

Supporting Information:

**Reactive Uptake of N₂O₅ to Internally Mixed Inorganic and Organic Particles:
The Role of Organic Carbon Oxidation State and Inferred Organic Phase
Separations**

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Experimental Set-Up:

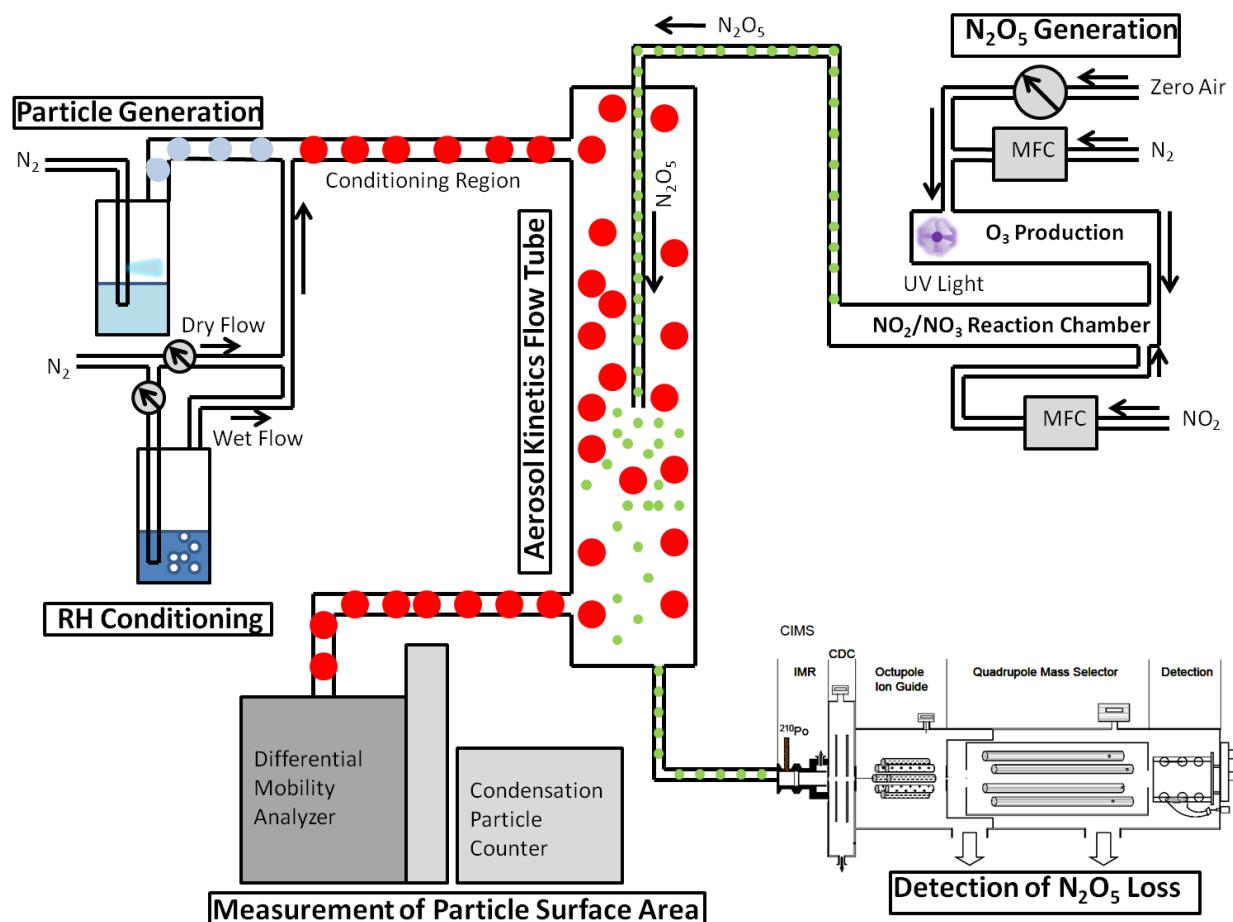


Figure S1: Schematic of the laboratory set up used to measure $\gamma\text{N}_2\text{O}_5$ on laboratory generated aerosols. A movable injector is used to change the amount of exposure time between N_2O_5 (represented by small green dots) and the generated particles (large red dots). The N_2O_5 decay is monitored using a chemical ionization mass spectrometer (CIMS) while total particle surface area (S_a) is monitored using a scanning mobility particle sizer (SMPS).

