we revised it as "Although the tracer and PMF approaches can at times agree (Kroll, 2014) and the tracer and molecular-ion approaches can sometimes agree as well (Smith et al., 2009), our results suggest that the heterogeneous kinetics of OA is underestimated when a non-molecular ion peak is used as the tracer to measure the particle phase concentration of OA based on UMR-AMS." In lines 489-491, we also pointed out that "The discrepancy between the tracer and PMF based methods for other compounds will depend upon a number of factors including: structure of products, OH exposure level, particle morphology, and organic species competing OH reactions.” Finally we have noted that: “the tracer approach and molecular-ion approaches can sometimes agree as well” (lines 497-498)

As you suggested, lines 494-496: “An improvement in the mixed-phase relative rates technique is achieved based upon PMF analysis of UMR-AMS derived spectra.” and “or 7.7 times greater than the Kessler’s value (Kessler et al. 2012)” has been deleted.

- Similarly, I would recommend a change to the title, since "improvement" is too strong. The authors show that PMF analysis gives a higher value of gamma, but without independent confirmation that this higher value is correct (i.e., via molecular detection of the reactants) this new approach has not yet been shown to lead to an improvement in accuracy.

Response: As you suggested, the title has been revised as “Application of positive matrix factor analysis in heterogeneous kinetics studies utilizing the mixed-phase relative rates technique”. In In your previous comments your re-analysis of data showed that the PMF based approach is in agreement with the tracer approach and when the products are quite different from the reactant. We have also found that PMF based kinetics is in good agreement with the M^+ tracer based kinetics for TPhP (a compound which has a M+ tracer in the AMS). In light this, we continue to believe that PMF based data is likely the better approach when a UMR-AMS is used to measure OA concentration and when the products are highly similar to the reactant, as stated in the revised manuscript. From this point of view, this approach could be considered an “improvement”. However, we agree that without any molecular based detection of reactants we cannot be sure that accuracy has been improved.

- Somewhere in the text (maybe in lines 299-315) it needs be highlighted that the drop in the PMF product factor is substantially greater than that of any of the individual ions. This is implied in the text, but never said explicitly - it’s important because it means that PMF (a highly complex mathematical procedure!) is required to analyze the oxidation kinetics, which the authors argue cannot be done by simpler means. Similarly, it should be stated that a large difference between the PMF-factor decay rate and the marker-ion decay rate is mathematically possible only when the two factors (reactants and products) are extremely similar.

Response: In lines 305-307, we had stated: "However, the relative loss of these tracers as a function of OH exposure in Figure 5C is much smaller than that of the CA factor derived from the PMF analysis (Figure 5B)". We have changed this sentence as you suggested to: "As shown in Figure 5 B and C, the drop in the PMF product factor is substantially greater than that of any of the individual ions." We have also added a sentence in lines 317-319: "In particular, the difference between the PMF-factor decay rate and the marker-ion decay rate is mathematically possible only when the two factors (reactants and products) are extremely similar".

- Page 24: I think this section needs to again highlight the usefulness of measurements (from CIMS, GC-MS, VUV-AMS, etc.) for the determination of heterogeneous loss rates. In truth such measurements probably are superior to both EI-AMS approaches discussed (tracer ions and PMF), and this should be discussed as the best way forward.

Response: Thank you. We added two sentences at the end of this section "As illustrated in this study, the kinetics derived with PMF may differ from that derived with tracer ions, with both based upon EI-AMS approaches. This highlights the usefulness of measurements from CIMS, GC-MS and VUV-AMS, for the determination of heterogeneous loss rates, since these instruments are more likely to retain the reactant molecular information." (lines 517-522)

2) Discussion of the chemistry:

- There needs to be some discussion of the high value (2.74) of the uptake coefficient determined by the PMF approach. This value of gamma is much higher than those measured by other groups for OH-initiated reactions. Moreover, it means that every OH-particle collision leads to the reaction of almost 3 citric acid molecules, (Alternatively, as discussed by Lambe et al 2009, it could mean that some fraction of the parent molecule is actually in the gas phase, but this is highly unlikely for citric acid.) What is the likely mechanism for this? And why have such large values of gamma not been observed for other systems?

