Atmospheric
Chemistry
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Supplement of

OH-initiated heterogeneous oxidation of tris-2-butoxyethyl phosphate: implications for its fate in the atmosphere

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Supporting information.

Mass transfer diffusion model.

From Fick's first law of diffusion, the rate of change of mass of a single, spherical, homogeneous drop of compound *A* can be described with

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 4\pi R^2 D_\mathrm{v} \frac{\mathrm{d}\rho_\mathrm{v}}{\mathrm{d}R} \qquad \text{Eq. (S1)}$$

where *m* is the mass of the drop (g), *R* is the radial distance from the center of the drop (cm), D_v is the molecular diffusion coefficient of *A* in air (cm^2 s^{-1}), ρ_v is the density of the vapor of A (g cm^{-3}), and $\mathrm{d}\rho_\mathrm{v}/\mathrm{d}R$ is the radial gradient of vapor density. When latent heat is taken into consideration during evaporation, Eq. (S1) becomes

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{4\pi D_\mathrm{v}(p_\mathrm{v}-p_\mathrm{v,s})}{\frac{D_\mathrm{v}L_\mathrm{e}p_\mathrm{v,s}}{k_\mathrm{a}T}\left(\frac{L_\mathrm{e}}{R_\mathrm{v}T}-1\right)+R_\mathrm{v}T} \qquad \text{Eq. (S2)}$$

Where p_v and $p_\mathrm{v,s}$ is the vapor pressure of *A* in bulk gas phase and on the particle surface, respectively (Pa), L_e is the latent heat of evaporation of *A* (J g^{-1}), κ_a is the thermal conductivity of moist air (J cm^{-1} s^{-1} K^{-1}), R_v is ideal gas constant (8.314 J K^{-1} mol^{-1}). Details regarding the derivation are also given elsewhere (Jacobson, 2005). According to a partition model (Kroll and Seinfeld, 2008;Pankow, 1994), the vapor pressure of *A* in bulk gas phase is calculated as

$$p_\mathrm{v} = \frac{R_\mathrm{v}T\rho_\mathrm{T}\rho_\mathrm{v,s}}{M+\rho_\mathrm{v,s}} \qquad \text{Eq. (S3)}$$

Where ρ_T is the total density of *A* in both gas and particle phase (g cm^{-3}), and *M* is the mass loading of organic aerosol in the atmosphere (g cm^{-3}). Both curvature and solute effects are corrected for p_v and $p_\mathrm{v,s}$. The Molecular diffusion coefficient (D_v) for OPEs

and OA are calculated and corrected according to (Jacobson, 2005).

Internally mixed particles (OPEs-OA) are considered an ideal solution for OPEs. The evaporation of OA and OPEs are treated separately in this model. Then, the mass of the drop in each step is calculated by

$$m_{i+1} = m_i + dm_i \qquad \text{Eq. (S4)}$$

Where, i=0, 1, 2…

The evaporation rate constant (k_e) of the OPE is obtained from the slope of the plot of $\ln(c_{OPE}/c_{OPE,0})$ against t. The following parameters are used as inputs in to the model.

Table S1 Inputs for the evaporation rate calculation.

	TBEP	OA	Air
ρ (g cm^{-3})	1.02 [a]	1.27 [b]	1.18×10^{-3} [c], 0.33 [d]
μ (kg m^{-1} s^{-1})	-	-	1.86×10^{-5} [e]
Vapor pressure (Pa)	3.3×10^{-6} [f]	3.3×10^{-7} [g]	-
M (g mol^{-1})	398	300 [h]	29
m_0 (µg m^{-3})	1.0×10^{-3}	5.0 [h]	-
D_v (cm^2 s^{-1}) [h]	0.1617	0.1635	-
P (Pa)		101325	
T (K)		298	

[a] (IPCS, 2000); [b] (Lee et al., 2010); [c] gas-phase; [d] liquid-phase ; [e] (Kadoya et al., 1985);

