Climate-Relevant Physical Properties of Molecular Constituents for Isoprene-Derived Secondary Organic Aerosol Material

Mary Alice Upshur,[1] Benjamin F. Strick,[1] V. Faye McNeill,[2*] Regan J. Thomson,[1*] and Franz M. Geiger[1*]

[1]Department of Chemistry, Northwestern University, Evanston, IL 60202, USA,

[2]Department of Chemical Engineering, Columbia University, New York, NY 10027

Abstract. Secondary organic aerosol (SOA) particles, formed from gas-phase biogenic volatile organic compounds (BVOCs), contribute large uncertainties to the radiative forcing that is associated with aerosols in the climate system. Reactive uptake of surface-active organic oxidation products of BVOCs at the gas-aerosol interface can potentially decrease the overall aerosol surface tension and therefore influence their propensity to act as cloud condensation nuclei (CCN). Here, we synthesize and measure some climate-relevant physical properties of SOA particle constituents consisting of the isoprene oxidation products α-, δ-, and *cis*- and *trans*-β-IEPOX (isoprene epoxide), as well as *syn*- and *anti*-2-methyltetraol. Following viscosity measurements, we use octanol-water partition coefficients to quantify the relative hydrophobicity of the oxidation products while dynamic surface tension measurements indicate that aqueous solutions of α- and *trans*-β-IEPOX exhibit significant surface tension depression. We hypothesize that the surface activity of these compounds may enhance aerosol CCN activity, and that *trans*-β-IEPOX may be highly relevant for surface chemistry of aerosol particles relative to other IEPOX isomers.

*Corresponding authors: vfm2103@columbia.edu; r-thomson@northwestern.edu, geigerf@chem.northwestern.edu

I. Introduction. Secondary organic aerosol (SOA) particles make up a substantial fraction of tropospheric aerosol and are known to lead to negative radiative forcing,[1-3] yet, their formation ranks among the least understood processes in the atmosphere.[1,4-7] Many studies[2,4,8-13] support the idea that the gas-phase oxidation products of biogenic volatile compounds can either a) partition to existing particles due to reduced volatility compared to the parent compounds or b) dissolve in aerosol or cloud water and participate in aqueous phase reactions to form low-volatility material. Surface tension is expected to be of particular importance for SOA formation and growth as it involves processes occurring at the interface between the SOA particle phase and the gas phase.[14,15] Moreover, atmospheric particles, once formed, can contain thousands of organic compounds or surfactants that can decrease the surface tension and thereby change aerosol particle properties such as cloud droplet formation, reactivity, and ice nucleation.[16-21] Specifically, it has been reported that organic surfactants can influence the propensity of atmospheric aerosol particles to act as cloud condensation nuclei (CCN) by depressing the surface tension at the moment of activation.[22-30] Lower surface tension values result in decreases in the water vapor supersaturation required for cloud droplet activation, depending on ionic content, pH, temperature, and meteorological conditions. McNeill and coworkers recently showed that volatile surfactant species such as methylglyoxal and acetaldehyde can suppress surface tension at the gas-aerosol interface beyond predictions based on bulk surface tension measurements, leading to significantly enhanced CCN activity.[28] Chemical reactions at the surface and in the bulk of the particle between aerosol components may also influence overall surface tension and thus impact the dependence

of CCN activity on the presence of surfactants. Yet, surface tension effects of many compounds relevant for SOA particle formation remain largely uncharacterized.[17,31]

Given their importance for global SOA particle formation,[2,32,33] we report here surface tension values, measured using pendant drop tensiometry, of suspended drops of deionized water and 1.0 M ammonium sulfate solutions containing 0.1 to 30 mM concentrations of synthetically prepared isoprene-derived SOA particle constituents. Specifically, we studied the isoprene oxidation products α-, δ- and *cis*- and *trans*-β-isoprene epoxide (IEPOX) (1–4, Figure 1), and *syn*- and *anti*-2-methyltetraol (5, 6). We are motivated by a recent study by Wennberg and coworkers reporting that *cis*-β-IEPOX (2) and *trans*-β-IEPOX (1) are produced in much higher yield than α-IEPOX (4) during isoprene oxidation by hydroxyl radicals with a ratio of α-IEPOX (4) to *cis*-β-IEPOX (2) to *trans*-β-IEPOX (1) of 1:20.5:27.9.[34] The δ-IEPOX (3) isomer was not detected in this study. We report octanol-water partitioning coefficients (K_{ow}) and viscosities of the compounds under investigation. These studies reveal that α-IEPOX (4) significantly decreases surface tension in water (19% at 30 mM) and in 1.0 M $(NH_4)_2SO_4$ (30% at 30 mM). The *trans*-β-IEPOX (1) isomer also decreases surface tension substantially with an overall decrease of 15% in water and in 1.0 M $(NH_4)_2SO_4$ at a concentration of 30 mM. Surface tension results indicate that these compounds may enhance aerosol CCN activity although further studies will be necessary to verify this experimentally.

II. Experimental.

II.A. Synthesis of Isoprene-derived SOA Particle Precursors. Synthesis of all compounds studied here are described in previous work.[35] The alkene diol (7) was prepared in order to examine the impact of the epoxide functional group on K_{ow} values.

Purity of synthesized compounds was determined based on NMR spectra. Surface tension measurements performed in this work are most likely insensitive to impurities below the detection limit of NMR spectroscopy due to the higher concentrations of IEPOX and tetraols used in this study (above micromolar amounts).

II.B. Partition Experiments. The octanol water partition coefficient, K_{ow}, was determined gas-chromatographically after thorough mixing of the two phases to reach the equilibrium using the shake flask method (mass-balance approach). For the IEPOX (1–4) and alkene diol (7) compounds, stock solutions (~45 mM) were prepared in high purity analytical grade 1-octanol (Sigma Aldrich) presaturated with water. Equal volumes of stock solutions and deionized water were mixed in three separate 15 mL propylene conical tubes. Due to the limited solubility of the 2-methyltetraol compounds in octanol, stock solutions (~45 mM) of the tetraol compounds were prepared in deionized water. Equal volumes of stock solution and 1-octanol presaturated with water were mixed in three separate 15 mL polypropylene conical tubes. In all cases, phases of the solvent systems were mutually saturated by shaking for ~24 hours on a mechanical shaker at room temperature. The three mixtures for each compound were subsequently centrifuged for 5 minutes at 3000 rpm to ensure complete phase separation. Three aliquots of the octanol phase were taken to determine the concentration of the IEPOX compounds (1–4), the tetraols (5, 6) and the alkene diol (7) compound.

The concentration of the compounds from the octanol phase for the epoxides and tetraols were determined using an Agilent 5973 gas chromatograph-mass spectrometer with a FFAP column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm) and a quadrupole analyzer and EI ionization. The injector and detector temperatures were

260°C and 250°C respectively. For the alkene diol and IEPOX compounds, the oven had an initial temperature of 40°C and a final temperature of 200°C with a ramp rate of 15°C/min. For the tetraol compounds, the oven had an initial temperature of 150°C and a final temperature of 220°C with a ramp rate of 30°C/min. The gas flow rate was 1.0 mL/min.