Response : Thank you for pointing this out. The γ_{OH} on a number of different organic particles have previously been measured, and are in the range of 0.3 – 2.0 (Kessler et al., 2010;George et al., 2007;Hearn and Smith, 2006;Lambe et al., 2007;Smith et al., 2009;Kessler et al., 2012). In fact, γ greater than 1 has been reported previously. For example, it was $2.0^{+0.6}_{-0.1}$ on BES (Hearn and Smith, 2006). Hearn and Smith (2006) also reported a γ of Cl on BES to be $2.0^{+0.8}_{-0.3}$, and 1.7±0.3 on DOS (Hearn et al., 2007). In their studies, the concentration of aerosol was measured using an Aerosol CIMS. Their results have been verified by a number of experiments (Hearn and Smith, 2006).

Hearn and Smith (2006) also discussed the influence of secondary reactions on the uptake coefficient and pointed out that secondary radical reactions (such as HO_2, RO and RO_2 (Hearn et al., 2007)) could play a significant role in heterogeneous chemistry. This indicates that the reaction of one OH radical from the gas phase could initiate the removal of multiple citric acid (or other) molecules through the formation of other secondary radicals in the particle resulting in a value of $\gamma > 1$. In the revised manuscript, we have discussed it as "The γ_{OH} for a number of different organic particles have previously been measured, and are in the range of 0.3 – 2.0 (Kessler et al., 2010;George et al., 2007;Hearn and Smith, 2006;Lambe et al., 2007;Smith et al., 2009;Kessler et al., 2012). As pointed out by Hearn and Smith (2006), the large γ implies that secondary radical reactions within the particles could play a significant role in heterogeneous chemistry, particularly since gaseous citric acid in these studies is insignificant" (lines 354-360).

- There should also be some discussion of the role of multigenerational chemistry in the present experiments. The implication of this work is that only early-generation chemistry is being probed, leading to the small differences in the reactant mass spectrum and derived product mass spectrum. However, at the highest level of OH oxidation, >80% of the product factor has reacted away (Figs 5b and 6a). At this level of oxidation, later-generation products ought to be formed as well (see Smith et al. 2009; Wilson et al. 2012). That assumes that 1st generation products exhibit oxidation kinetics that are reasonably similar to that of citric acid; but they probably should given their chemical similarity. Yet no further evolution of the mass spectrum (which could show up in a 3rd PMF factor) is observed. Why is this?

Response: As shown in Smith's and Wilson's work (Smith et al., 2009;Wilson et al., 2012), when the OH exposure is ~1.5×10^{12} molecules cm^{-3} s, the second generation product reached its maximum value ($[SqO_2]/[Sq]_0$: ~0.08). Our highest OH exposure is ~7.0×10^{11} molecules cm^{-3} s. Under this OH exposure, the first generation product reached its maximum level ($[SqO_1]/[Sq]_0$:~0.3) and the $[SqO_2]/[Sq]_0$ is ~0.05 accompanied with $[Sq]/[Sq]_0$ of ~0.7 (Fig. R1. Compared with the first generation product, the ratio of second generation products is very low. It suggests that the second generation product will have little influence on the mass spectrum of the products (measured with EI-AMS). Although it is difficult to directly extrapolate their results to our system due to differences in reaction conditions and mechanism, it is possible to form a low concentration of higher generation products for citric acid because the reactant is highly oxidized to begin with. On the other hand, a VUV HR-ToF-AMS is used to detect the aerosol composition in their work, which is more sensitive to chemical structure than Aerodyne C-ToF-AMS used in this study. We have tried 3 factors for PMF analysis, which results in the splitting of citric acid but not a second product factor. This is likely related to the ability of PMF to separate such small differences, since the uncertainty for each factor is 10-20 %. We have discussed these points in our revised manuscript (lines 389-396): "In studies of the OH oxidation of squalane (Sq) (Smith et al., 2009;Wilson et al., 2012), the first generation product (SqO) was the primary contributor to the products when the OH exposure was the same as the highest OH level in the current study (7.0×10^{11} molecules cm^{-3} s), while higher generation products were predominant at OH exposures was greater than ~2×10^{12} molecules cm^{-3} s. Although not directly comparable, it is reasonable to assume that lower OH exposure in the current work should lead primarily to the first generation products, which are highly similar to CA. However, the formation of multi-generation products cannot be completely ruled out. "

