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Supplement of

Reactive uptake of N_2O_5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations

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Further Details on the *Anttila et al. [2006]* Parameterization:

As mentioned in the main body of the manuscript, we used the core-shell model provided by *Anttila et al. [2006]* to account for organic coatings using the following equations:

$$\frac{1}{\gamma} = \frac{\omega R_p}{4D_{gas}} + \frac{1}{\alpha} + \frac{\omega R_p}{4RTH_{org}D_{org}(q_{org}F-1)} \quad (1)$$

γ is the uptake coefficient of N_2O_5 measured for different organics, R_p is the total particle radius (m), D_{gas} is the gas phase diffusion coefficient for N_2O_5 taken to be $1 \times 10^{-5} \text{ m}^2/\text{s}$ (*Anttila et al., 2006*), α is the dimensionless mass accommodation coefficient (*Anttila et al., 2006; Riemer et al., 2009*), R is the universal gas constant ($\text{m}^3 \text{ atm}/\text{K mol}$), T is temperature in K, H_{org} is the Henry's law coefficient for N_2O_5 in the organic layer ($\text{mol}/\text{m}^3 \text{ atm}$), D_{org} is the diffusion coefficient of N_2O_5 in the organic layer (m^2/s), q_{org} is the dimensionless diffuso-reactive parameter in the organic layer, which describes the competition between diffusion and reaction in the organic layer, defined as:

$$q_{org} = R_p \sqrt{\frac{k_{org}}{D_{org}}} \quad (2)$$

where k_{org} is the reaction rate constant of N_2O_5 in the organic layer (s^{-1}). The parameter F in equation 1 is described by the following equations:

$$F = \frac{\coth(q_{org}) + h(q_{aq}, q_{org}^*)}{1 + \coth(q_{aq})h(q_{aq}, q_{org}^*)} \quad (3)$$

where q_{aq} is aqueous diffuse-reactive parameter defined as:

$$q_{aq} = R_c \sqrt{\frac{k_{aq}}{D_{aq}}} \quad (4)$$

where R_c is the radius of the particle core (in meters), D_{aq} is the aqueous diffusion coefficient of N_2O_5 taken to be $1 \times 10^{-9} \text{ m}^2/\text{s}$ (Anttila et al., 2006; Griffiths et al., 2009), and k_{aq} is the reaction rate constant of N_2O_5 in the aqueous phase (s^{-1}). We use the model of *Bertram and Thornton* [2009] to constrain k_{aq} using the particulate nitrate, chloride, and water content in the following equation:

$$k_{aq} = k'_{2f} = \beta - \beta e^{(-\delta[H_2O(l)])} \quad (5)$$

$\beta = 1.15 \times 10^6 \text{ s}^{-1}$ and $\delta = 1.3 \times 10^{-1} \text{ M}^{-1}$. The parameter $h(q_{aq}, q_{org}^*)$ is defined by the following equation:

$$h(q_{aq}, q_{org}^*) = -\tanh(q_{org}^*) * \frac{\frac{H_{aq}D_{aq}}{H_{org}D_{org}}(q_{aq} \coth(q_{aq}) - 1) - (q_{org}^* \coth(q_{org}^*) - 1)}{\frac{H_{aq}D_{aq}}{H_{org}D_{org}}(q_{aq} \coth(q_{aq}) - 1) - (q_{org}^* \tanh(q_{org}^*) - 1)} \quad (6)$$

$$q_{org}^* = \frac{R_c}{R_p} q_{org} \quad (7)$$

where H_{aq} is the aqueous Henry's law coefficient for N_2O_5 taken to be $5000 \text{ mol/m}^3 \text{ atm}$ (Anttila et al., 2006; Griffiths et al., 2009; Mentel et al., 1999).

Decays of N_2O_5 in the Presence and Absence of Aerosol

N_2O_5 decays are represented in this paper by moving the injector to the top and bottom of the aerosol flow tube. Figure S1 shows a full decay of N_2O_5 as a function of injector position in the presence and absence of ammonium bisulfate. The linear decays shown in logarithmic space indicates that first order kinetics can be assumed.