For IEPOX and alkene diol compounds, the quantity of the compound present at equilibrium in the aqueous phase was calculated from difference between the quantity of the compound originally introduced and the quantity in the octanol phase determined using the mass balance technique.

II.C. Viscosity Studies. All viscosities were measured using solutions of 0.325 g/mL of the compound of interest and 0.1625 g/mL $(NH_4)_2SO_4$. Viscosity measurements are relative to a control solution (0.1625 g/mL $(NH_4)_2SO_4$ in deionized H_2O) and were determined using a technique similar to a Cannon-Fenske viscometer, by measuring the time taken for the solutions to pass through a 1 mL plastic syringe as reported by McNeill and Drozd.[36]

II.D. Dynamic Surface Tension Measurements. Pendant drop tensiometry (PDT) was used to measure surface tension over time for all solutions in this study on a FTA125 goniometer. Solutions were prepared in dH_2O or with 1.0 M $(NH_4)_2SO_4$. The pH of solutions containing $(NH_4)_2SO_4$ ranged from approximately 5.0 to 6.0 while pH ranged from approximately 6.0 to 7.0 in dH_2O. All solutions fell within the bounds of atmospherically relevant pH for aerosols in the troposphere (pH 0-8).[37,38] Solutions containing 100 mM IEPOX compounds in 1 M $(NH_4)_2SO_4$ were allowed to stir at room temperature for one week and monitored by NMR. No conversion into the organosulfate

or tetraols was observed during this time. All solutions for surface tension experiments were measured within a week of their formation and were stored in glass vials at ~4 °C in between measurements in order to further reduce the probability of conversion of IEPOX compounds into the organosulfate or tetraol products. Concentrations of compounds in solutions ranged from 0-30 mM although in some cases higher concentrations (50 mM, 100 mM) were also analyzed. All surface tension experiments were performed at ambient temperature and pressure. Relative humidity ranged from 15% to 45%, and the laboratory temperature ranged from 20°C to 23°C.

Droplets of sample solutions were formed at the tip of a flat stainless steel needle 1 mL syringe mounted on the instrument and inserted ~1 cm into a quartz cuvette containing 0.5 mL of dH_2O. All droplets were approximately 7 μL in volume and varied between 2.1 and 2.4 mm in diameter. After formation, the droplet was allowed to stabilize and images were captured ~5 seconds after droplet formation. Images were taken every 0.3 seconds for 10 minutes, resulting in 1500 images for each experiment and measurements were repeated 5-7 times for each solution. Recent dynamic surface tension studies using the extracted total surfactant component of the PM10 size fraction of aerosol particles collected in an urban setting reported similar equilibration times.[39] Surface tension for each image was determined by fitting the shape of the drop to the Young-Laplace equation, which relates interfacial tension to drop shape as described by Adamson and Gast:[40]

$$\Delta\rho g h = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \quad (1)$$

where $\Delta\rho$ is the difference in densities of the drop and the surrounding media, g is acceleration due to gravity, h is the height generally measured from the apex of the drop, γ is the surface tension and R_1 and R_2 are the radii of curvature. To calculate the surface tension of the drop, images were captured using a RS170 CCD camera equipped with a microscope lens. FTA32 v2.0 software fit each drop profile and determined distances analytically. A regression then obtains the best overall fit to the Laplace-Young equation with the fitting parameter being interfacial tension with units of mN/m.

III. Results and Discussion

III.A. Partitioning and Viscosity Studies. The octanol water partition coefficient, K_{ow}, is defined as the ratio between the concentrations of a compound of interest in octanol to the one in water once equilibrium is established.[41] Experimental values of K_{ow} serve as a measure of hydrophobicity while also allowing for the prediction of other physical values relevant to cloud formation that can be more difficult to experimentally measure.[42-44] Since particles can undergo liquid-liquid phase separation and often contain an aqueous and an organic-rich phase,[45] K_{ow} values indicate the phase these compounds will preferentially partition to. Our gas-chromatographically determined K_{ow} values are listed in Figure 1.

In general, K_{ow} values followed the expected trends in hydrophobicity for each of the compounds. The *trans*- and *cis*-β-IEPOX compounds 1 and 2 were found to have the most negative K_{ow} values, which is consistent with the presence of two primary hydroxyl groups. These compounds also displayed the longest GC retention times (~16.5 min) with nearly identical fragmentation patterns (Figure S1). δ-IEPOX (3), with its secondary and primary hydroxyl groups, had a slightly higher partition coefficient. α-IEPOX (4) proved

159 to be the most hydrophobic epoxide with the least negative K_{ow} value of all the epoxides.
160 These results are consistent with α-IEPOX (4) having the least accessible hydroxyl
161 groups of the epoxides due to the placement of the methyl group and possibly indicate
162 that α-IEPOX (4) would be the isomer most likely to partition into the organic-rich phase
163 of particles. Replacement of the epoxide group in α-IEPOX (4) with a simple alkene (7)
164 shifted the log(K_{ow}) upward by about 0.4 units. This demonstrates that removal of the
165 polar epoxide group significantly increases hydrophobicity.
166 The exact K_{ow} values of the two tetraol diastereomers (5 and 6) could not be determined,
167 possibly due to their very limited solubility in octanol. GC traces of the octanol fraction
168 in tetraol partitioning experiments showed that concentrations of the tetraols in the
169 octanol fractions were below the detection limit. This indicates that the log(K_{ow}) values
170 for tetraol compounds 5 and 6 would be much more negative than the values found for
171 the IEPOX compounds.
172 Relative viscosities are listed in Figure 1. The substances tested are all viscous liquids
173 from room temperature down to –40 ºC. The epoxides (1–3) have a viscosity similar to
174 glycerol (1.98 ± 0.03), whereas the 2-methyltetraols (5, 6) are slightly more viscous and
175 almost gelatinous.
176 **III.B. Dynamic Surface Tension Measurements.** Based on the relevance of surface
177 tension measurements in the prediction of new particle formation and aerosol CCN
178 properties, the effect of concentration on surface tension over time was measured for the
179 four epoxide isomers (1–4) and the two tetraol diastereomers (5, 6) in dH_2O and in 1.0 M
180 $(NH_4)_2SO_4$. As shown in Fig. 2, results in dH_2O showed that the α-IEPOX (4) is by far
181 the most surface active of the epoxide compounds. At the highest concentration measured

(30 mM), interfacial tension for α-IEPOX (4) was lowered by 5% at t=0 seconds and decreased an additional 14% over the course of 10 minutes relative to dH_2O. While some of this decrease may be due to evaporation, the majority of the effect is most likely due to the migration of α-IEPOX (4) to the surface of the droplet. Based on partitioning coefficients, α-IEPOX (4) is the most hydrophobic of the epoxides and therefore would be more likely to partition from the bulk of the aqueous droplet to the surface.