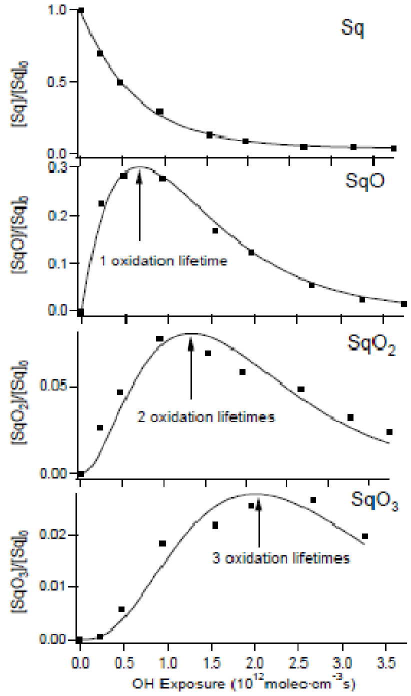

Figure R1. The evolution of squalane and the first three generations of oxidation products (SqO, SqO_2, SqO_3) as a function of the average OH exposure. (Smith et al., 2009)

- Lines 371-373 (and 402): There actually is some overlap between the OH exposures in the present study and those in Kessler et al. 2012, so the difference in exposures alone probably cannot explain the differences observed (i.e., differences in change to m/z 68). Some of the more subtle effects given in lines 404-422 may be at play here. The work of Che et al. (PCCP 11:7885), which finds uptake coefficients can vary with different timescales and concentrations, may also be helpful here.

Response: Thank you. We have added a sentence in the revised manuscript (lines 397-398). "Secondly, the difference in OA and oxidant concentrations as well as timescale may also have an influence on the product distribution".

Because the lines 404-422 (lines 423-443, in the revised manuscript) discussed the influence of OH concentration, O_3 concentration, timescale as you suggested, and morphology on reaction rate. We think it is more reasonable to discuss it here but not after the issue of m/z 68. A sentence has been added in lines 435-436 in the revised manuscript. “Different timescales and concentrations of reactants might also lead to different rate constants (Che et al., 2009).”

Minor comments:

Lines 124-131: The authors need to be specific about how AMS tracer ions are typically chosen – that they are usually the fastest-decaying ions in the spectrum (meaning the technique is equivalent to spectral subtraction).

Response: It has been pointed out in the revised manuscript: “In utilizing this approach, a specific fragment (usually the fastest-decaying ions in the spectrum) is often chosen as a tracer for the particle phase compound of interest.” (lines 125-126)

Line 217: Ulbrich et al. 2009 should probably be cited here.

Response: It has been cited here. (line 218)

Lines 292-293: Here it is stated that m/z 68 consumption is observed; this is in direct contradiction with line 369, which states “no significant consumption of m/z 68 was observed”. Which is correct?

Response: Thanks. The changes of AMS signal for m/z 68 and 129 are shown in Figure R2. It can be seen that m/z 68 doesn’t significantly change with OH exposure. So, in line 294, “m/z 68” has been deleted, and it is correct in line 379.

