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**Reversible and
irreversible
processing of
biogenic olefins**

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Reversible and irreversible processing of biogenic olefins on acidic aerosols

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Abstract

Recent evidence has suggested that heterogeneous chemistry of oxygenated hydro-carbons, primarily carbonyls, plays a role in the formation of secondary organic aerosol (SOA); however, evidence is emerging that direct uptake of alkenes on acidic aerosols does occur and can contribute to SOA formation. In the present study, significant up-take of monoterpenes, oxygenated monoterpenes and sesquiterpenes to acidic sulfate aerosols is found under various conditions in a reaction chamber. Proton transfer mass spectrometry is used to quantify the organic gases, while an aerosol mass spectrom-eter is used to quantify the organic mass uptake and obtain structural information for heterogeneous products. Aerosol mass spectra are consistent with several mecha-nisms including acid catalyzed olefin hydration, cationic polymerization and organic ester formation, while measurable decreases in the sulfate mass on a per particle ba-sis suggest that the formation of organosulfate compounds is also likely. A portion of the heterogeneous reactions appears to be reversible, consistent with reversible olefin hydration reactions. A slow increase in the organic mass after a fast initial uptake is attributed to irreversible reactions, consistent with polymerization and organosulfate formation. Uptake coefficients (γ) were estimated for a fast initial uptake governed by the mass accommodation coefficient (α) and ranged from 1×10^{-6}–2.5×10^{-2}. Up-take coefficients for a subsequent slower reactive uptake ranged from 1×10^{-7}–1×10^{-4}. These processes are estimated to potentially produce greater than $2.5\,\mu\mathrm{g\,m^{-3}}$ of SOA from the various biogenic hydrocarbons under atmospheric conditions, which can be highly significant given the large array of atmospheric olefins.

1 Introduction

Gas-phase oxidation of hydrocarbons has been considered a key step in the formation of secondary organic aerosols (SOA) in the atmosphere. This process is an area of significant interest due to its climatic relevance (Pilinis et al., 1995), its effect on

regional visibility (Eldering and Cass, 1996), and its potential for negative health effects (Goldberg et al., 2003; Hannigan et al., 1998). Comprehension of these effects is further complicated by the fact that the composition of SOA greatly determines the extent of these effects. Consequently, there is a need to determine the mechanisms of
5   formation and the nature of SOA composition, particularly from biogenic sources.

Emissions from terrestrial vegetation are a significant source of non methane hydrocarbons (NMHCs) globally, contributing upwards of 850 Tg of organic carbon per year, considerably surpassing annual anthropogenic emissions (125 Tg/year) (Hoffmann et al., 1997). Emissions of these biogenic NMHCs, including isoprene, monoterpenes,
10   oxygenated terpenes and sesquiterpenes, are an important source of secondary organic aerosol (SOA), particularly due to their high atmospheric concentrations and their intense reactivities with atmospheric oxidants. Although many products from the oxidation of biogenic NMHCs are volatile and remain in the gas-phase, a significant number possess vapor pressures sufficiently low such that their partitioning to aerosols occurs.
15   Many of these low volatility products have been observed in both laboratory generated biogenic SOA (Böge et al., 2006; Kroll et al., 2006) and ambient aerosols over forested regions (Kavouras et al., 1999).

Recent work has shown heterogeneous and liquid phase reactions as a potential route for SOA formation from volatile and semi-volatile oxidation products of biogenic
20   and anthropogenic origin (Jang et al., 2003; Kroll et al., 2005; Liggio and Li, 2006b; Noziere and Riemer, 2003). This pathway may aid in explaining the current underestimation of SOA mass by global models (Heald et al., 2005), and could prove important with respect to CCN activity. Heterogeneous reactions have been proposed to lead to the transformation of VOCs and SVOCs to various high molecular weight compounds,
25   oligomers or organosulfate species, specifically via compounds containing oxygenated functional groups (carbonyls and alcohols). Several mechanisms, including oligomer formation, hydration, hemi-acetal, acetal formation, polymerization (Jang and Kamens, 2001), aldol condensation (Noziere and Riemer, 2003) and organosulfate formation (Iinuma et al., 2007; Liggio and Li, 2006a; Surratt et al., 2007), have been proposed

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to explain observed heterogeneous products and possible acid catalysis in laboratory studies.