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:

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

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).

Linear Fits for $\gamma(\text{N}_2\text{O}_5)$ vs Organic Mass Fraction for ABS/ PEG and Ambient Measurements:

The main manuscript shows similar uptake of $\gamma(\text{N}_2\text{O}_5)$ as a function of organic mass fraction onto particles composed of ABS/ 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 ABS/ PEG and ambient aerosol, respectively.

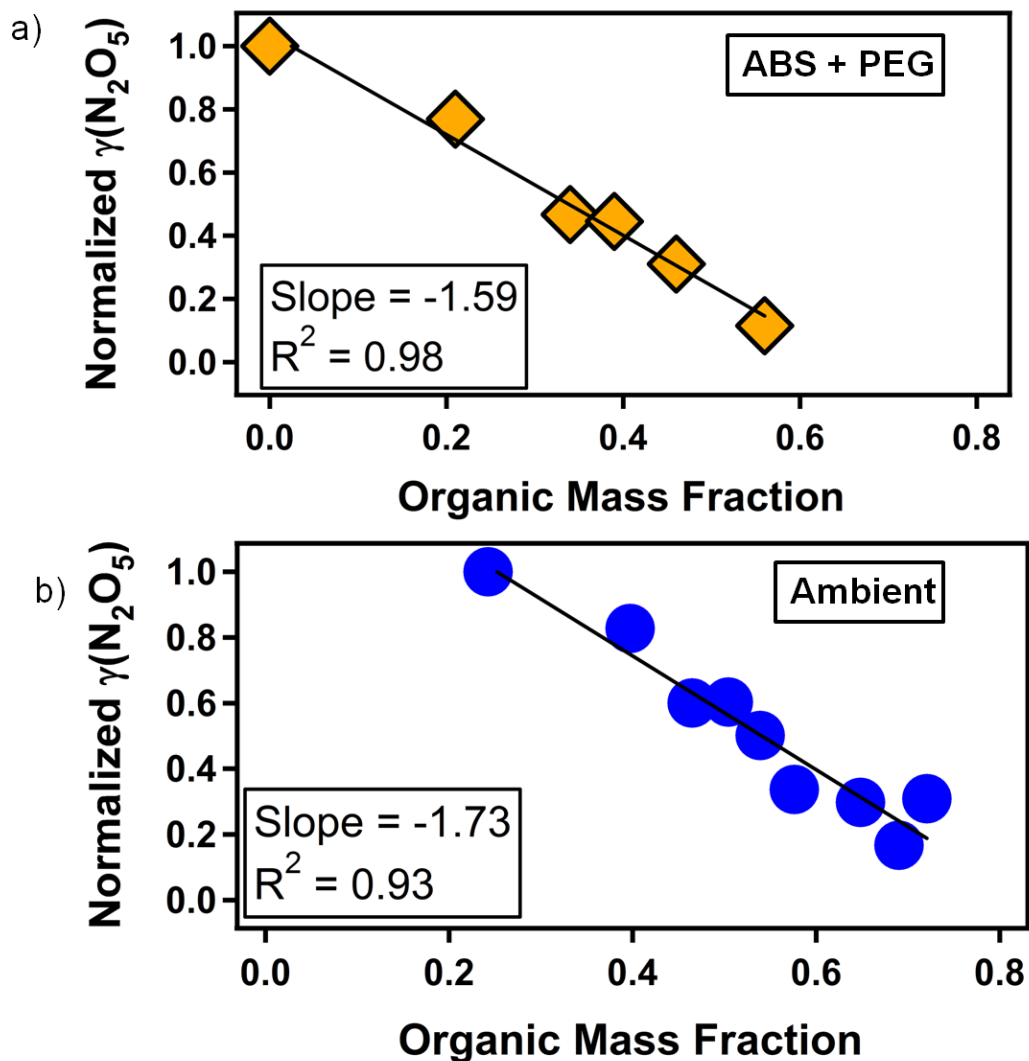


Figure S2: Linear fits of normalized $\gamma(\text{N}_2\text{O}_5)$ for particles generated from ABS/PEG (a) and for uptake onto ambient aerosol (b).

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 $C_2H_3O^+$ 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 $\gamma(N_2O_5)$ measurements were also being made.