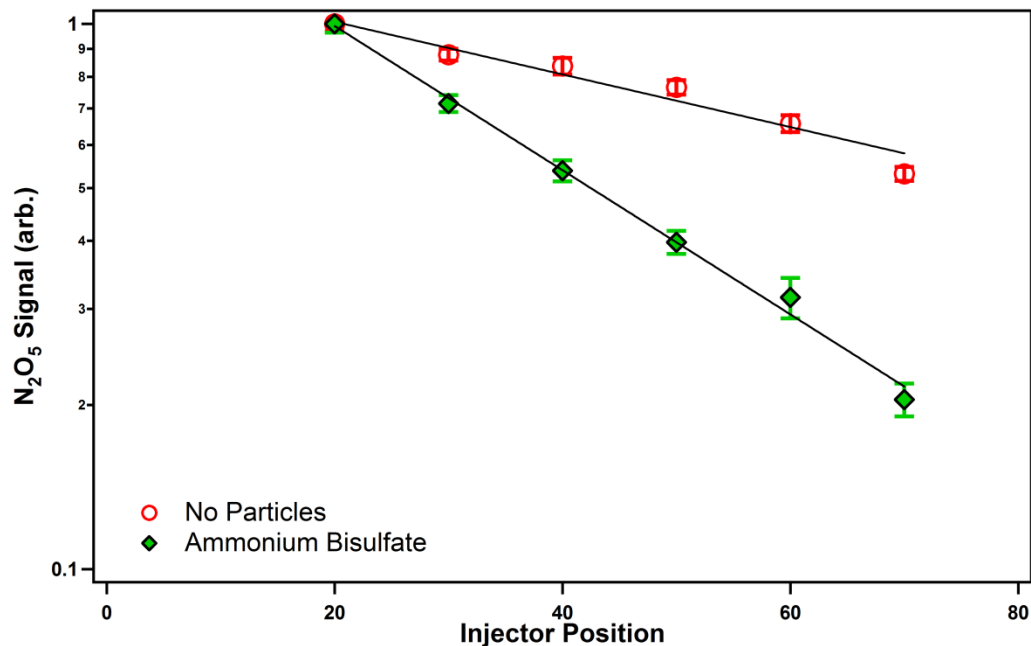


Figure S1: Representative N_2O_5 decays at 50% RH in the absence (red open circles with connected lines) and presence of ammonium bisulfate (green diamonds with connected lines).

Linear Fits for $\gamma(N_2O_5)$ vs Organic Mass Fraction for Ammonium Bisulfate/PEG and Ambient Measurements:

The main manuscript shows similar uptake of $\gamma(N_2O_5)$ as a function of organic mass fraction onto particles composed of Ammonium Bisulfate/PEG and onto ambient particles in Seattle, WA during the summer. As shown in Figure S2, both systems show linear behavior with similar, steep slopes of 1.59 and 1.73 for Ammonium Bisulfate/PEG and ambient aerosol, respectively.

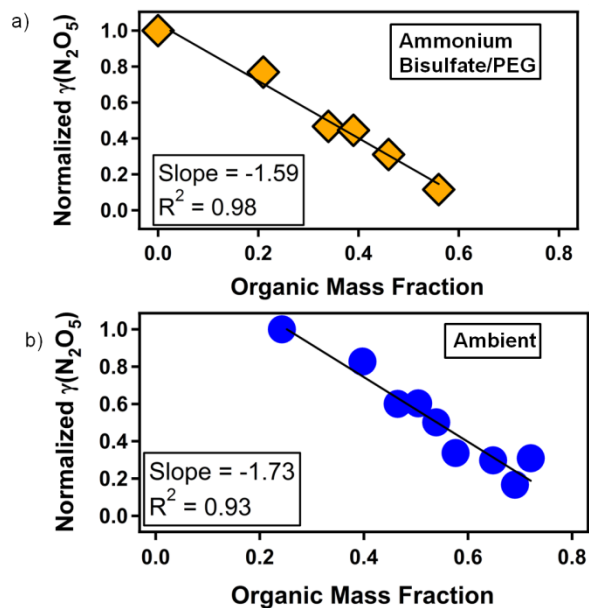


Figure S2: Linear fits of normalized $\gamma(\text{N}_2\text{O}_5)$ for particles generated from Ammonium Bisulfate/PEG (a) and for uptake onto ambient aerosol (b).