[f] (Bergman et al., 2012);[g] (Abramson et al., 2013); [h] (Vogel et al., 2013).
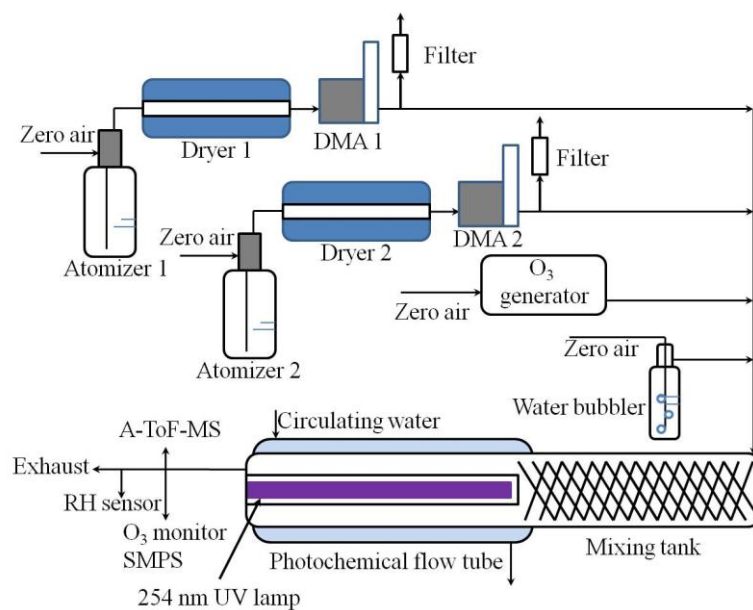
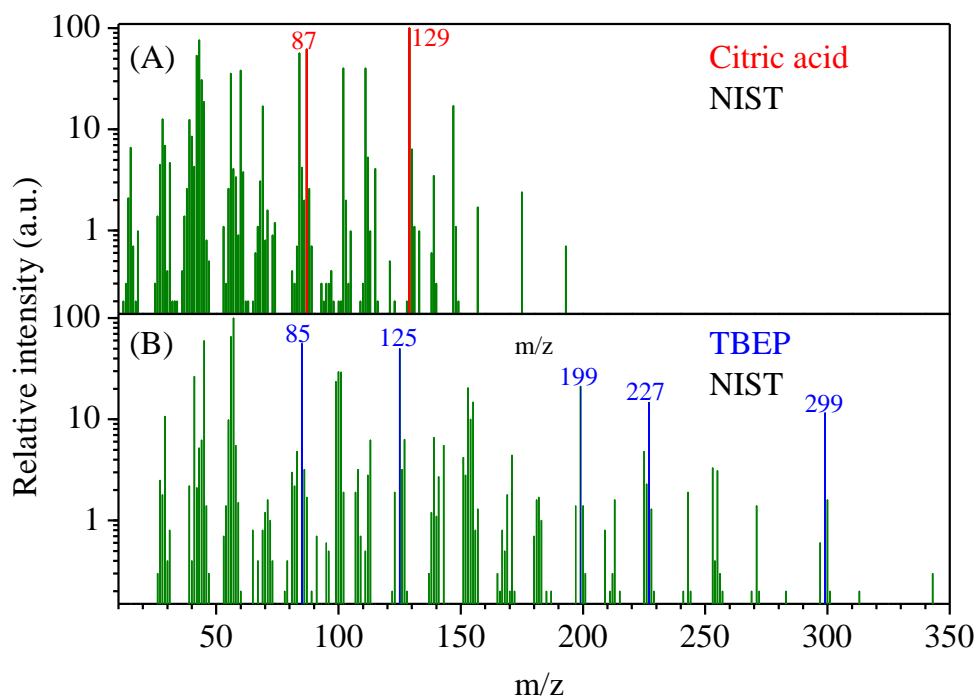Figure S1. Experimental schematic for heterogeneous oxidation studies

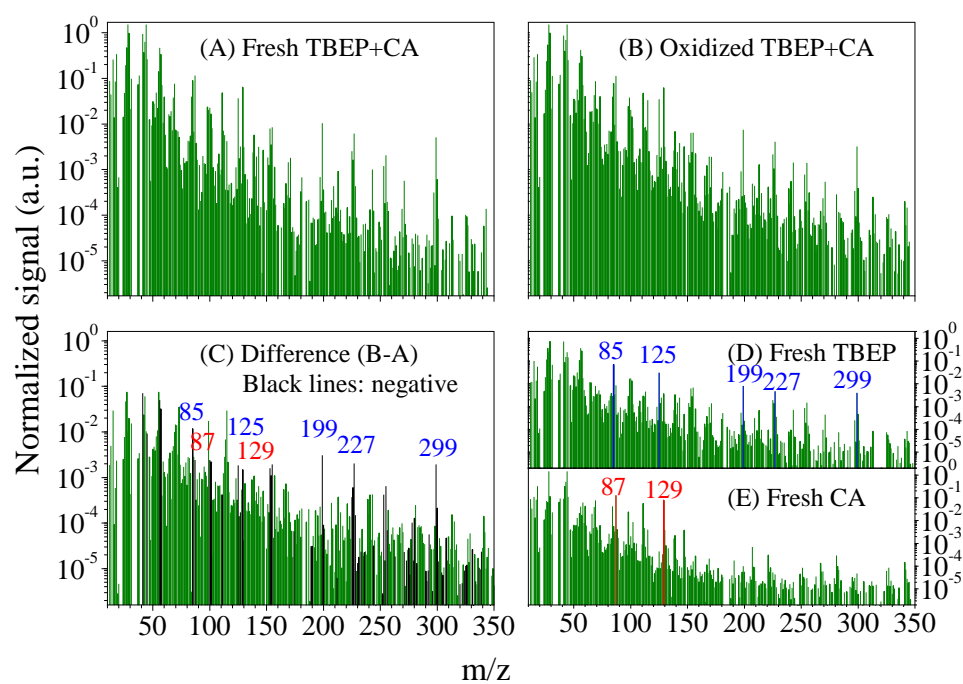**Figure S2.** NIST mass spectra of (A) citric acid (B) TBEP.