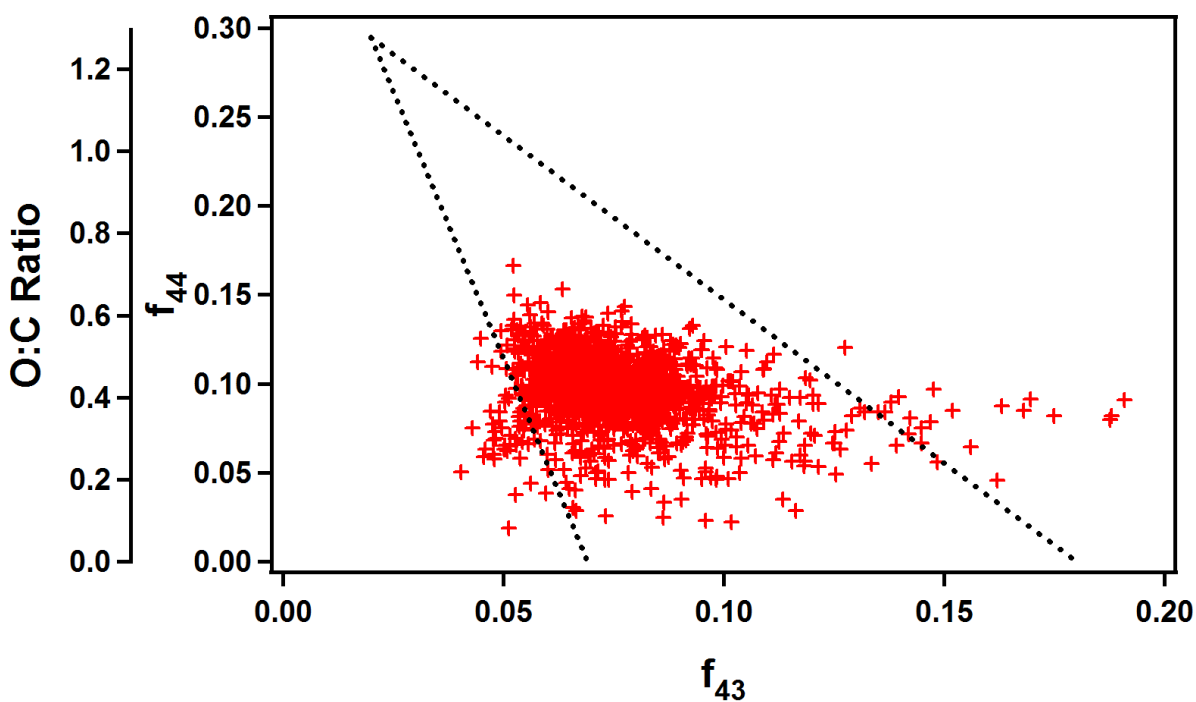


Figure S3: AMS measurements of ambient organic aerosol in Seattle, WA when concurrent measurements of $\gamma(N_2O_5)$ were being made on ambient aerosol (*Bertram et al.*, 2009). Comparison of f_{43} and f_{44} are used to determine the campaign average O:C ratio following the procedure of *Ng et al.* [2010].

Comparison of ABS + Azelaic Acid Experiments to ABS + Low O:C Mixtures:

In addition to experiments with ABS and mixtures of organics with low O:C ratios, experiments were also conducted with ABS + 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 ABS and single organic component and ABS 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%.