Determination of the O:C Ratio of Organic Aerosol Obtained from Ambient Data:

Measurements of $\gamma(\text{N}_2\text{O}_5)$ were made on ambient particles in Seattle, WA during August 2008 (Bertram et al., 2009). Concurrent measurements of submicron mass concentrations of non-refractory aerosol components were also made using a quadrupole aerosol mass spectrometer (Q-AMS). In addition to probing how the mass fraction of organic aerosol affected $\gamma\text{N}_2\text{O}_5$, the role of the O:C ratio was also probed. The majority of the OA is secondary, hence we will expect that m/z 43 is mostly from the $\text{C}_2\text{H}_3\text{O}^+$ fragment. Following the work of Ng *et al.*, [2010], the O:C ratio was probed by plotting f_{43} and f_{44} , which are ratios of m/z 43 and m/z 44 to the total organic mass concentration, respectively; Figure S3 is scaled to the O:C ratio providing a campaign average value (Ng et al., 2010). Using available AMS data, the average O:C ratio of

organic aerosol was 0.45 for the entire campaign when $\gamma(\text{N}_2\text{O}_5)$ measurements were also being made.

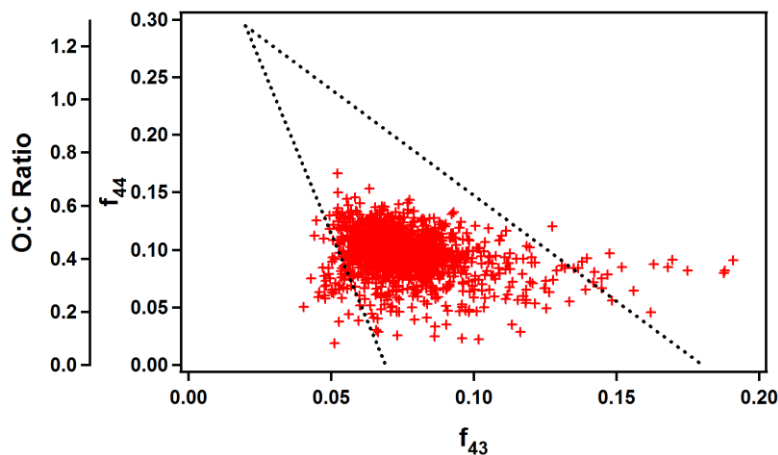


Figure S3: AMS measurements of ambient organic aerosol in Seattle, WA when concurrent measurements of $\gamma(\text{N}_2\text{O}_5)$ were being made on ambient aerosol (Bertram et al., 2009). Comparison of f_{43} and f_{44} are used to determine the campaign average O:C ratio following the procedure of Ng *et al.* [2010].

Comparison of Ammonium Bisulfate/Azelaic Acid Experiments to Ammonium Bisulfate/Low O:C Mixtures:

In addition to experiments with ammonium bisulfate and mixtures of organics with low O:C ratios, experiments were also conducted with ammonium bisulfate/azelaic acid, one of the components used in the low O:C mixture. Figure S4 shows a comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for both experiments, which show striking similarity at 30%, 50%, and 70% RH for both the ammonium bisulfate and single organic component and ammonium bisulfate and the low O:C mixture. Both azelaic acid and the low O:C mixture have similar atomic O:C ratios of 0.44 and 0.475, respectively, and both systems show a rapid drop in $\gamma(\text{N}_2\text{O}_5)$ of ~60-70% with an organic mass fraction of as little as 10-15%.