Figure S3. (A) Mass spectra of unreacted, (B) oxidized and (C) difference mass spectra for externally mixed TBEP and CA; (D) and (E) mass spectra of unreacted TBEP and CA.
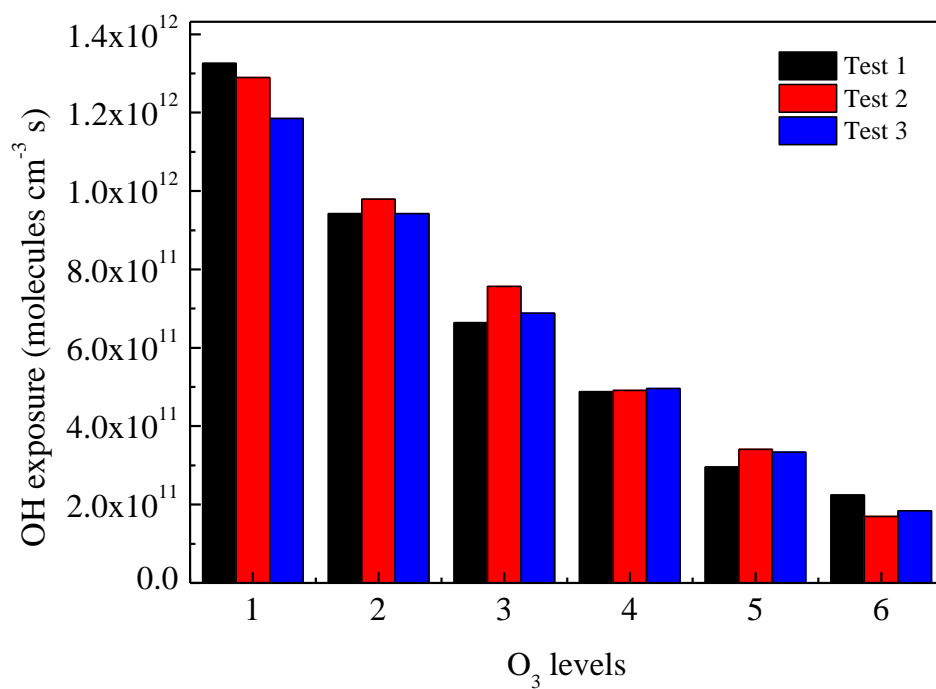
Figure S4. Repeatability of OH exposures under the identical experimental conditions. OH concentrations were calibrated with methanol as a reference compound. The gas flow rate is 1.03 L min^{-1} and the RH is 40 ± 2 %.
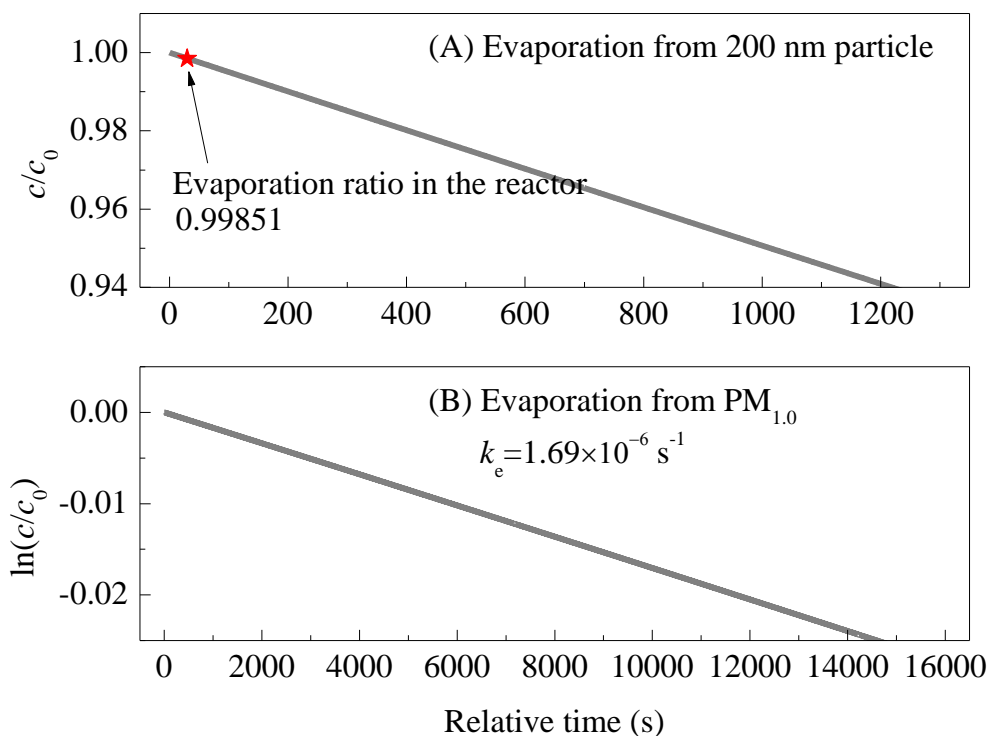
Figure S5. Calculated evaporation curves of TBEP from (A) 200 nm particles for laboratory experiment, and (B) ambient $PM_{1.0}$.

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