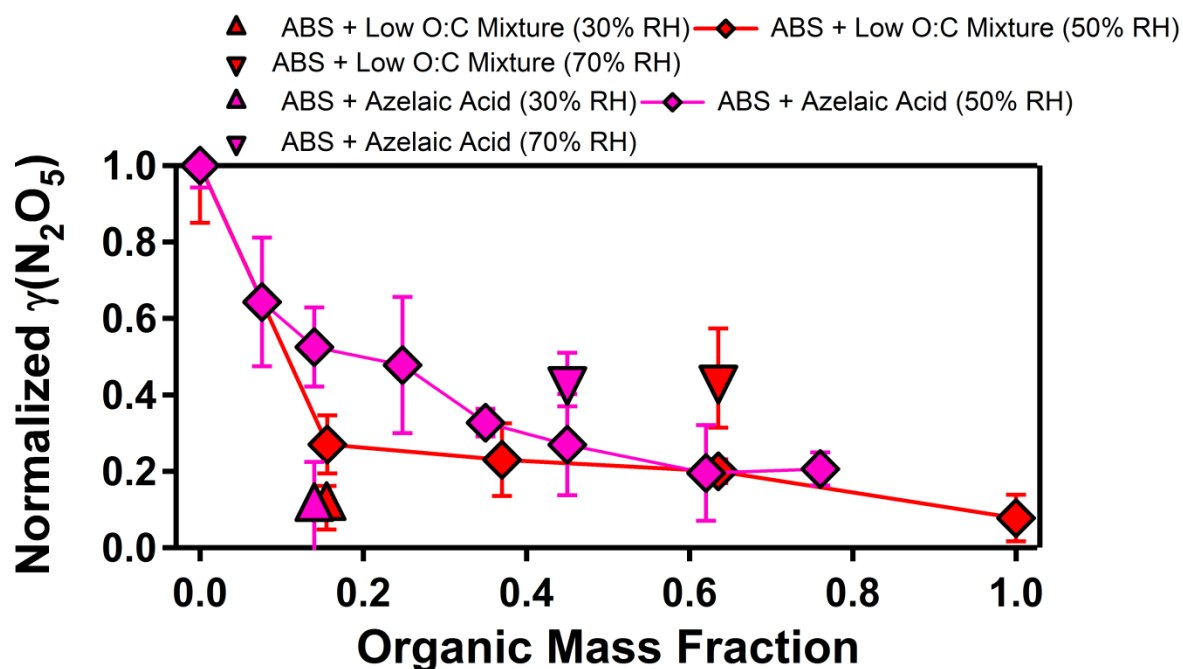


Figure S4: Comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ABS and azelaic acid (pink markers) and ABS and a mixture of organics with low O:C ratios (red markers) at 30%, 50%, and 70% RH.

Linear Fits for $\gamma\text{N}_2\text{O}_5$ vs. Organic Mass Fraction for ABS + 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 ABS and a high O:C organic mixture. As shown in Figure S5, this system shows linear behavior with a slope of 0.78.

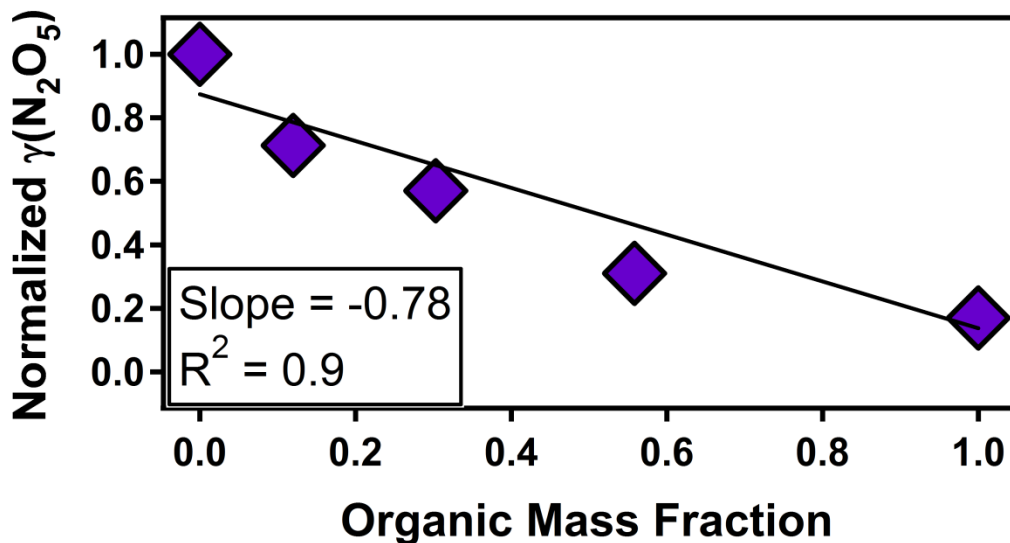


Figure S5: Linear fit of normalized $\gamma(N_2O_5)$ for mixtures of ABS and a mixture of organics with high O:C ratios (dark purple markers) at 50% RH.

Experiments with ABS + Succinic Acid:

Experiments were also conducted with ABS + succinic acid, one of the components used in the high O:C mixture. Figure S6 shows normalized $\gamma(N_2O_5)$ 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 ABS is observed suggesting the absence of phase separations and, possibly, a lack of organic coatings in general.

