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 reviewers and have revised the manuscript accordingly. These revisions are described in detail below

Reviewer 1#

General comments:

This paper (acp-2014-547) reported an experimental study on the heterogeneous reaction between OH radicals and TBEP using particle-phase relative rates technique. The second-order rate constant for the reaction was obtained and the atmospheric lifetimes of TBEP and other OPEs were estimated. The influence of mixing state of multi-component particle on TBEP oxidation was also investigated. TBEP is a widely used flame retardant, which can be emitted in the atmosphere primarily in the particle phase. The results reported in this paper are important for assessing the persistence of TBEP and its fate in the atmosphere. This paper matches the merit of Atmospheric Chemistry and Physics. However, there are still some problems and mistakes that need to be addressed prior to possible publication.

Response: Thank you for your positive comments.

(1) The usage of equation (Eq. 5) for calculating uptake coefficient γ_{OH} is questionable. First, the second-order reaction constant $k_{2,TBEP}$ should be in the numerator other than denominator. Second, this equation is appropriate for calculating the γ_{OH} involving pure particles other than mixed particles. According to the original author Smith et al., derivation of γ_{OH} is as follows:

$$\gamma_{OH} = \frac{-d[TBEP]/dt}{f \cdot J_{coll} \cdot A \cdot C_p}$$

Where f is the fraction of TBEP molecules remaining within the particle (i. e. $[TBEP]/[TBEP]_0$); J_{coll} is the OH flux at the particle surface ($\frac{1}{4}\bar{c}[OH]$); A is the particle surface area, and C_p is the particle number concentration. Then, the γ_{OH} is,

$$\gamma_{OH} = \frac{k_{2,TBEP}[TBEP][OH]}{\frac{[TBEP]}{[TBEP]_0}\cdot J_{coll}\cdot A\cdot C_p}$$

$$= \frac{k_{2,TBEP}[TBEP]_0[OH]}{J_{coll}\cdot A\cdot C_p}$$

Here, if the TBEP particles used in this experiment are single-component pure TBEP particles, like the particles used in the study of Smith et al, the initial concentration of TBEP ($[TBEP]_0$, in molec cm^{-3}) can be calculated in terms of the initial particle-phase density ρ_{TBEP}.

$$[TBEP]_0 = \frac{C_p \cdot V \cdot \rho_{TBEP} \cdot N_A}{M_{TBEP}}$$

Where V is the particle volume, M_{TBEP} is the molar mass of TBEP, N_A is Avogadro's number. Put it in the above equation of γ_{OH},

$$\gamma_{OH} = \frac{k_{2,TBEP}\frac{C_p \cdot V \cdot \rho_{TBEP} \cdot N_A}{M_{TBEP}}[OH]}{\frac{1}{4}\bar{c}[OH]\cdot A\cdot C_p}$$

Since V/A equals to $\frac{D_p}{6}$ (D_p is the surface-weighted particle diameter), the final expression for γ_{OH} should be,

$$\gamma_{OH} = \frac{2k_{2,TBEP}D_p\rho_{TBEP}N_A}{3\bar{c}M_{TBEP}}$$

To sum up, ρ_{TBEP} in this equation to calculate the initial concentration of TBEP ($[TBEP]_0$) is improper. The obtained $[TBEP]_0$ is the initial concentration of pure TBEP particles. However, in fact, a fraction of particles is occupied by other substances such as ammonium nitrate in this experiment. Thus, the exact value of $[TBEP]_0$ must be not accordance with the calculated value of this study.

Response: Thank you very much for your correction. We carefully checked our original manuscript submitted to Atmos. Phys. Chem. Discuss. Equation (5) (Eq. (7) in the revised manuscript) is a typsetting error but we did not catch it during proof-reading. The original equation is

$$\gamma_{OH} = \frac{2D_p\rho_{TBEP}N_A}{3v_{OH}M_{TBEP}}k_{2,TBEP} \qquad \text{(Eq. R1)}$$

We have corrected it in the revised manuscript (page 17, line 367 in the revised manuscript).

