

Reviewer 2#

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 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.

Response: Thank you for your positive comments.

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.

Response: Thank you for your suggestion. We'll add the general principles of PMF analysis in the Section 2.2 (line 3, page 19438) as follows. "The principles of, and the procedures involved in the utilization of PMF analysis have been described elsewhere (Liu et al., 2014;Ulbrich et al., 2009). Briefly, PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into factor contributions and factor profiles (Paatero and Tapper, 1994).

$$x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij} \quad (1)$$

Where i and j refer to row and column indices in the matrix, respectively, p is the number of factors in the solution, x_{ij} is an element of the $m \times n$ matrix \mathbf{X} of measured data elements to be fit, and e_{ij} is the residual. The PMF solution minimizes the object function Q (Eq.2), based upon the uncertainties (u) (Norris and Vedantham, 2008), and is constrained so that no sample can have a negative source contribution.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{u_{ij}} \right)^2 \quad (2)$$

If all points in the matrix are fit to within their expected error, the $\text{abs}(e_{ij})/u_{ij}$ is ~ 1 and the expected $Q(Q_{\text{exp}})$ equals the degrees of freedom of the fitted data ($mn - p(m+n)$) (Paatero et al., 2002;Ulbrich et al., 2009). For AMS datasets, $mn \gg p(m+n)$, so $Q_{\text{exp}} \approx mn$, the number of points in the data matrix. If the assumptions of the bilinear model

are appropriate for the problem (data is the sum of variable amounts of components with constant mass spectra) and the estimation of the errors in the input data is accurate, solutions with numbers of factors that give Q/Q_{exp} near 1 should be obtained (Ulbrich et al., 2009).”

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)?

Response: Thank you for your suggestion. Figure R1 compares the mass concentration and the mass spectra of TBEP in the dark to that in the light. After atomization and drying, 200 nm TBEP particles selected by a DMA were introduced into the reactor in the dark. The RH in the reactor was 30 %. O_3 was absent in the reactor. The mass concentration and mass spectrum of TBEP were measured with the C-ToF-AMS. When the signal was stable, the 254 nm UV lamp was turned on. As can be seen from Figure R1A, the particle phase concentration of TBEP decreased significantly (~44 %) after UV light was turned on. There are two reasons which explain this decrease. Firstly, the temperature, which was measured with a thermocouple, in the reactor increased 3-4 degrees after the UV light was turned on, subsequently, leading to evaporation of TBEP from the particle phase. Secondly, as pointed out in our manuscript, photolysis might occur under irradiation of 254 nm UV light. Figure R1B shows the mass spectra measured under the dark and the light. Although the mass spectra were highly similar, the normalized signals of m/z 299, 227, 199, 125 and 85, which have been assigned to the typical fragments of TBEP in our manuscript, decreased (~15 %) when the UV light was turned on. At the same time, the signal of m/z 44 increased slightly (~10 %). This suggests that photolysis of TBEP is also possible under UV irradiation, although evaporation is likely more prevalent.

