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) is a typsetting error but we did not catch it during proof-reading. The original equation is

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

, and will be correct 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).

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

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 will add the following discussion in our revised manuscript at the end of Section 3.3.

"It should be pointed out that Eq. (5) 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 diffusion drying. Therefore, TBEP is very likely enhanced 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 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 line 1, page 16 should be Fig. 6C. These errors will be 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" should be replaced with "particulate". It will be corrected in the revised manuscript.

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 will be added in Section 2.2 (line 3, page 19438) as follows. "The principles of, and the procedure 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 analytical tool that decomposes a matrix of speciated sample data into factor contributions and factor profiles (Paatero and Tapper, 1994).

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

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.

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

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 $Q_{exp} \approx mn$, 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 will be corrected in the revised manuscript.

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

Response: We do not think there should be a comma there as suggested.

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 should be a comma there as suggested.

Page 11, Line 11: Replace "citric acid" by "CA".

Response: It will be corrected in the revised manuscript.

Page 11, Line 14: Add comma "," after "oxidized".

Response: We do not think there should be a comma there as suggested.

Page 11, Line 15: "is" should be "are".

Response: It should be “are” and will be corrected in the revised manuscript.

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 will be replaced with “Thus” in the revised manuscript.

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 has been revised as “As shown in Fig. 4, the 4-factor solution successfully separates 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 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 will be corrected in the revised manuscript.

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 will be corrected in the revised manuscript.

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

Response: Thanks, it will be corrected in the revised manuscript.

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 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 will be removed from this sentence in the revised manuscript.

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

Response: Thanks, it will be corrected in the revised manuscript.

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 will be 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.