We agree with you that, strictly speaking, this equation will cause some uncertainty when applied to a multi-component particle, especially, for a solution or solid solution. However, we used it to calculate the γ_{OH} in our study despite some additional uncertainty that might be introduced for following reasons. In Eq. (R2) (your first equation), f is the fraction of the surface area covered by TBEP (or reactant) in the terms of the collision theory. It is usually expressed as the fraction of reactant molecules remaining within the particles (Smith et al., 2009) (The surface area fraction is the same as the volume or mass fraction when the components are well mixed in a solution).

$$\gamma_{OH} = \frac{-d[TBEP]/dt}{f \cdot J_{coll} \cdot A \cdot C_p} \qquad \text{(Eq. R2)}$$

However, TBEP is a surfactant with a surface tension of 0.0342 N m^{-1} (Karsa., 1999). The internally mixed particles of TBEP and NH_4NO_3 (TBEP-AN) were generated using an atomizer from aqueous solution followed by a diffusion dryer. Therefore, TBEP is very likely present (and enhanced) on the surface layer in the dried particles (NH_4NO_3 as a core) as confirmed by the influence of mixing state on the kinetics (Section 3.4). In this case, the accessibility of TBEP molecules to OH radicals should be similar to that in the pure TBEP particles. We have added this discussion in our revised manuscript at the end of Section 3.3 (pages 17-18, lines 373-380 in the revised manuscript).

"It should be pointed out that Eq. (7) may introduce an additional uncertainty to γ_{OH} for a mixed particle, especially, for a solution or solid solution. However, as will be discussed below, TBEP is a surfactant with a surface tension of 0.0342 N m^{-1} (Karsa., 1999). The internally mixed particles of TBEP-AN were generated using an atomizer from aqueous solution followed by a diffusion dryer. Therefore, TBEP is highly likely to be present on the surface layer in the dried particles (NH_4NO_3 as a core). In this case, the accessibility of TBEP molecules to OH radicals should be similar to that in the pure TBEP particles."

(2) Page 16, Lines 4-6: The author states that "the diffusion rate of CA or OH radicals in the particle phase increases at higher RH, subsequently enhancing the potential for reaction with OH". However, from Figure 7(c) we can see that the consumption of CA under higher RH was less than that under lower RH. These experimental results do not support the conclusion.

Response: Thank you for catching this. In Figure 7C, the number "57 %" is not correct. It should be 30 % as noted in the Figure caption. At the same time, the figure number ("Fig. 7C") in page 20, line 431 should be Fig. 6C. These errors have been corrected in the revised manuscript.

Minor comments:

Page 2, Line 20: Show the full name of "PM" for its first appearance in the article.

Response: The "PM" has been replaced with "particulate" in the revised manuscript (page 2, line 42).

Page 8: Since PMF analysis is not a widely-used method in data processing, a brief description for its principle can be added in the Section 2.2. For example, Q/Q_{exp} (Page 10, Line 1) first appears in the paper but without an explanation.

Response: Thank you. PMF is factor analysis tool and has been widely used in source apportionment. In our previous paper (Liu et al., 2014), we have described the theory and parameter settings for PMF analysis. As you suggested, a brief introduction about the principles of PMF has been added in Section 2.2 (pages 9-10, lines 189-207) as follows. "The principles and the procedure 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).

$$x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij} \qquad \text{Eq. (1)}$$

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 **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.

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

If all points in the matrix are fit to within their expected error, the abs(e_{ij})/u_{ij} is ~ 1 and the expected Q(Q_{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, $mn >> p(m+n)$, so $Q_{\mathrm{exp}} \approx mn$, 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).”

Page 10, Line 20: “a small fraction factor 4” may be “a small fraction of factor 4”.

Response: Yes, it is “a small fraction of factor 4”. It has been corrected in the revised manuscript (page 13, line 272).

Page 10, Line 25: “227 and 299” should be “227, and 299”.

Response: We do not think there is an issue with the comma.

Page 11, Line 2: “Figure 3a-d further compares…” should be “Figures 3a-d further compare…”.

Response: It should be Figure 3a-d. This was confirmed by the editor.

Page 11, Line 9: Add comma “,” after “227”.

Response: We do not think there is an issue with the comma.

Page 11, Line 11: Replace “citric acid” by “CA”.

Response: It has been corrected in the revised manuscript (page 14, line 292).

Page 11, Line 14: Add comma “,” after “oxidized”.

Response: We do not think there is an issue with the comma (page 14, line 295).

Page 11, Line 15: “is” should be “are”.

Response: It should be “are” and has been corrected in the revised manuscript (page 14, line 296).

Page 11, Lines 16 and 17: “Fig. S3a-c” should be “Figs. S3a-c”. Please unify the expression of Figure in the full text. For example, the full names “Figures 1 and 2” and “Figure 3a-d” were used in the Page 9, Line 24 and Page 11, Line 2, but the abbreviation “Fig. S3a-c” was used here and other places.

Response: Thanks. But according to the guidelines for authors, the abbreviations “Fig.” should be used when they appear in running text and should be followed by a number unless they come at the beginning of a sentence, e.g.: “The results are depicted in Fig. 5. Figure 9 reveals that...”. So, it is unnecessary to unify them throughout the paper.