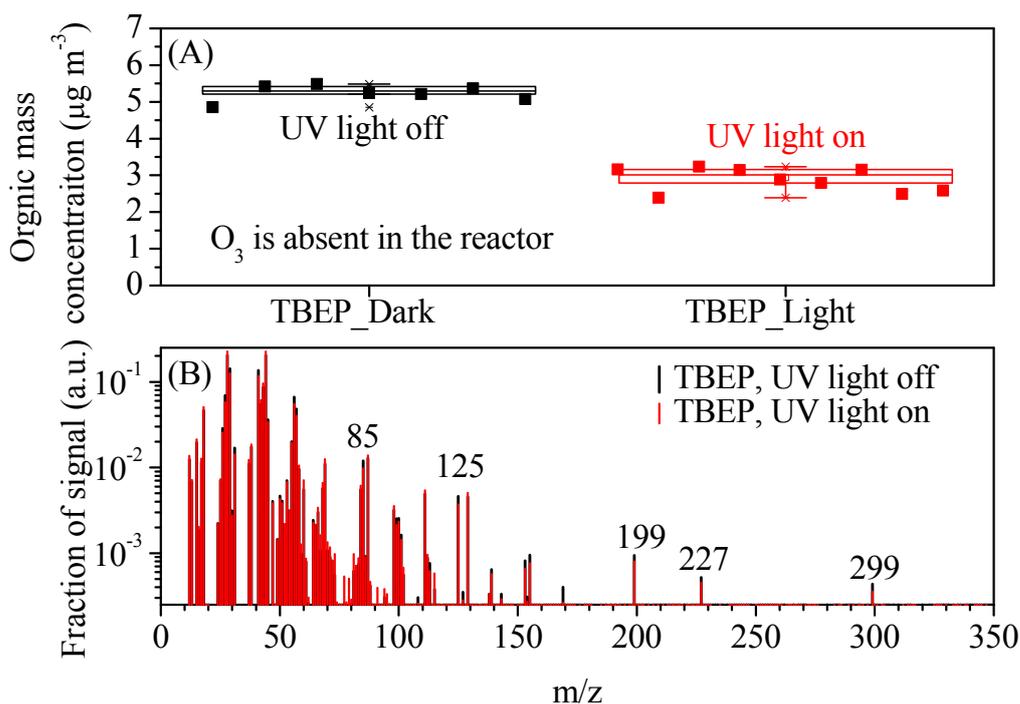


Figure R1. (A) Mass concentration and (B) normalized mass spectra (to mass concentration) of TBEP in the dark and light.

However, the above effects (warming and photolysis by UV light) on the kinetic calculations can be ruled out because the particles were always irradiated by UV light using our experiment procedure. This is because these factors have been considered when measuring the c_0 of TBEP. When OH (generated by photolysis O₃ and H₂O) was introduced into the reactor, the decrease of TBEP concentration should solely be explained by OH oxidation. Although the products of TBEP photolysis might have a small influence on OH oxidation kinetics, there is no better way at the present time. This should not be an issue if the products of OH oxidation are the dominant products during the experiment. It should also be noted that the mass spectrum of TBEP from the PMF analysis is highly consistent with that of pure TBEP. This implies that PMF analysis should correctly extract the concentration of TBEP and might partly exclude the interference from photolysis products.

As pointed out in our manuscript (Section 3.3 and 3.5), the loss of TBEP due to evaporation in the reactor is less than 0.3 % because of a short residence time (52 s). It is negligible compared to the total consumption of TBEP. However, in the ambient atmosphere, the lifetime of particles is up to a week. This means that a large fraction of TBEP might be evaporated from the particle phase even though the evaporation kinetics is the same as that in the flow tube reactor. As discussed in the Section 3.5,

the contribution of evaporation to the overall lifetime of TBEP and other OPEs is significant. This can be seen in Figure 8. Therefore, we think it is necessary to consider the effect of the evaporation process on the atmospheric lifetimes of these semi-volatile organic compounds.

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?

Response: The Q_{exp} and the meaning of Q/Q_{exp} has been answered in the Question 1# and will be added into Section 2.2 in the revised manuscript.

We think it is better to add the explanation regarding the factors after “4 factors” in line 22, page 19439 as “, namely, two factors refer to parent and product...”.

There are several criteria to determine the number of factors and to assign them. Firstly, the PMF results were verified by the Q/Q_{exp} as pointed out in Question #1. We have investigated the oxidation of CA by OH in our previous work (Liu et al., 2014). Two factors, which were assigned to the unreacted CA and its oxidation products, explained the AMS data ($Q/Q_{\text{exp}}=0.9998$) very well. In this study, 4 factors (two factors refer to parent and product, $Q/Q_{\text{exp}}=0.996$) also explained the AMS data very well. Secondly, PMF analysis provides a mass spectrum (factor profile) and a time series of mass concentration (factor contribution) for each factor. As shown in Figure 3, we can directly compare the mass spectra from PMF analysis and experimental spectra of unreacted CA or TBEP. Finally, as shown in Figures 1 and 4, the time series of mass concentration for each factor also contains useful information. Since the CA and TBEP particles were alternatively introduced into the reactor and oxidized under controlled conditions (OH concentration) in Exp. I, we know in advance when the CA or TBEP particles should be detected and when the products should be produced. These points have been discussed in Section 3.1 and 3.2.

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?

Response: The error bars only represent the error resulting from the mathematical procedure. It has been pointed out in line 6, page 19440.

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?

Response: In our manuscript, we compared the k_r ($=k_{2,TBEP}/k_{2,CA}$) among the externally mixed CA and TBEP-AN (1.33), internally mixed TBEP-CA (4.59) and internally mixed TBEP-AN-CA (19.53). We cannot measure the absolute value of $k_{2,TBEP}$ in the internally mixed particles because the k_2 of CA (the reference) is influenced by the mixing state.