As shown in Fig. 3, the surface tension lowering effect of α-IEPOX (4) was greatly enhanced by the presence of 1.0 M $(NH_4)_2SO_4$. The presence of 1.0 M $(NH_4)_2SO_4$ in water raises the surface tension of the droplets by approximately 3%. Addition of 30 mM α-IEPOX (4) to the 1.0 M $(NH_4)_2SO_4$ solution prompted a 20% drop in surface tension at t=0 seconds and decreased an additional 10% over the course of 10 minutes (resulting in an overall 30% decrease compared to interfacial tension of dH_2O). The presence of inorganic salt most likely decreased the solubility of α-IEPOX (4) in water, increasing the concentration of α-IEPOX (4) at the surface of the droplet due to "salting out". These types of nonreactive salt-organic interactions may have a significant influence of surface tension of atmospheric aerosols.[46-50] *Trans*-β-IEPOX (1) also demonstrated significant surface activity. However, addition of 1.0 M $(NH_4)_2SO_4$ did not appear to greatly enhance these surface tension lowering effects. Both with and without inorganic salt, a solution of 30 mM *trans*-β-IEPOX (1) resulted in an overall decrease of 15% in surface tension relative to dH_2O after 10 minutes. δ-IEPOX (3) and *cis*-β-IEPOX (2) both showed minimal surface tension-lowering effects. A more concentrated solution of 100 mM δ-IEPOX (3) was required in order to achieve the 15% surface tension depression seen for the 30 mM *trans*-β-IEPOX (1) solution. Addition of 1.0 M $(NH_4)_2SO_4$ also did not appear

205 to greatly enhance the surface tension lowering effects of either δ-IEPOX (3) or *cis*-β-
206 IEPOX (2).

207 Regarding the tetraols, Fig. 4 shows a sharp drop in surface activity between 20 mM and
208 10 mM *anti*-2-methyltetraol (6) solutions in dH_2O. Specifically, *anti*-2-methyltetraol (6)
209 showed surface activity comparable to *trans*-β-IEPOX (1) at 30 mM in dH_2O. The *syn*-2-
210 methyltetraol (5) showed less surface activity compared to the *anti*-2-methyltetraol (6)
211 but did exhibit a similar increase in surface activity between the 20 mM and 10 mM
212 solutions in dH_2O. This phenomenon was also observed for the *anti*-2-methyltetraol (6) in
213 1.0 M $(NH_4)_2SO_4$ solutions but was less pronounced for the *syn*-2-methyltetraol (5) under
214 the same conditions. This result could be an indication of the increased solubility of the
215 2-methyltetraol diastereomers in water and therefore a smaller concentration of the 2-
216 methyltetraols at the surface of the droplet. We conclude that the 2-methyltetraol
217 diastereomers may be completely soluble with little effect on droplet surface tension until
218 a critical concentration above 10 mM is reached.

219 Droplets of pure water and 1.0 M $(NH_4)_2SO_4$ were also exposed to the vapor pressure
220 over neat IEPOX compounds, however, no change in the surface tension of the droplets
221 was observed on a timescale of twenty minutes. We caution here that the partial pressure
222 of IEPOX used in these experiments was much higher than its typical pressure in the
223 atmosphere, and that gas and particle phase diffusion limitations for this experiment
224 would also differ for submicron-sized aerosol particles: a recent chamber study of
225 methylglyoxal demonstrated enhanced CCN activity for ammonium sulfate aerosols
226 exposed to methylglyoxal and/or acetaldehyde over 3-5 hours, but not when exposure
227 occurred in an aerosol flow tube on a timescale of seconds or minutes.[28]

Taken together, our surface tension and partitioning studies reveal that α-IEPOX (4) is both the most hydrophobic and most surface active of all the compounds studied. However, there does not appear to be a consistent correlation between hydrophobicity/viscosity and surface activity of the compounds studied here. For example, *cis*-β-IEPOX (2) and *trans*-β-IEPOX (1) were found to possess nearly identical K_{ow} values and therefore similar levels of hydrophobicity but *trans*-β-IEPOX (1) demonstrated greater surface activity relative to *cis*-β-IEPOX (2). The difference in surface activity of *trans*-β-IEPOX (1) and *cis*-β-IEPOX (2) may be a reflection of the different relative orientations of the two hydroxyl and the single epoxide groups in *cis*- and *trans*-β-IEPOX (1, 2) as well as the difference in their propensity to form hydrogen bonds with water molecules inside the water droplet. The greater surface tension depression of *trans*-β-IEPOX (1) may indicate that this compound forms fewer hydrogen bonds than *cis*-β-IEPOX (2), which could be verified through computational chemistry, such as molecular dynamics simulations."

IV. Implications for Atmospheric Chemistry. Experimental and field studies have shown that surface tension depression by organic compounds is a critical component of predicting aerosol particle behavior.[15,19-21,26,51-61] These studies have demonstrated that the amount of solute present in an aerosol particle (known as the dry diameter) as well as the surface tension of the droplet can alter its propensity to act as a cloud condensation nucleus. Köhler theory describes cloud droplet activation and growth from soluble particles.[62,63] The Köhler curve is given by:

$$s = \frac{A}{D_p} - \frac{B}{D_p^3} \qquad (2)$$

with

$$A = \frac{4M_w\sigma}{RT\rho_w} \quad \text{and} \quad B = \frac{6n_sM_w}{\pi\rho_w} \tag{3}$$

where s is the supersaturation, D_p is the diameter of the aqueous droplet, M_w is the molecular of water and ϱ_w its density, R is the gas constant, T is temperature, σ is surface tension, and n_s is the number of moles of solute. A decrease in surface tension due to the presence of surfactants would therefore decrease parameter A and result in increased CCN activation. If the bulk solute content of the particle remains constant, the effect of organic surfactants on equilibrium CCN activity can be assumed to be purely surface tension based. This assumption is valid based on the fact that gas-phase isoprene oxidation products will be continuously taken up at the gas-aerosol interface as they are consumed in heterogeneous reactions within the bulk and at the surface of the aerosol.[49] Using this assumption, the critical supersaturation for particles of a given size can be described as follows:

$$s_c^* = \left(\frac{\sigma}{\sigma_w}\right)^{3/2} s_c \tag{4}$$

Here, s_c^* is the critical supersaturation, σ_w and σ are the surface tension of water and the particle, respectively, and s_c is the critical supersaturation of particle with the surface tension of water (72.8 mN/m).[64] For all IEPOX and 2-methyltetraol compounds, dynamic surface tension measurements were fit to exponential curves in order to determine the equilibrium surface tension at t=∞ (Table 1). The equilibrium surface tension was used in Eq. 4 to calculate the critical supersaturation ratio (s_c^* / s_c), which are listed in Table 2.