Page 11, Line 24: Substitute the oral language “In doing so” by some written words.

Response: It has been replaced with “Thus” in the revised manuscript (page 14, line

305).

Page 11, Line 27 and Page 12, Line 1: The present tense and past tense are in one sentence. Please revise it.

Response: This sentence (pages 14-15, line 307-310) has been revised as "As shown in Fig. 4, the 4-factor solution successfully separated the signals of CA, TBEP, and their oxidation products, regardless of whether the particles were introduced into the reactor together (Exp. II) or via alternating particle sources (Exp. I)."

Page 12, Lines 8-10: The same problem as above.

Response: This sentence (page 15, line 316-318) has been revised as "When exposed to OH radicals, the concentrations of CA (factor 1) and TBEP (factor 3) decreased synchronously with OH exposure, which was accompanied with an increase of factors 2 and 4".

Page 13, Lines 23, 25, 27…: The units of rate constants for many places in this paper are incorrect. "cm^3 molecule s^{-1}" should be "cm^3 $molecule^{-1}$ s^{-1}".

Response: These typo errors have been corrected in the revised manuscript (page 17, lines 361,363,365; page 21, lines 450, 455, 458, 459).

Page 14, Line17: "Fig. 6a and b" should be "Figs. 6a and b". Please use the plural form of Fig., if necessary, for other places throughout the article.

Response: It has been corrected in the revised manuscript (page 18, line 388).

Page 17, Line 1: The "10^{-1}" should be "10^{-10}".

Response: Thanks, it has been corrected in the revised manuscript (page 21, line 447).

Page 17, Line 22: Add comma "," after "TEHP". There are still many similar problems in this paper. Please revise the format "A, B and C" with "A, B, and C".

Response: We don't think a comma is required here.

Page 20, Lines 10-13: There is a grammatical mistake in this sentence: "*In particular, the measurements of TPhP in PM in remote regions (Möller et al., 2012), despite its dominant gas-phase loss contribution (based upon our model results) highlights the effect of multi-component particle mixtures on the kinetics of particle degradation.*"

Response: This sentence (page 25, lines 541-544) has been revised as "In particular, the measurements of TPhP in PM in remote regions (Möller et al., 2012), despite its dominant gas-phase loss contribution (based upon our model results), highlights the effect of multi-component particle mixtures on the kinetics of particle degradation."

Page 20, Line 22: Delete the word "show" after "that".

Response: It has been removed from this sentence in the revised manuscript (page 26, line 553).

Page 31, the caption of Figure 1: Replace "Exp 1, 2, 3 represent…" by "Error bars represent…".

Response: Thanks, it has been corrected in the revised manuscript (page 34, line 823).

Page 37, the caption of Figure 7: Please state clearly that the RH of experiments (A) and (B) are (30 ± 3)%, and that of (C) is (57 ± 2)%".

Response: It is also (30 ± 3)% in Fig. 7C. It has been corrected in the revised manuscript.

Reference:

Karsa., D. R.: Design and Selection of Performance Surfactants, Sheffield Academic Press, P260, 1999.

Liu, Y., Li, S.-M., and Liggio, J.: Technique Note: Application of positive matrix factor analysis in heterogeneous kinetics studies utilizing the mixed-phase relative rates technique, Atmos. Chem. Phys. Discuss., 14, 8695-8722, doi:10.5194/acpd-14-8695-2014, 2014.

Norris, G., and Vedantham, R.: EPA positive matrix factorization (PMF) 3.0 fundamentals & user guide, U.S. Environmental Protection Agency, www.epa.gov, 2008.

Paatero, P., and Tapper, U.: Positive matrix factorization: a nonnegative factor model with optimal utilization of error estimates of data values, Environmetrics 5, 111-126, 1994.

Paatero, P., Hopke, P. K., Song, X.-H., and Ramadan, Z.: Understanding and controlling rotations in factor analytic models, Chemometrics and Intelligent Laboratory Systems, 60, 253-264, http://dx.doi.org/10.1016/S0169-7439(01)00200-3, 2002.

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.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, 2009.

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 (pages 9-10, lines 189-207) 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).

$$x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij} \qquad \text{Eq. (1)}$$

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.

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

If all points in the matrix are fit to within their expected error, the abs(e_{ij})/u_{ij} is ~ 1 and the expected Q(Q_{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, $mn >> p(m+n)$, so $Q_{\mathrm{exp}} \approx mn$, 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.