Compared to the externally mixed CA and TBEP-AN, the internally mixed TBEP-CA showed a larger k_r . AN in the internally mixed TBEP-CA-AN further increased the k_r . It should be noted that either increase of $k_{2,TBEP}$ or decrease of $k_{2,CA}$ can lead to the increase of the k_r . As shown in Figure 7b and c (the RH in Figure 7c was 30 % but not 57 %), the fraction of consumed TBEP in the internally mixed TBEP-CA and TBEP-CA-AN was comparable, while less CA was consumed in the internally mixed TBEP-CA-AN. This means that the increase of the k_r in the internally mixed TBEP-CA-AN is a result of a decrease of $k_{2,CA}$. Therefore, we can deduce that the accessibility of OH to TBEP in both cases is comparable and AN mainly effects the kinetics of CA but not TBEP. This implies that TBEP should be at the surface. On the other hand, because both AN and CA are water soluble, it is reasonable to postulate that AN and CA are the inner core of the particles. In our manuscript (lines 11-25, page 19444 and lines 1-24, page 19445), we have discussed this in detail. The possible formation mechanism will be discussed below.

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.

Response: Thank you so much for your suggestion. Yes, we generated the particles by atomization and not by coating of existing aerosols. As pointed in lines 34-35, page 19445, TBEP may be enriched on the surface of internally mixed particles containing CA during diffusion drying from liquid droplets. In the droplets, it is well known that the surfactant (TBEP) will stay at the surface to reduce the surface free energy. It is reasonable to deduce then, that TBEP stays at the surface after water has evaporated. Figure R2 shows the possible formation mechanism of internally mixed TBEP-CA-AN. On the other hand, even for well mixed liquid particles of organic

(secondary organic matters (SOM) from ozonolysis of α -pinene, photooxidation of 1,2,4-trimethylbenzene, or organic sulfate) and inorganic compound (ammonium sulfate, AS), phase separation has been confirmed during efflorescence, from which the inner phase was an inorganic-rich phase and the outer phase was an organic-rich phase (You et al., 2012). Here, CA or AN is similar to AS, and TBEP corresponds to SOM. Although several methods, such as fluorescence microscopy and optical light-reflectance microscopy, can be used to characterize the morphology of particles, at the present time, these methods are unavailable to us. Other methods such as scanning or tuning electronic microscopy (SEM or TEM) cannot be applied in our system because of the volatility of these compounds.

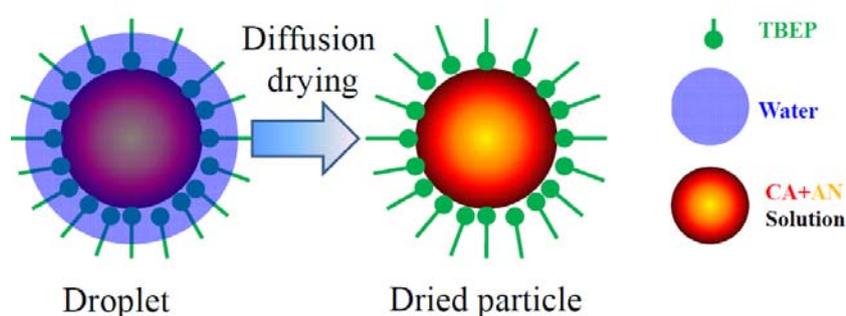


Figure R2. Schematic of formation process of internally mixed particle.

The above discussion will be added in line 12, page 19445 of the revised manuscript as: “In droplets, it is well known that surfactants (TBEP) will remain at the surface to reduce the surface free energy. TBEP may remain at the surface after water loss during efflorescence, and be enriched on the surface of internally mixed particles containing CA during the diffusion drying from liquid droplets. This assumption is consistent with the phase separation observed during efflorescence of internally mixed liquid particles of secondary organic materials and ammonium sulfate, from which the inner phase was an inorganic-rich phase and the outer phase was an organic-rich phase (You et al., 2012).”

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 any way at the surface why is it more sensitive?

Response: A lower k_r ($=k_{2,\text{TBEP}}/k_{2,\text{CA}}$) was observed at 57 % RH ($k_r=12.2$) than at 30 % RH ($k_r=19.5$) in the internally mixed TBEP-CA-AN particle. It reflects an increase in

reactivity of CA over TBEP, but not the inverse as you pointed out. Therefore, it is consistent with the explanation that CA is present in the core because high RH favors the diffusion of OH into the aerosol.

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?