While there is some uncertainty regarding the in-particle concentrations of IEPOX and its reaction products, we can make reasonable estimates of these values based on field and

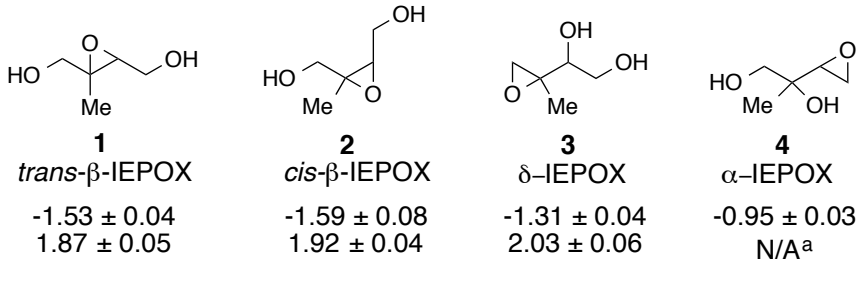
modeling studies. Chan et al.[65] reported up to 24 ng m^{-3} of IEPOX in Yorkville, GA during the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS). During that period, they also measured 33.4 mg m^{-3} of $PM_{2.5}$. Therefore, the observed IEPOX loading corresponds to an in-particle concentration of ~7 mM, assuming 1.2 g cm^{-3} for the particle density. The McNeill group's coupled gas-aqueous aerosol chemistry model, Gas Aerosol Model for Mechanism Analysis (GAMMA),[66] has been updated to include the latest aqueous phase IEPOX chemistry and physical parameters.[67] GAMMA 1.4 simulations predict in-particle concentrations of unreacted IEPOX between 2 and 23 mM in a rural scenario (see Supporting Information). Therefore, we take here 7.5 mM as an example of an atmospherically relevant IEPOX in-particle concentration and find that α-IEPOX (4) exhibited the largest decrease in s_c^* / s_c (9%), with an even larger decrease observed (23%) in 1.0 M $(NH_4)_2SO_4$. *Trans*-β-IEPOX (1) was also observed to lower surface tension and therefore is also expected to lead to decreased supersaturation ratios and enhanced CCN activity. The potential of *trans*-β-IEPOX to enhance CCN activity is particularly significant based on recent studies demonstrating that *trans*-β-IEPOX is the most abundantly produced isomer relative to other IEPOX isomers during isoprene oxidation.[34] At 10 mM, s_c^* / s_c for *trans*-β-IEPOX (1) is predicted to decrease by 8% in dH_2O and in $(NH_4)_2SO_4$. Surface tension depression, and therefore the predicted impact on CCN activity, was less significant for *cis*-β-IEPOX (2), δ-IEPOX (3) and the 2-methyltetraols (5, 6). On a per-mole basis, surface tension depression by *trans*-β-IEPOX is similar to that observed for methylglyoxal in bulk solutions.[49] The Henry's Law constant for IEPOX is several orders of magnitude higher than that of methylglyoxal,[67] leading to a greater potential for suppression of aerosol surface tension by these species

via bulk effects. That being said, as demonstrated by McNeill and coworkers,[28] bulk absorption of surface-active gases is apparently not a requirement for surface tension depression and enhanced CCN activity. In fact, while reactive uptake may be important in other systems, and is certainly important for SOA particles, it is not relevant for our aqueous model experiments, as complementary NMR studies discussed in the Supporting Information show no hydrolysis of the epoxides in ammonium sulfate solution over the course of one week. Our results thus set the stage for future investigations of the effects of *trans*-β-IEPOX on the CCN activity of aqueous aerosols.

V. Conclusions. In conclusion, we report dynamic surface tension measurements, using pendant drop tensiometry, of synthetically prepared isoprene-derived SOA particle constituents. Specifically, we studied the isoprene oxidation products α-, δ- and *cis*- and *trans*-β-isoprene epoxide (IEPOX) (1–4) and *syn*- and *anti*-2-methyltetraol (5, 6) compounds. In addition, we experimentally determined octanol-water partitioning coefficients (K_{ow}) and viscosities of these compounds. Results these experiments revealed that α-IEPOX (4) is the most hydrophobic and surface active of the compounds studied here, however the hydrophobicity of these compounds did not coincide with surface activity for all compounds. Calculation of supersaturation ratios from surface tension values demonstrated that *trans*-β-IEPOX (1) lowers supersaturation ratios significantly while the largest decrease in supersaturation ratios was calculated for α-IEPOX (4). Other compounds measured, *cis*-β-IEPOX (2), δ-IEPOX (3), and the 2-methyltetraols (5, 6), demonstrated less significant surface activity and therefore minimal decreases in supersaturation ratios at higher concentrations.

The enhanced surface activity of *trans*-β-IEPOX (1) and its potential to significantly decrease supersaturation ratios is particularly important based on its correlation with recent sum frequency generation (SFG) spectroscopy studies towards the identification of molecular constituents on the surfaces of isoprene-derived SOA particles.[35] This surface specific study identified *trans*-β-IEPOX (1) as the closest match to the SFG spectra of isoprene-derived SOA surfaces, which coupled with surface tension experiments presented here, strongly indicates that *trans*-β-IEPOX (1) may be present in higher concentrations at the surface of aerosol particles relative to other IEPOX isomers. This conclusion is also supported by the study by Wennberg and coworkers where *trans*-β-IEPOX (1) was found to be produced in higher yields relative to other IEPOX isomers during isoprene oxidation by hydroxyl radicals. Reactive uptake of IEPOX compounds into aerosol particles by acid-catalyzed epoxide ring opening can also lead to formation of organosulfate and organonitrate derivatives[68-70] so future studies will involve synthesizing these derivatives and analyzing their surface activity and other atmospherically relevant properties.

VI. Acknowledgments. MAU gratefully acknowledges support from a NASA Earth and Space Fellowship. This work was supported by the Initiative for Sustainability and Energy at Northwestern (ISEN) and the National Science Foundation (NSF) Environmental Chemical Sciences Program in the Division of Chemistry under Grant No. 1212692.



a. α-IEPOX (4) was insoluble in dH_2O at higher concentrations used for viscosity experiments b. 2-methyltetraols (5,6) had concentrations in octanol below the detection limit c. Viscosity for alkene diol (7) was not measured due to its increased hydrophobicity relative to α–IEPOX (4) observed during partitioning experiments.

Figure 1. Octanol-water partition coefficients and viscosity values for epoxides 1–4 and tetraols 5 and 6.