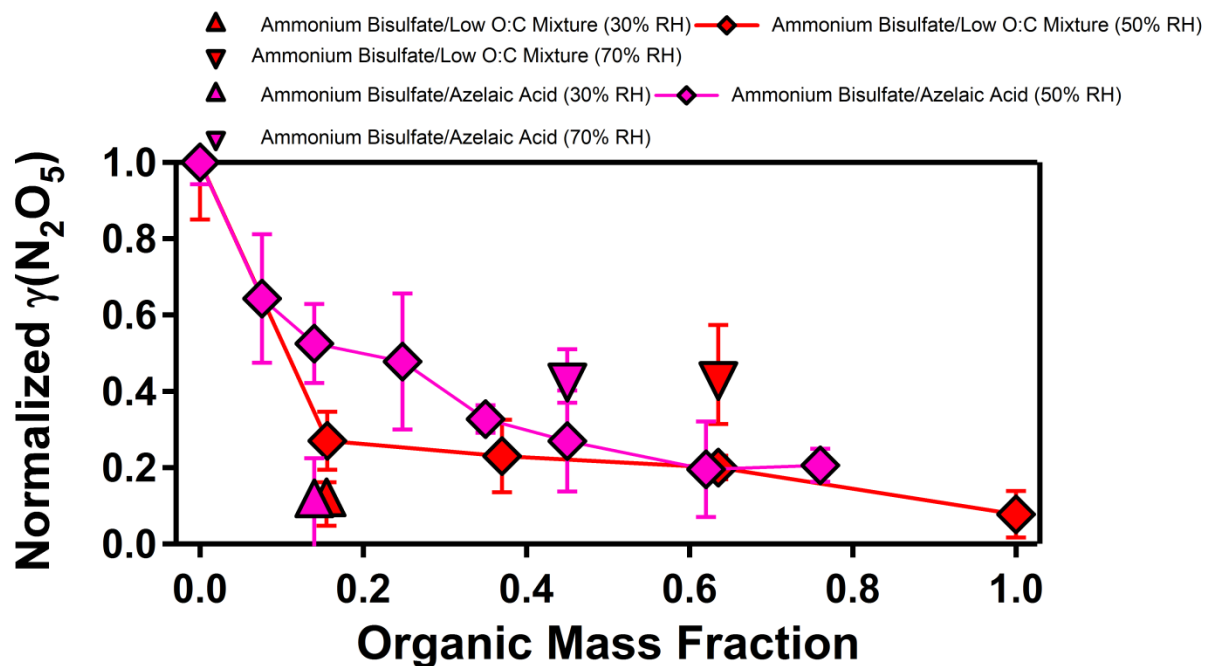


Figure S4: Comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ammonium bisulfate and azelaic acid (pink markers) and ammonium bisulfate and a mixture of organics with low O:C ratios (red markers) at 30%, 50%, and 70% RH.

Linear Fits for $\gamma\text{N}_2\text{O}_5$ vs. Organic Mass Fraction for Ammonium Bisulfate/High O:C Mixture

The main manuscript shows uptake of $\gamma(\text{N}_2\text{O}_5)$ as a function of organic mass fraction onto particles composed of ammonium bisulfate and a high O:C organic mixture. As shown in Figure S5, this system shows linear behavior with a slope of 0.78.