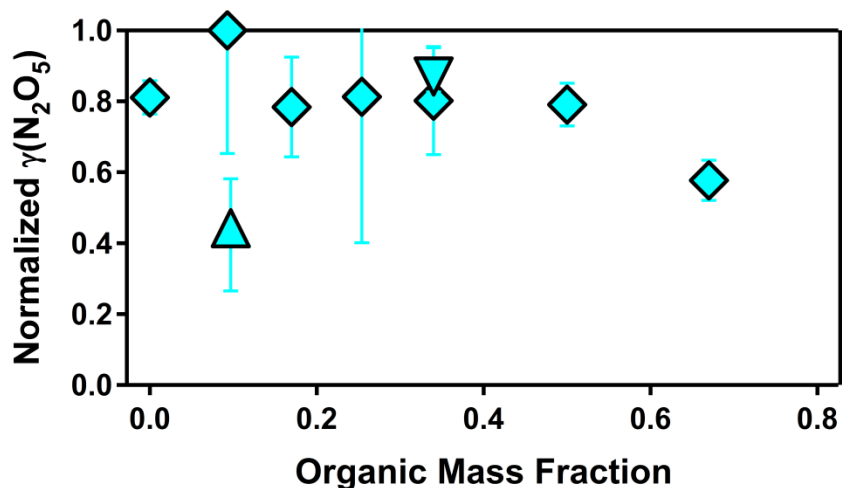


Figure S6: Normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ABS and succinic acid (cyan markers) at 30% (right-side up triangle), 50% (diamonds), and 70% (upside-down triangle) RH.

Comparison of ABS + Citric Acid Experiments to ABS + High O:C Mixtures:

In addition to experiments with ABS and mixtures of organics with high O:C ratios, experiments were also conducted with ABS + 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 ABS and single organic component and ABS 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 ABS and citric acid mixtures show a sharper increase at 70% RH than ABS 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.

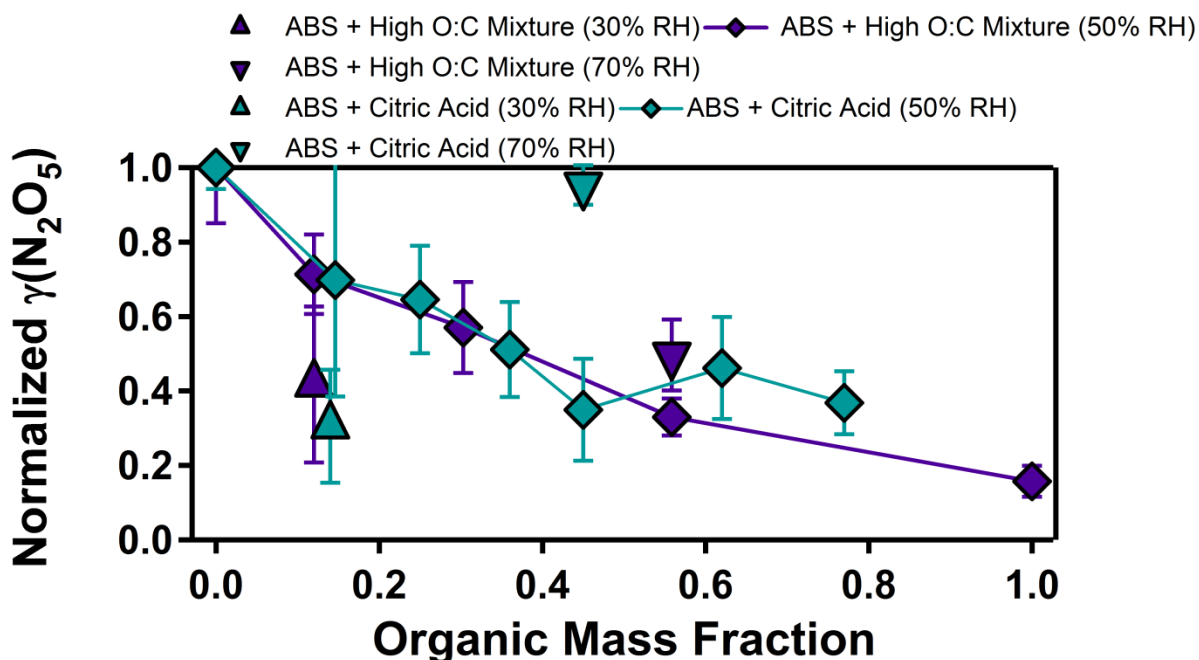


Figure S7: Comparison of normalized $\gamma(\text{N}_2\text{O}_5)$ for mixtures of ABS and citric acid (teal markers) and ABS and a mixture of organics with high O:C ratios (dark purple markers) at 30%, 50%, and 70% RH.