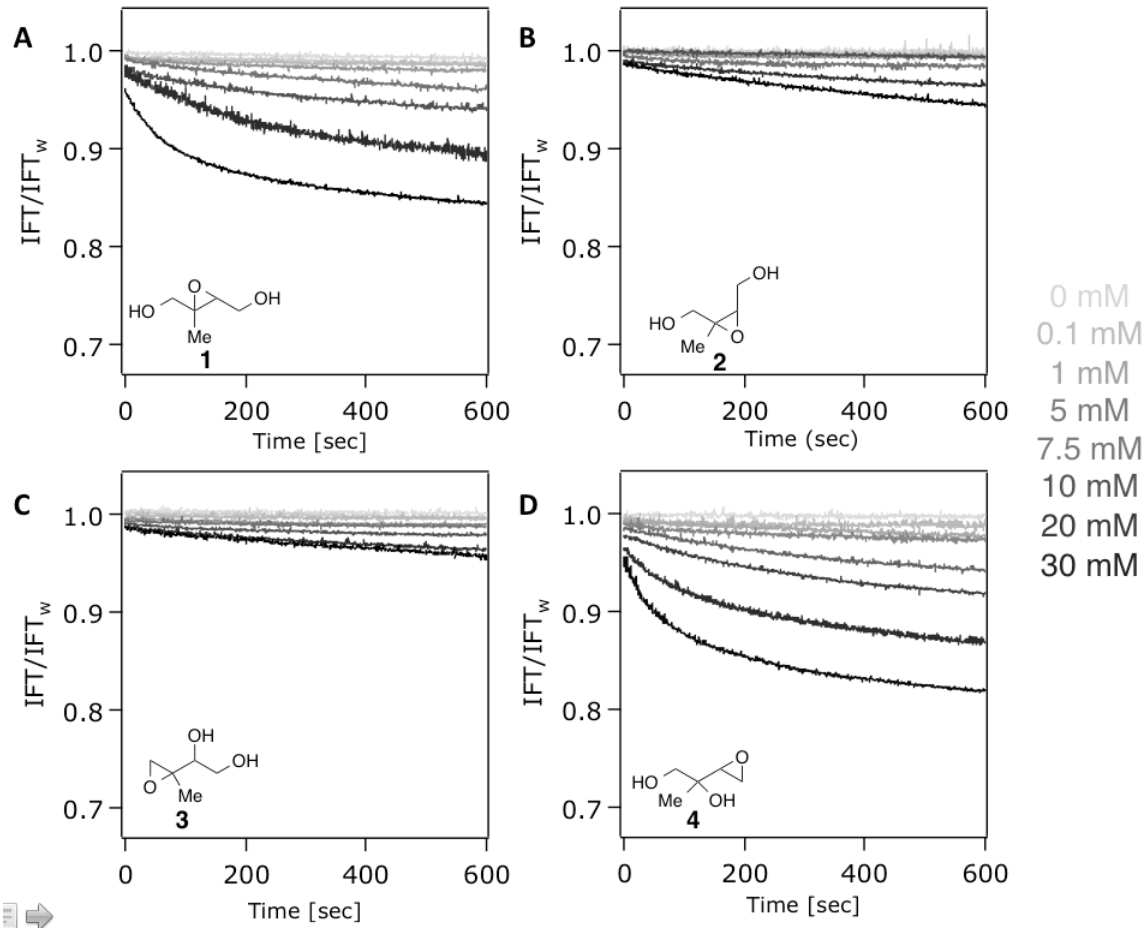
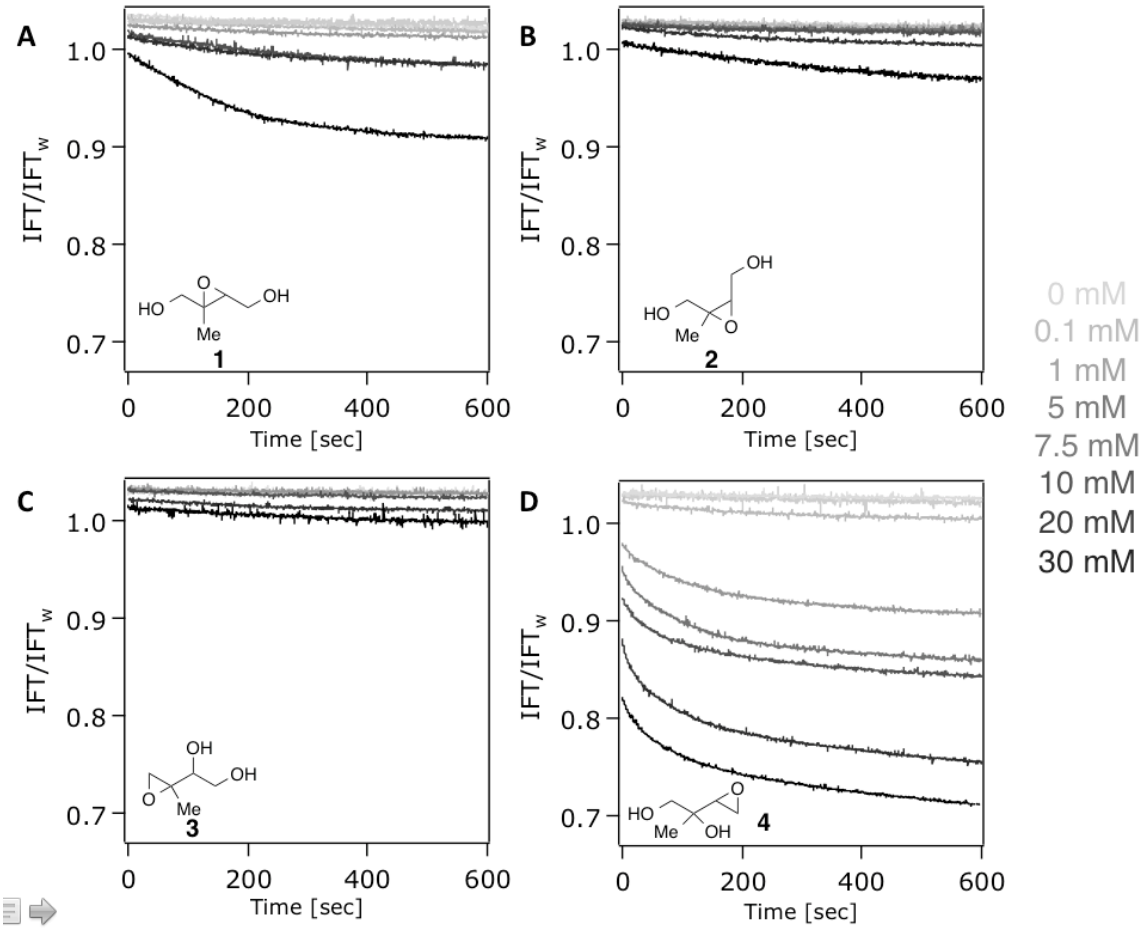


Figure 2. Dynamic surface tension measurements for IEPOX compounds in dH_2O. A) trans-β-IEPOX (1) B) cis-β-IEPOX (2) C) δ-IEPOX (3) D) α-IEPOX (4).



353

354 **Figure 3**. Dynamic surface tension measurements for IEPOX compounds in 1 M
355 $(NH_4)_2SO_4$. A) trans-β-IEPOX (1) B) cis-β-IEPOX (2) C) δ-IEPOX (3) D) α-IEPOX (4).
356