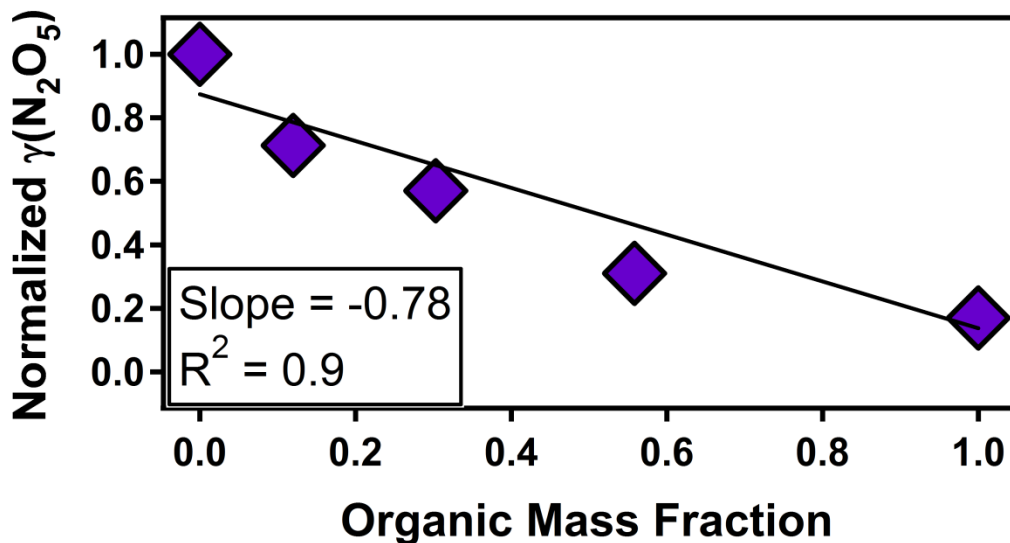


Figure S5: Linear fit of normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ammonium bisulfate and a mixture of organics with high O:C ratios (dark purple markers) at 50% RH.

Experiments with Ammonium Bisulfate/Succinic Acid:

Experiments were also conducted with ammonium bisulfate/succinic acid, one of the components used in the high O:C mixture. Figure S6 shows normalized $\gamma(\text{N}_2\text{O}_5)$ as a function of organic mass fraction; little change is observed in N_2O_5 uptake with increasing organic mass fraction and little deviation from the N_2O_5 uptake value obtained from pure ammonium bisulfate is observed suggesting the absence of phase separations and, possibly, a lack of organic coatings in general.

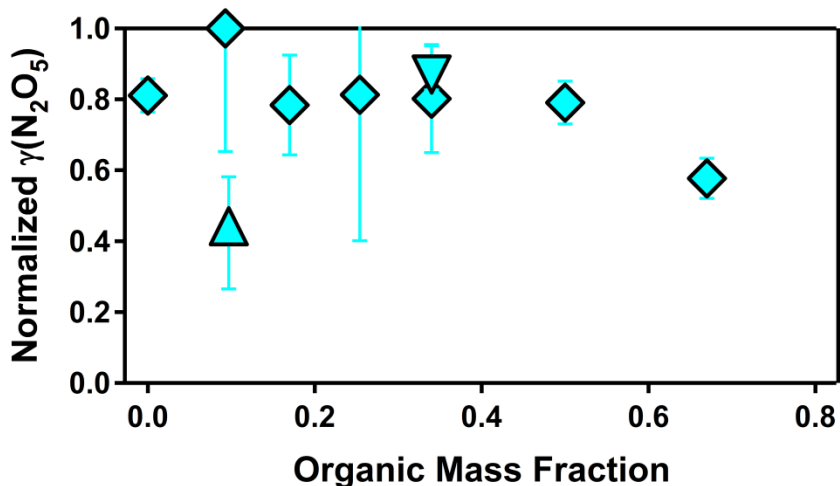


Figure S6: Normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ammonium bisulfate and succinic acid (cyan markers) at 30% (right-side up triangle), 50% (diamonds), and 70% (upside-down triangle) RH.

Comparison of Ammonium Bisulfate/Citric Acid Experiments to Ammonium Bisulfate/High O:C Mixtures:

In addition to experiments with ammonium bisulfate and mixtures of organics with high O:C ratios, experiments were also conducted with ammonium bisulfate/citric acid, one of the components used in the high O:C mixture. Figure S7 shows a comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for both experiments, which show striking similarity at 50% RH for both the ammonium bisulfate and single organic component and ammonium bisulfate and the high O:C mixture. Both citric acid and the high O:C mixture show a similar slightly linear decrease as the organic mass fraction increases and have similar O:C ratios of 1.17 and 1.125, respectively. However, the ammonium bisulfate and citric acid mixtures show a sharper increase at 70% RH than ammonium bisulfate and the high O:C mixtures used. This is likely due to semi-solid phase transitions known to occur for citric acid (Baustian et al., 2013; Koop et al., 2011); the use of organic mixtures minimizes occurrence of this crystallization.