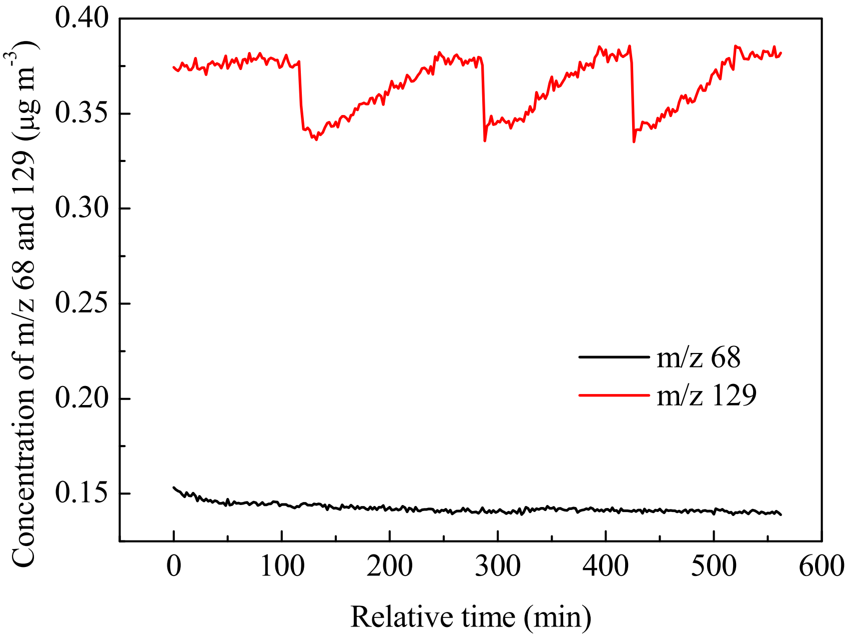

Figure R2. Changes of AMS signal for m/z 68 and 129 during OH oxidation of citric acid.

Line 349: This correction should be included in Eq. 7 (or at least referred to in the text just below the equation).

Response: Thanks. A correction factor has been included in Eq. 7.

$$\gamma_{OH} = \frac{2D_p\rho_{CA}N_A}{3v_{OH}M_{CA}}\varphi k_2$$

φ is a correction factor for diffusion of OH from the gas phase to particle phase. (line 248)

Line 349: the uncertainty value appears to be incorrect. (Possibly high by a factor of 10?) Response: Thanks. You are right. It's 0.66±0.05 (line 353).

Lines 398-403: I don't follow this sentence, especially the part marked "2" – the numbers themselves (not the potential differences in product distributions) indicate that the rate constants are different.

Response: We have deleted the ", and (2) that the two derived rate constants are indeed different" (line 419).

Lines 432-433 (and Scheme 2): This is only one product; somewhere there should be text mentioning other possible reaction products. Might fragmentation products (which can look quite different) play a role? Also, the citation should be modified to reflect that this follows the general chemistry described by Atkinson et al. (since citric acid wasn't studied directly).

Response: In lines 460-461, a new sentence has been added as "Other possible reaction products might also play similar roles in the fragments." We revised the description about this in lines 451-455 as "For example, scheme 2 illustrates the possible fragmentation pathways of 2,3-dihydroxypropane-1,2,3-tricarboxylic acid, which is one of the possible products from the OH oxidation of citric acid in terms of the general chemistry described by Atkinson et al. (Atkinson, 1986)". The caption for Scheme 2 has also been revised.

Typos/language: Line 70 ("particles make"), 103 (lower case c), 112 ("has been widely"), 117 ("detection").

Response: The errors in lines 70, 103, 112, 117 have been corrected.

Reference:

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Smith, J. D., Kroll, J. H., Cappa, C. D., Che, D. L., Liu, C. L., Ahmed, M., Leone, S. R., Worsnop, D. R., and Wilson, K. R.: The heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidative aging of ambient aerosols, Atmos. Chem. Phys., 9, 3209-3222, 10.5194/acp-9-3209-2009, 2009.

Wilson, K. R., Smith, J. D., Kessler, S. H., and Kroll, J. H.: The statistical evolution of multiple generations of oxidation products in the photochemical aging of chemically reduced organic aerosol, Phys. Chem. Chem. Phys., 14, 1468-1479, 10.1039/c1cp22716e, 2012.