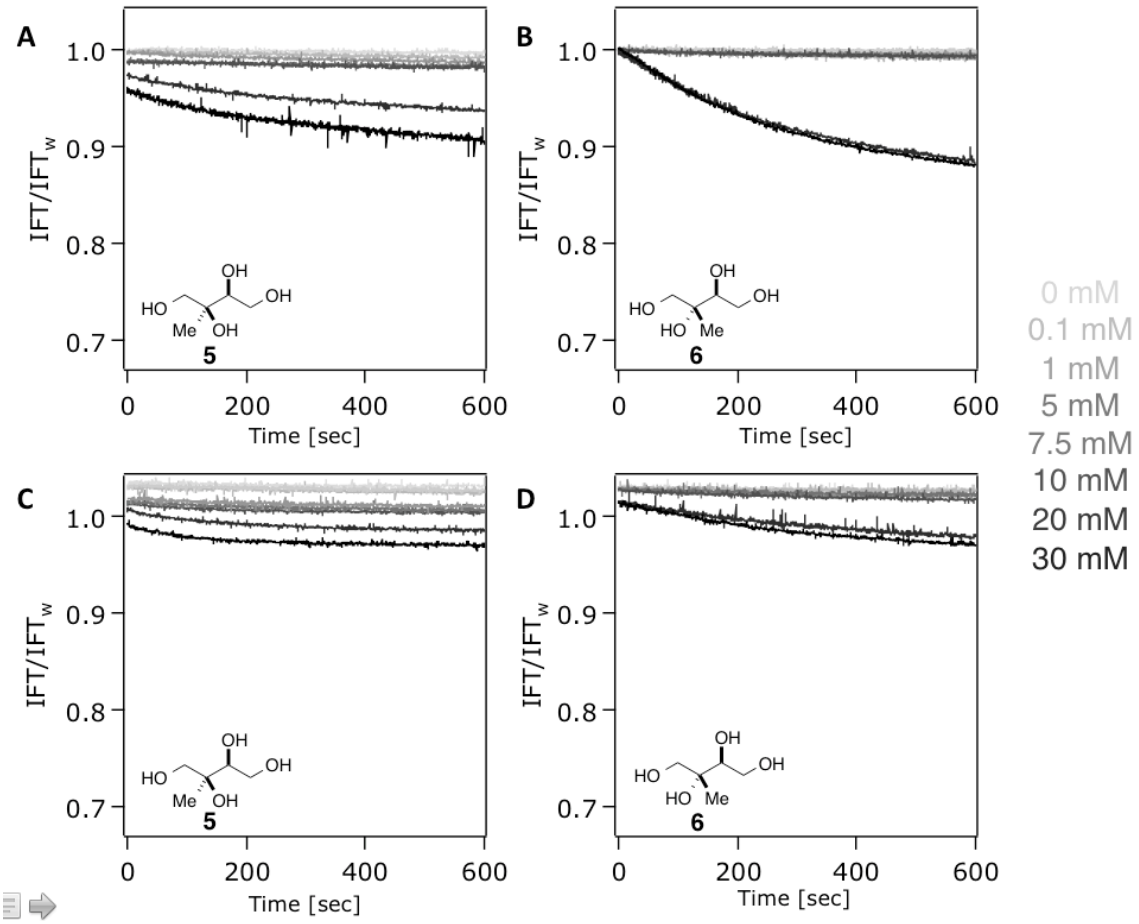
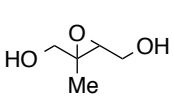
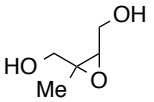
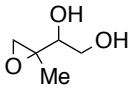
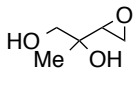
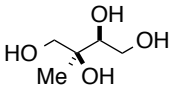
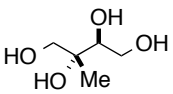


Figure 4. Dynamic surface tension measurements for 2-methyltetraol compounds in dH_2O (A and B) and 1 M $(NH_4)_2SO_4$ (C and D). A/C) syn-2-methyltetraol (5) B/D) anti-2-methyltetraol (6).

370 **Table 1.** Equilibrium surface tension (at t=∞) for IEPOX (1–4) and 2-methyltetraols (5,6).

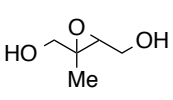
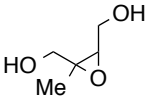
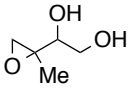
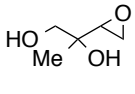
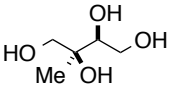
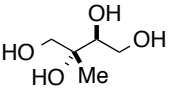
Concentration (mM)	 1	 2	 3	 4	 5	 6
0	71.8 (73.87)	72.73 (74.38)	72.84 (74.85)	72.4 (74.59)	72.48 (75.01)	72.47 (74.67)
0.1	71.4 (74.63)	72.59 (74.28)	72.3 (74.63)	71.96 (74.0)	72.06 (74.54)	72.36 (74.69)
1	71.68 (73.81)	72.31 (74.25)	72.46 (74.4)	70.7 (73.01)	71.8 (74.2)	71.30 (74.72)
5	71.20 (73.56)	72.32 (74.17)	71.96 (74.80)	70.69 (66.09)	71.68 (73.47)	71.70 (74.27)
7.5	68.72 (73.49)	71.67 (74.14)	71.85 (74.32)	67.64 (62.70)	71.48 (73.18)	71.27 (74.37)
10	67.87 (71.11)	71.7 (74.00)	71.09 (74.39)	65.95 (61.45)	71.1 (73.09)	71.34 (73.74)
20	64.57 (71.39)	69.01 (72.93)	69.31 (73.46)	62.99 (55.14)	67.78 (71.72)	61.45 (70.36)
30	61.62 (65.89)	65.5 (69.21)	67.4 (72.09)	59.46 (51.89)	65.35 (70.64)	60.96 (69.97)

a. Surface tension values at t=∞ for solutions of IEPOX (1–4) and 2-methyltetraols (5, 6) in dH_2O based on exponential fits. All values have units of mN/m b. Values in parentheses denote surface tension values in 1 M $(NH_4)_2SO_4$. c. Error in exponential fit varied from 0.01-0.2 for IEPOX 1-3 and *syn*-2-methyltetraol 5, 0.01-0.1 for IEPOX 4, and from 0.01-0.06 for *anti*-2-methyltetraol 6.

371

372

373 **Table 2.** Supersaturation ratios for IEPOX (1–4) and 2-methyltetraols (5, 6).

Concentration (mM)	 1	 2	 3	 4	 5	 6
0	1.0 (1.02)	1.00 (1.0)	1.00 (1.04)	1.0 (1.04)	0.99 (1.05)	0.99 (1.04)
0.1	1.0 (1.04)	1.00 (1.03)	1.0 (1.04)	0.98 (1.0)	0.99 (1.0)	0.99 (1.04)
1	0.98 (1.02)	0.99 (1.03)	0.99 (1.0)	0.9 (1.00)	1.0 (1.0)	0.97 (1.04)
5	0.97 (1.02)	0.99 (1.03)	0.98 (1.04)	0.96 (0.86)	0.98 (1.01)	0.98 (1.03)
7.5	0.92 (1.01)	0.98 (1.03)	0.98 (1.03)	0.90 (0.80)	0.97 (1.00)	0.97 (1.03)
10	0.90 (0.96)	1.0 (1.02)	0.96 (1.03)	0.86 (0.78)	1.0 (1.00)	0.97 (1.02)
20	0.84 (0.97)	0.9 (1.00)	0.93 (1.01)	0.80 (0.66)	0.90 (0.98)	0.78 (0.95)
30	0.78 (0.86)	0.9 (0.93)	0.9 (1.0)	0.74 (0.60)	0.85 (0.96)	0.77 (0.94)

a. Supersaturation ratios (s^*_c/s_c) for solutions of IEPOX (1–4) and 2-methyltetraols (5, 6) in dH_2O b. Values in parentheses denote supersaturation ratios (s^*_c/s_c) in 1 M $(NH_4)_2SO_4$. Errors in ratios varied from 0.01-0.2 for IEPOX 1-3 and *syn*-2-methyltetraol 5, 0.01-0.1 for IEPOX 4, and 0.01-0.09 for *anti*-2-methyltetraol 6.