Response: Yes, it is based upon the measured k_2 in particle phase in this study and the k_2 for the gas phase estimated with the AOPWIN model. Below we compared the experimental and model k_2 for some organophosphate esters (OPEs) (Table R1). For trimethyl phosphate (TMP) and triethyl phosphate (TEP) (both exist in gas phase), the measured k_2 in gas phase are comparable to the estimated ones with the AOPWIN model. In condensed phases (aqueous or particle phase), however, the measured k_2 of other OPEs are much lower than those in gas phase estimated based on SAR. We don't know the exact uncertainties of k_2 estimations based on SAR for TBEP, TPhP, TEHP and TDCPP discussed in this paper because their gas phase kinetics are unavailable, while the uncertainties are ~13 % for TMP and TEP.

Table R1. Comparisons between measured and estimated k_2 for OPEs.

OPs	k_2 (cm ³ molecule ⁻¹ s ⁻¹)	
	Laboratory	AOPWIN model (gas phase)
TMP	7.4×10^{-12} , ^a	8.4×10^{-12}
TEP	$(5.1 \pm 0.3) \times 10^{-11}$, ^b	5.8×10^{-11}
TCEP	9.3×10^{-13} , ^c	2.2×10^{-11}
TCPP	3.3×10^{-13} , ^c	4.5×10^{-11}
TBEP	1.7×10^{-11} , ^c	1.3×10^{-10}
TnBP	1.1×10^{-11} , ^c	7.9×10^{-11}
TPhP	$(2.0 \pm 0.43) \times 10^{-12}$, ^d	1.1×10^{-11}
TEHP	$(4.3 \pm 0.78) \times 10^{-12}$, ^d	9.8×10^{-11}
TDCPP	$(1.1 \pm 0.29) \times 10^{-13}$, ^d	1.8×10^{-11}
TBEP	$(4.4 \pm 0.45) \times 10^{-12}$, ^e	1.3×10^{-10}

^a in gas phase, Tuazon et al. (Tuazon et al., 1986); ^b in gas phase, Aschmann et al. (Aschmann et al., 2006, 2008); ^c in aqueous phase, calculated based on Watts and Linden's results (Watts and Linden, 2009); ^d in particle phase, (Liu et al., 2014); ^e in particle phase, in this study.

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

Response: Salamova et al. (Salamova et al., 2013) have reported the concentration of several OPEs in atmospheric particles in the Great Lakes region. The concentrations of TBEP and TEHP are comparable with the other OPEs, while they are significantly lower in the polar regions (Möller et al., 2012). This implies that the atmospheric

sinks of TBEP and TEHP should be faster than other OPEs. OH oxidation is the most important sink for these saturated hydrocarbon-OPEs. Therefore, we think the larger k_2 of TBEP and TEHP should explain this difference.

Based on the experimental data summarized in Table R1, we think it is significant enough to support this statement. For example, we performed the t -test for TBEP and TPhP. The k_2 of TBEP is significantly different from that of TPhP at 0.05 level with t and P value of 24.7 and <0.05 ($1.2E-6$), respectively.

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.

Response: Yes, they are. The figure caption has been revised to “Typical temporal concentration profiles of the 4-factor solution for oxidation of externally mixed TBEP-AN and CA particles. On the left shaded column, the curves are the same as those in Fig. 1 (Exp. I); they represent the oxidation of externally mixed TBEP - NH_4NO_3 and CA as function of OH concentrations on the right column (Exp. II)”.

Technical comments

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

Response: Thank you. It has been added in the revised manuscript.

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

Response: Thanks. “for organic aerosol” has been replaced with “for their” in our revised manuscript.

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

Response: Thank you for your corrections. It has been corrected in the revised manuscript.

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

Response: Yes, it’s molecules cm^{-3} s. It has been corrected.

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

Response: “PMF” has been replaced with “Positive Matrix Factor (PMF)”.

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.

Response: The followed sentences (lines 17-21, page 19443) have been rewritten as “However, additional gas-phase diffusion corrections for TBEP are unnecessary in this study due to the following reasons. Firstly, both CA (the reference) and TBEP are present in the particle phase, and a gas-phase diffusion correction for OH from gas-phase to the CA particle surface has been performed by applying a previously utilized empirical formula (Fuchs and Sutugin, 1970; Worsnop et al., 2002; Widmann and Davis, 1997). Secondly, the k_r is approximately unity and the particle size for CA is the same as that of TBEP-AN in this study.”

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

Response: It has been replaced with “ 1.29×10^{-10} ”.

8. Page 19447 L12; missing “of” before “ongoing”.

Response: It has been added.

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