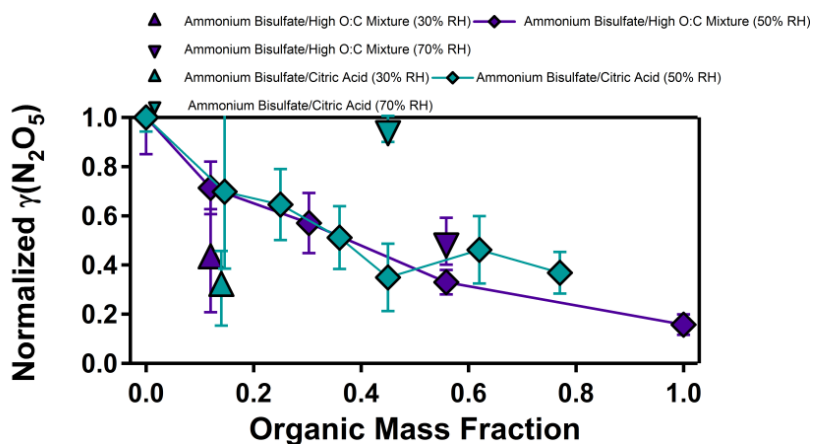


Figure S7: Comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ammonium bisulfate and citric acid (teal markers) and ammonium bisulfate and a mixture of organics with high O:C ratios (dark purple markers) at 30%, 50%, and 70% RH.

Ambient AMS Measurements

In the manuscript, we describe ambient AMS measurements from 25 data sets that are detailed in previous publications (Jimenez et al., 2009), the AMS global datasets website (<https://sites.google.com/site/amsglobaldatabase/>), and in Table S1, which details the location of where the data set was taken, the type of location, the organic aerosol mass fraction and average O:C ratio. Most of the data was taken from urban locations; however, 10 data sets were taken in urban downwind or remote locations. The O:C ratio are campaign averages for all types of organic aerosol including hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA) (Zhang et al., 2005). The average O:C ratio was taken by mass spectral analysis of each different organic aerosol type to determine the O:C ratio for each organic aerosol factor; these O:C ratios are then multiplied by the fraction of each organic aerosol type (e.g., HOA, OOA) representative of the total organic aerosol (Ng et al., 2010).

Table S1: AMS data set, the type of environment sampled in, the campaign average organic aerosol mass fraction, and campaign average O:C ratio of the organic aerosol.

Data Set	Type	Organic Aerosol Mass Fraction	Average O:C
Riverside, CA (SOAR-1)	urban	0.47	0.42
Mexico City (Milagro T0)	urban	0.65	0.35
Houston, TX 2000	urban	0.47	0.49
Beijing, China	urban	0.35	0.36
Boulder, CO	urban	0.68	0.40
Edinburgh, UK	urban	0.63	0.49
Mainz, Germany	urban	0.44	0.42
Manchester, UK	urban	0.34	0.55
Manchester, UK	urban	0.58	0.17
New York City 2001—Summer	urban	0.48	0.51
New York City 2004—Winter	urban	0.42	0.30
Pittsburg, PA	urban	0.30	0.41
Tokyo 2003	urban	0.49	0.38
Tokyo 2004	urban	0.43	0.30
Vancouver, Canada	urban	0.70	0.35
Taunus, Germany	urban downwind	0.58	0.50
Chelmsford, UK (Torch 1)	urban downwind	0.47	0.38
Cheju, Korea	remote	0.40	0.79
Duke Forest, NC	remote	0.46	0.42
Hyytialia, Finland (QUEST)	remote	0.60	0.42
Chebogue Pt., Nova Scotia (ICARTT)	remote	0.55	0.61
Okinawa, Japan	remote	0.22	0.82
Pinnacle State Park, NY	remote	0.46	0.64
Thompson Farm, NC	remote	0.56	0.48
Fukue, Japan	remote	0.37	0.60

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