374
375

376

377
378
379
380
381
382
383

References.

(1) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. *Atmos Chem Phys* **2005**, *5*, 1053.

(2) Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. *Atmos Chem Phys* **2009**, *9*, 4987.

(3) Williams, J.; Crowley, J.; Fischer, H.; Harder, H.; Martinez, M.; Petäjä, T.; Rinne, J.; Bäck, J.; Boy, M.; Dal Maso, M.; Hakala, J.; Kajos, M.; Keronen, P.; Rantala, P.; Aalto, J.; Aaltonen, H.; Paatero, J.; Vesala, T.; Hakola, H.; Levula, J.; Pohja, T.; Herrmann, F.; Auld, J.; Mesarchaki, E.; Song, W.; Yassaa, N.; Nölscher, A.; Johnson, A. M.; Custer, T.; Sinha, V.; Thieser, J.; Pouvesle, N.; Taraborrelli, D.; Tang, M. J.; Bozem, H.; Hosaynali-Beygi, Z.; Axinte, R.; Oswald, R.; Novelli, A.; Kubistin, D.; Hens, K.; Javed, U.; Trawny, K.; Breitenberger, C.; Hidalgo, P. J.; Ebben, C. J.; Geiger, F. M.; Corrigan, A. L.; Russell, L. M.; Ouwersloot, H. G.; Vilà-Guerau de Arellano, J.; Ganzeveld, L.; Vogel, A.; Beck, M.; Bayerle, A.; Kampf, C. J.; Bertelmann, M.; Köllner, F.; Hoffmann, T.; Valverde, J.; González, D.; Riekkola, M. L.; Kulmala, M.; Lelieveld, J. *Atmos Chem Phys* **2011**, *11*, 10599.

(4) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T. F.; Monod, A.; Prevot, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. *Atmos Chem Phys* **2009**, *9*, 5155.

(5) Goldstein, A. H.; Galbally, I. E. *Environ Sci Technol* **2007**, *41*, 1514.

(6) Galbally, I. E.; Lawson, S. J.; Weeks, I. A.; Bentley, S. T.; Gillett, R. W.; Meyer, M.; Goldstein, A. H. *Environ Chem* **2007**, *4*, 178.

(7) Riipinen, I.; Pierce, J. R.; Yli-Juuti, T.; Nieminen, T.; Häkkinen, S.; Ehn, M.; Junninen, H.; Lehtipalo, K.; Petäjä, T.; Slowik, J.; Chang, R.; Shantz, N. C.; Abbatt, J.; Leaitch, W. R.; Kerminen, V. M.; Worsnop, D. R.; Pandis, S. N.; Donahue, N. M.; Kulmala, M. *Atmos Chem Phys* **2011**, *11*, 3865.

(8) Kroll, J. H.; Seinfeld, J. H. *Atmos Environ* **2008**, *42*, 3593.

(9) Lin, Y. H.; Zhang, Z. F.; Docherty, K. S.; Zhang, H. F.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D. *Environ Sci Technol* **2012**, *46*, 250.

(10) Worton, D. R.; Surratt, J. D.; Lafranchi, B. W.; Chan, A. W.; Zhao, Y.; Weber, R. J.; Park, J. H.; Gilman, J. B.; de Gouw, J.; Park, C.; Schade, G.; Beaver, M.; Clair, J. M.; Crounse, J.; Wennberg, P.; Wolfe, G. M.; Harrold, S.; Thornton, J. A.; Farmer, D. K.; Docherty, K. S.; Cubison, M. J.; Jimenez, J. L.; Frossard, A. A.; Russell, L. M.; Kristensen, K.; Glasius, M.; Mao, J.; Ren, X.; Brune, W.; Browne, E. C.; Pusede, S. E.; Cohen, R. C.; Seinfeld, J. H.; Goldstein, A. H. *Environ Sci Technol* **2013**, *47*, 11403.

(11) Kourtchev, I.; Fuller, S. J.; Giorio, C.; Healy, R. M.; Wilson, E.; O'Connor, I.; Wenger, J. C.; McLeod, M.; Aalto, J.; Ruuskanen, T. M.; Maenhaut, W.; Jones, R.;

Venables, D. S.; Sodeau, J. R.; Kulmala, M.; Kalberer, M. *Atmos Chem Phys* **2014**, *14*, 2155.

(12) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipila, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I. H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurten, T.; Nielsen, L. B.; Jorgensen, S.; Kjaergaard, H. G.; Canagaratna, M.; Maso, M. D.; Berndt, T.; Petaja, T.; Wahner, A.; Kerminen, V. M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.; Mentel, T. F. *Nature* **2014**, *506*, 476.

(13) Claeys, M.; Wang, W.; Ion, A. C.; Kourtchev, I.; Gelencsér, A.; Maenhaut, W. *Atmos Environ* **2004**, *38*, 4093.

(14) Wang, J.; Wexler, A. S. *Geophys Res Lett* **2013**, *40*, 2834.

(15) Djikaev, Y. S.; Tabazadeh, A. *Journal of Geophysical Research* **2003**, *108*, 4689.

(16) Schwier, A. N.; Viglione, G. A.; Li, Z.; Faye McNeill, V. *Atmos Chem Phys* **2013**, *13*, 10721.

(17) McNeill, V. F.; Sareen, N.; Schwier, A. N. *Top. Curr. Chem.* **2014**, *339*, 201.

(18) Aumann, E.; Tabazadeh, A. *Journal of Geophysical Research* **2008**, *113*, D23205.

(19) Tabazadeh, A. *Atmos Environ* **2005**, *39*, 5472.

(20) Taraniuk, I.; Graber, E. R.; Kostinski, A.; Rudich, Y. *Geophys Res Lett* **2007**, *34*, L16807.

(21) Taraniuk, I.; Kostinski, A. B.; Rudich, Y. *Geophys Res Lett* **2008**, *35*, L19810.

(22) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. *Nature* **1999**, *401*, 257.

(23) Kiss, G.; Tombacz, E.; Hansson, H. C. *J Atmos Chem* **2005**, *50*, 279.

(24) Shulman, M. L.; Jacobson, M. C.; Carlson, R. J.; Synovec, R. E.; Young, T. E. *Geophys Res Lett* **1996**, *23*, 277.

(25) Asa-Awuku, A.; Sullivan, A. P.; Hennigan, C. J.; Weber, R. J.; Nenes, A. *Atmos Chem Phys* **2008**, *8*, 799.

(26) Facchini, M. C.; Decesari, S.; Mircea, M.; Fuzzi, S.; Loglio, G. *Atmos Environ* **2000**, *34*, 4853.

(27) Novakov, T.; Penner, J. E. *Nature* **1993**, *365*, 823.

