

Interactive comment on “OH initiated heterogeneous oxidation of tris-2-butoxyethyl phosphate: implications for its fate in the atmosphere” by Y. Liu et al.

Anonymous Referee #2

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The paper is a continuation of two previous papers by these authors that look on heterogeneous oxidation of organic aerosols by OH radicals using time-of-flight aerosol mass spectrometer. In previous paper (Liu et al, 2014) they have shown that Positive Matrix Factor (PMF) analysis improves the kinetic estimation obtained via the common mixed-phase relative rates technique, and provided rate constants for heterogeneous oxidation of citric acid and three organophosphates. In the current paper these authors use the same technique to investigate the oxidation kinetics of another organophosphates flame retardant (TBEP) and the effect of mixing phase (internal vs. external) on the reactivity of citric acid and TBEP. An effort is also done to apply the obtained kinetic

C6257

information for evaluating the affect of OH oxidation and gas-particle partitioning on atmospheric fate of TBEP. The paper provides good scientific data and fits the scopes of ACPD and therefore I recommend accepting it for publication after the comments below are addressed.

Specific Comments

1. Although the PMF procedure was discussed in previous publications, it would be helpful if a short and general description of its principles will be given in current paper.
2. Page 19437 L 23; the authors mention that blank experiments in which the aerosols were exposed only to UV were performed to exclude the effect of photolysis. Can you provide the information of how significant was the photochemical loss in these experiments? (Absolutely and relatively to the loss due to reaction with OH). By the way, if photochemical loss was negligible than it already implies that evaporation in the reactor was negligible too (without need for the theoretical evaporation model). If it was very large how much error does it introduce in the calculation of the reactivity toward OH (i.e., subtracting two large numbers)?
3. Pages 19439-40; Please explain what Q/Q_{exp} are and add some explanation regarding the factors used in the analysis (e.g., two factors refer to parent and product). Some explanation is given on page 19441 but it needs to be before the second paragraph on page 19440. Furthermore, how did you determine these factors; based on mathematical fitting (chemometric tools) or previous knowledge on the fragmentation pattern of the parent compounds and their products?
4. Page 19442 L. 6; Do the presented error bars represent only the error resulting from the mathematical procedure or also from variability between replicate experiments?
5. Page 19445 L. 19; If TBEP remains at the surface, as claimed, how do you explain the big difference in its reactivity toward OH when internally mixed with AN and with CA? Is it possible that with AN there is more competition on surface sites?

C6258

6. Page 19445 second paragraph; the authors' explanation regarding changes in CA reactivity upon addition of AN or TBEP is based on the assumption that the internally mixed aerosols present core-shell morphology. How likely that this is correct considering that the aerosols were generated via atomization of mixed solution and not by coating of existing aerosols (as was done by Katrib et al, 2005)? In general, considering the focus of current paper on the effect of mixing phase on oxidation kinetics, it would be very beneficial if the authors can provide independent information (from other analytical techniques) on the morphology of these internally mixed aerosols.

7. Page 19446 L. 1-2; the lower K_r observed at higher RH is said to reflect faster kinetics. Did RH increased loss rates of both compounds? If so, the increase in K_r should reflect faster increase in reactivity of TBEP than of CA [since $K_r = R(\text{TBEP})/R(\text{CA})$]. How does that fit with your explanation that CA is present in the core and increasing RH increases diffusion of OH into the aerosol? If TBEP is in any way at the surface why is it more sensitive?

8. Page 19446 L 20; do you believe that the heterogeneous rate constant is lower than the gaseous one? How accurate are the kinetic estimations based on SAR?

9. Page 19447 L 5; Are the differences in the measured heterogeneous rate constants significant enough to support this statement?

10. In figure 4: are the temporal changes in concentrations along the experiments a result of changes in OH concentrations? Needs to be stated in the figure caption.

Technical comments

1. Page 19433 L. 15; missing "information regarding" before "heterogeneous"

2. Page 19433 L. 21; suggest "for their" instead of "for OA"

3. Figure S3; I think it should be B-A not B-C

4. Page 19437 l 6; units of OH exposure, I believe it should be second not seconds⁽⁻¹⁾.

C6259

5. Page 19434 L 18 give full name of PMF as it is the first time it is mentioned in the text.

6. Page 19443 L 16; consider omitting the second part of the sentences (regarding gaseous reference compounds) since your reference compound is also in the condensed phase and it may be confusing for the reader.

7. Page 19447 L 1; Typo in the power of the TBEP rate constant (10^{-1} ...)

8. Page 19447 L12; missing "of" before "ongoing".

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C6260