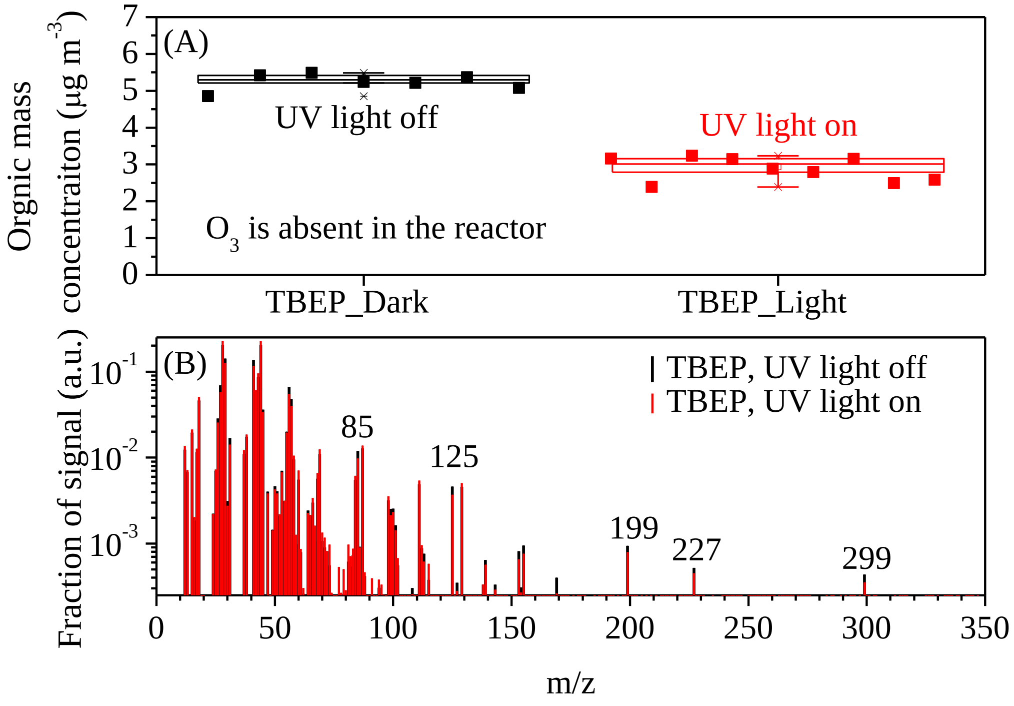

Figure R1. (A) Mass concentration and (B) normalized mass spectra (to mass concentration) of TBEP in the dark and light.

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 O_3 and H_2O) 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/Qexp 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 response to Question 1# and has been added into Section 2.2 in the revised manuscript (page 10, line 201).

We think it is better to add the explanation regarding the factors after "4 factors" in page 12, lines 249-250 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_{exp}=0.9998) very well. In this study, 4 factors (two factors refer to parent and product, Q/Q_{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 page 12, lines 258-259.

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 (pages 18-20, lines 382-425), 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 theses 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 page 19, lines 408-412, 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.

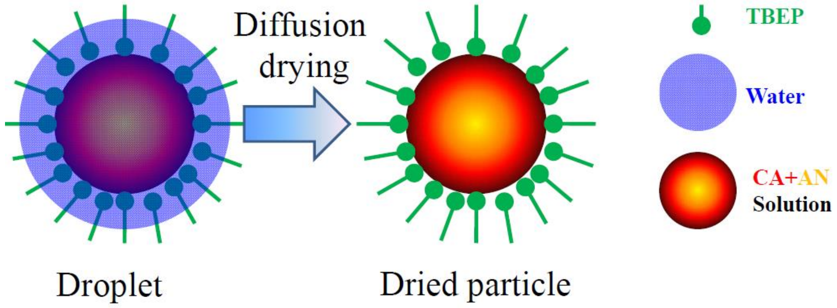

Figure R2. Schematic of formation process of internally mixed particle.

The above discussion has been added in page 19, lines 408-415 in the revised manuscript as: “In droplets, it is well known that a surfactant (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 inorganic-rich and the outer phase was organic-rich (You et al., 2012).”

7. Page 19446 L. 1-2; the lower Kr observed at higher RH is said to reflect faster kinetics. Did RH increased loss rates of both compounds? If so, the increase in Kr should reflect faster increase in reactivity of TBEP than of CA [since Kr=R(TBEP)/R(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 ($=k_{2,\mathrm{TBEP}}/k_{2,\mathrm{CA}}$) 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	$(5.1\pm0.3)\times10^{-11}$, [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	$(2.0\pm0.43)\times10^{-12}$, [d]	1.1×10^{-11}
TEHP	$(4.3\pm0.78)\times10^{-12}$, [d]	9.8×10^{-11}
TDCPP	$(1.1\pm0.29)\times10^{-13}$, [d]	1.8×10^{-11}
TBEP	$(4.4\pm0.45)\times10^{-12}$, [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); the oxidation of externally mixed TBEP -NH_4NO_3 and CA as function of OH concentrations is represented in 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 (page 3, line 64).