(28) Sareen, N.; Schwier, A. N.; Lathem, T. L.; Nenes, A.; McNeill, V. F. *Proceedings of the National Academy of Sciences of the United States of America* **2013**, *110*, 2723.

(29) Salma, I.; Ocskay, R.; Varga, I.; Maenhaut, W. *Journal of Geophysical Research* **2006**, *111*, 205.

(30) Hitzenberger, R.; Berner, A.; Kasper-Giebl, A.; Loflund, M.; Puxbaum, H. *Journal of Geophysical Research* **2002**, *107*, 4752.

(31) Woo, J. L.; Kim, D. D.; Schwier, A. N.; Li, R.; McNeill, V. F. *Faraday Discuss.* **2013**, *165*, 357.

(32) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kurten, A.; St Clair, J. M.; Seinfeld, J. H.; Wennberg, P. O. *Science* **2009**, *325*, 730.

(33) Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W. *Science* **2004**, *303*, 1173.
(34) Bates, K. H.; Crounse, J. D.; St Clair, J. M.; Bennett, N. B.; Nguyen, T. B.; Seinfeld, J. H.; Stoltz, B. M.; Wennberg, P. O. *J Phys Chem A* **2014**, *118*, 1237.
(35) Ebben, C. J.; Strick, B. F.; Upshur, M. A.; Chase, H. M.; Achtyl, J. L.; Thomson, R. J.; Geiger, F. M. *Atmos Chem Phys* **2014**, *14*, 2303.
(36) Drozd, G. T.; McNeill, V. F. *Environ. Sci. Process Impacts* **2014**, *16*, 741.
(37) Keene, W. C. *Journal of Geophysical Research* **2004**, *109*.
(38) Zhang, Q.; Jimenez, J. L.; Worsnop, D. R.; Canagaratna, M. *Environ Sci Technol* **2007**, *41*, 3213.
(39) Noziere, B.; Baduel, C.; Jaffrezo, J. L. *Nature communications* **2014**, *5*, 3335.
(40) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; 6th ed. ed.; John Wiley & Sons, Inc.: New York, 1997.
(41) Leo, A.; Hansch, C.; Elkins, D. *Chem. Rev.* **1971**, *71*, 525.
(42) Finizio, A.; Mackay, D.; Bidleman, T.; Harner, T. *Atmos Environ* **1997**, *31*, 2289.
(43) Klopffer, W.; Rippen, G.; Frische, R. *Ecotoxicol. Environ. Saf.* **1982**, *6*, 294.
(44) Meylan, W. M.; Howard, P. H. *Chemosphere* **2005**, *61*, 640.
(45) Yuan, Y.; Renbaum-Wolff, L.; Carreras-Sospedra, M.; Hanna, S. J.; Hiranuma, N.; Kamal, S.; Smith, M. L.; Zhang, X.; Weber, R. J.; Shilling, J. E.; Dabdub, D.; Martin, S. T.; Bertram, A. K. *Proceedings of the National Academy of Sciences of the United States of America* **2012**, *109*, 13188.
(46) Li, Z.; Williams, A. L.; Rood, M. J. *J. Atmos. Sci.* **1998**, *55*, 1859.
(47) Matijevic, E.; Pethica, B. A. *Trans. Faraday Soc.* **1958**, *54*, 1383.
(48) Schwier, A.; Mitroo, D.; McNeill, V. F. *Atmos Environ* **2012**, *54*, 490.
(49) Sareen, N.; Schwier, A. N.; Shapiro, E. L.; Mitroo, D.; McNeill, V. F. *Atmos Chem Phys* **2010**, *10*, 997.
(50) Li, Z.; Schwier, A. N.; Sareen, N.; McNeill, V. F. *Atmos Chem Phys* **2011**, *11*, 11617.
(51) Cruz, C. N.; Pandis, S. N. *Journal of Geophysical Research* **1998**, *103*, 13111.
(52) Ekstrom, S.; Noziere, B.; Hansson, H. C. *Atmos Chem Phys* **2009**, *9*, 973.
(53) Corrigan, C. E.; Novakov, T. *Atmos Environ* **1999**, *33*, 2661.
(54) Cruz, C. N.; Pandis, S. N. *Atmos Environ* **1997**, *31*, 2205.
(55) Henning, S.; Rosenorn, T.; D'Anna, B.; Gola, A. A.; Svenningsson, B.; Bilde, M. *Atmos Chem Phys* **2005**, *5*, 575.
(56) Prenni, A. J.; DeMott, P. J.; Kreidenweis, S. M.; Sherman, D. E. *J Phys Chem A* **2001**, *105*, 11240.
(57) Raymond, T. M. *Journal of Geophysical Research* **2003**, *108*, 4469.
(58) Raymond, T. M. *Journal of Geophysical Research* **2002**, *107*, 4787.
(59) Liu, P. S. K.; Leaitch, W. R.; Banic, C. M.; Li, S. M.; Ngo, D.; Megaw, W. J. *Journal of Geophysical Research* **1996**, *101*, 28971.

519 (60) Broekhuizen, K.; Kumar, P. P.; Abbatt, J. P. D. *Geophys Res Lett* **2004**, *31*,
520 107.
521 (61) Kumar, P. P.; Broekhuizen, K.; Abbatt, J. P. D. *Atmos Chem Phys* **2003**, *3*,
522 509.
523 (62) Kohler, H. *Trans. Faraday Soc.* **1936**, *32*, 1152.
524 (63) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: from*
525 *air pollution to climate change*; Wiley: New York, 1998.
526 (64) Engelhart, G. J.; Asa-Awuku, A.; Nenes, A.; Pandis, S. N. *Atmos Chem*
527 *Phys* **2008**, *8*, 3937.
528 (65) Chan, M. N.; Surratt, J. D.; Claeys, M.; Edgerton, E. S.; Tanner, R. L.;
529 Shaw, S. L.; Zheng, M.; Knipping, E. M.; Eddingsaas, N. C.; Wennberg, P. O.; Seinfeld,
530 J. H. *Environmental Science & Technology* **2010**, *44*, 4590.
531 (66) McNeill, V. F.; Woo, J. L.; Kim, D. D.; Schwier, A. N.; Wannell, N. J.;
532 Sumner, A. J.; Barakat, J. M. *Env. Sci. Technol.* **2012**, *46*, 8075.
533 (67) Nguyen, T. B.; Coggon, M. M.; Bates, K. H.; Zhang, X.; Schwantes, R.
534 H.; Schilling, K. A.; Loza, C. L.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. *Atmos*
535 *Chem Phys* **2014**, *14*, 3497.
536 (68) Surratt, J. D.; Kroll, J. H.; Kleindienst, T. E.; Edney, E. O.; Claeys, M.;
537 Sorooshian, A.; Ng, N. L.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Flagan, R. C.;
538 Seinfeld, J. H. *Environ Sci Technol* **2007**, *41*, 517.
539 (69) Surratt, J. D.; Chan, A. W.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.;
540 Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. *Proceedings*
541 *of the National Academy of Sciences of the United States of America* **2010**, *107*, 6640.
542 (70) Darer, A. I.; Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. *Environ*
543 *Sci Technol* **2011**, *45*, 1895.
544
545