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

References:

- Anttila, T., A. Kiendler-Scharr, R. Tillmann, and T.F. Mentel (2006), On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5 , *J. Phys. Chem. A*, *110*, 10435-10443.
- Baustian, K.J., M.E. Wise, E.J. Jensen, G.P. Schill, M.A. Freedman, and M.A. Tolbert (2013), State transformations and ice nucleation in amorphous (semi-)solid organic aerosol, *Atmos. Chem. Phys.*, *13*, 5615-5628.
- Bertram, T.H., J.A. Thornton, T.P. Riedel, A.M. Middlebrook, R. Bahreini, T.S. Bates, P.K. Quinn, and D.J. Coffman (2009), Direct observations of N_2O_5 reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, *36*, L19803, doi:10.1029/2009GL040248.
- Griffiths, P.T., C.L. Badger, A. Cox, M. Folkers, H.H. Henk, and T.F. Mentel (2009), Reactive uptake of N_2O_5 by aerosols containing dicarboxylic acids. Effect of particle phase, composition, and nitrate content, *J. Phys. Chem. A*, *113*, 5082-5090.
- Jimenez, J.L., M.R. Canagaratna, N.M. Donahue, A.S.H. Prevot, Q. Zhang, J.H. Kroll, P.F. DeCarlo, J.D. Allan, H. Coe, N.L. Ng, A.C. Aiken, K.S. Docherty, I.M. Ulbrich, A.P. Grieshop, A.L. Robinson, J. Duplissy, J.D. Smith, K.R. Wilson, V.A. Lanz, C. Hueglin, Y.L. Sun, J. Tian, A. Laaksonen, T. Raatikainen, J. Rautiainen, P. Vaattovaara, M. Ehn, M. Kulmala, J.M. Tomlinson, D.R. Collins, M.J. Cubison, E.J. Dunlea, J.A. Huffman, T.B. Onasch, M.R. Alfarra, P.I. Williams, K. Bower, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, D. Salcedo, L. Cottrell, R. Griffin, A. Takami, T. Miyoshi, S. Hatakeyama, A. Shimono, J.Y. Sun, Y.M. Zhang, K. Dzepina, J.R. Kimmel, D. Sueper, J.T. Jayne, S.C. Herndon, A.M. Trimborn, L.R. Williams, E.C. Wood, A.M. Middlebrook, C.E. Kolb, U. Baltensperger, and D.R. Worsnop (2009), Evolution of organic aerosols in the atmosphere, *Science*, *326* (5959), 1525-1529.
- Koop, T., J. Bookhold, M. Shiraiwa, and U. Poschl (2011), Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, *Phys. Chem. Chem. Phys.*, *13*, 19238-19255.
- Mentel, T.F., M. Sohn, and A. Wahner (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, *1*, 5451-5457.
- Ng, N.L., M.R. Canagaratna, Q. Zhang, J.L. Jimenez, J. Tian, I.M. Ulbrich, J.H. Kroll, K.S. Docherty, P.S. Chhabra, R. Bahreini, S.M. Murphy, J.H. Seinfeld, L. Hildebrandt, N.M. Donohue, P.F. DeCarlo, V.A. Lanz, A.S.H. Prevot, E. Dinar, Y. Rudich, and D.R. Worsnop (2010), Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, *Atmos. Chem. Phys.*, *10*, 4625-4641.
- Riemer, N., H. Vogel, B. Vogel, T. Anttila, A. Kiendler-Scharr, and T.F. Mentel (2009), Relative importance of organic coatings for the heterogeneous hydrolysis of N_2O_5 during summer in Europe, *J. Geophys. Res.*, *114*, D17307, doi:10.1029/2008JD011369.
- Zhang, Q., M.R. Alfarra, D.R. Worsnop, J.D. Allan, H. Coe, M.R. Canagaratna, and J.L. Jimenez (2005), Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *Environ. Sci. Tech.*, *39* (13), 4938-4952.