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 (page 4, line 71).

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 SI.

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

Response: Yes, it's molecules cm^{-3} s. It has been corrected (page 8, line 166).

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 Factorization (PMF)" (page 5, line 96).

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 (page 17, lines 353-359) 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 (10ˆ-1…)

Response: It has been replaced with "1.29×10^{-10}" (page 21, line 447).

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

Response: It has been added (page 22, line 470).

References:

Aschmann, S. M., Long, W. D., and Atkinson, R.: Temperature-Dependent Rate Constants for the Gas-Phase Reactions of OH Radicals with 1,3,5-Trimethylbenzene, Triethyl Phosphate, and a Series of Alkylphosphonates, J. Phys. Chem. A, 110, 7393-7400, 2006.

Aschmann, S. M., Long, W. D., and Atkinson, R.: Rate Constants for the Gas-Phase Reactions of OH Radicals with Dimethyl Phosphonate over the Temperature Range of 278-351 K and for a Series of Other Organophosphorus Compounds at ~280 K, J. Phys. Chem. A 112, 4793-4799, 2008.

Fuchs, N. A., and Sutugin, A. G.: Highly Dispersed Aerosols, Butterworth-Heinemann, Newton, MA, 1970.

Karsa., D. R.: Design and Selection of Performance Surfactants, Sheffield Academic Press, P260, 1999.

Liu, Y., Li, S.-M., and Liggio, J.: Technique Note: Application of positive matrix factor analysis in heterogeneous kinetics studies utilizing the mixed-phase relative rates technique, Atmos. Chem. Phys. Discuss., 14, 8695-8722, doi:10.5194/acpd-14-8695-2014, 2014.

Möller, A., Sturm, R., Xie, Z., Cai, M., He, J., and Ebinghaus, R.: Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the polar regions: Evidence for global occurrence, Environmental Science and Technology, 46, 3127-3134, 2012.

Norris, G., and Vedantham, R.: EPA positive matrix factorization (PMF) 3.0 fundamentals & user guide, U.S. Environmental Protection Agency, www.epa.gov, 2008.

Paatero, P., and Tapper, U.: Positive matrix factorization: a nonnegative factor model with optimal utilization of error estimates of data values, Environmetrics 5, 111-126, 1994.

Paatero, P., Hopke, P. K., Song, X.-H., and Ramadan, Z.: Understanding and controlling rotations in factor analytic models, Chemometrics and Intelligent Laboratory Systems, 60, 253-264, http://dx.doi.org/10.1016/S0169-7439(01)00200-3, 2002.

Salamova, A., Ma, Y., Venier, M., and Hites, R. A.: High Levels of Organophosphate Flame Retardants in the Great Lakes Atmosphere, Environ. Sci. Technol. Lett., 1, 8-14, 2013.

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.

Tuazon, E. C., Atkinson, R., Aschmann, S. M., Arey, J., Winer, A. M., and Pitts, J. N.: Atmospheric loss processes of 1,2-dibromo-3-chloropropane and trimethyl phosphate, Environ. Sci Technol., 20, 1043-1046, 1986.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, 2009.

Watts, M. J., and Linden, K. G.: Advanced Oxidation Kinetics of Aqueous Trialkyl Phosphate Flame Retardants and Plasticizers, Environ. Sci. Technol., 43, 2937-2942, 2009.

Widmann, J. F., and Davis, E. J.: Mathematical models of the uptake of ClONO2 and other gases by atmospheric aerosols, J. Aerosol. Sci., 28, 87-106, 1997.

Worsnop, D. R., Morris, J. W., Shi, Q., Davidovits, P., and Kolb, C. E.: A chemical kinetic model for reactive transformations of aerosol particles, Geophys. Res. Lett., 29, 1996, 10.1029/2002gl015542, 2002.

You, Y., Renbaum-Wolff, L., Carreras-Sospedra, M., Hanna, S. J., Hiranuma, a., Kamal, S., Smith, M. L., Zhang, X., Weber, R. J., Shilling, J. E., Dabdub, D., Martine, S. T., and Bertram, A. K.: Images reveal that atmospheric particles can undergo liquid–liquid phase separations, Proc. Nat. Acad. Sci. USA, 109, 13188-13193, 2012.