Although oligomer formation from oxidized products of primary hydrocarbons is now well known, comparatively little is known regarding the SOA forming potential of primary unsaturated biogenic hydrocarbons (e.g. alkenes). Bulk liquid studies suggested that acid catalyzed polymerization of isoprene may be feasible (Limbeck et al., 2003), and more elaborate chamber studies have demonstrated that than indeed isoprene and α-pinene can be taken up significantly by acidic aerosols via polymerization of these olefins and subsequent polymer hydration (Liggio et al., 2007). However, it has been unclear whether reactions leading to polymers and oligomers are reversible, which in turn determines their importance to SOA formation in the atmosphere. Evidence for both scenarios has been observed with respect to the heterogeneous uptake of glyoxal (Hastings et al., 2005; Kroll et al., 2005; Liggio et al., 2005).

Extending the previous work on isoprene and α-pinene (Liggio et al., 2007), the present paper reports on the results of a series of lab studies on the direct uptake of biogenic olefin species, including various monoterpenes, oxygenated monoterpenes, and sesquiterpenes, to acidic sulfate aerosols. The organic mass uptake, reaction mechanisms for the heterogeneous reactions of several of these compounds, the reversibility of such reactions, and the importance of this process in the ambient atmosphere are discussed.

2 Methodology

Eight terpenoid species were exposed to acidic sulfate seed aerosols in a $2\,\text{m}^3$ Teflon reaction chamber, enclosed in a framed aluminium container to prevent potential photochemistry. The details of the chamber design and configuration have been given previously (Liggio and Li, 2006b), with slight modifications described herein. A summary of the initial aerosol composition, the hydrocarbon gases and other initial conditions is given in Table 1. In a typical experiment, the chamber was filled first with aerosols of

known $H_2SO_4/(NH_4)_2SO_4$ composition and size, to a concentration of approximately 1000–3000 cm^{-3}, followed by the addition of a gaseous monoterpene or sesquiterpene (Sigma-Aldrich, >98%) at a given relative humidity (RH, 1.4–73%). The relative humidity was controlled by injecting de-ionized and organic free water onto the surface of a resistively heated element within the chamber, prior to and during the addition of aerosols.

2.1 Aerosol generation

Aerosols were generated by atomizing a solution of $H_2SO_4/(NH_4)_2SO_4$ with a constant volume atomizer (TSI Inc.). Depending on the experiment, the ratio of H_2SO_4 to $(NH_4)_2SO_4$ in the solution was chosen to give different acidities in the aerosols (Table 1). Approximately mono-dispersed aerosols, of 463–527 nm in diameter, were selected with a scanning differential mobility analyzer (DMA, TSI Inc.) and introduced into the chamber over a period of several hours or until a sufficient particle concentration was obtained. Drifting of the DMA sheath and aerosol flows over this time, and differences in water uptake from one experiment to the next, account for the stated size range.

2.2 Gas delivery and measurement

The terpenoid gases were introduced to the chamber, one for each experiment, by injecting their pure liquids into a stream of zero air (Aadco Inc.) which contains no measurable levels of oxidant or other contaminants. The terpenoid compounds were chosen to span the range of compound classes that are commonly observed in the ambient atmosphere. These include non-oxygenated and oxygenated monoterpenes and sesquiterpenes (Table 1). Structures associated with the studied compounds are given in Fig. 1 – Supporting Information. The gas phase concentration in the chamber during a given experiment was monitored on a 1 s time resolution with a Proton Transfer Reaction Mass Spectrometer (PTR-MS, Ionicon Analytik Inc.), the operation principles

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and application of which have been described previously (Steinbacher et al., 2004). Briefly, H_3O^+ ions are used to ionize gases via the transfer of a proton, yielding primarily M+1 ions with little or no fragmentation. The ionization efficiency is based upon the proton affinity, which is significant for most unsaturated compounds. Ions are then accelerated into a quadrupole mass spectrometer for detection which was operated in the single ion mode. The response of the PTR-MS for a species was calibrated with a known gas phase concentration, produced by injection of a given mass of the species into a known flow of zero air. The PTR-MS was directly connected to the chamber via a 10 cm length of 1/8" Teflon tubing which was continuously heated to approximately 60 C, to minimize adsorption of gases and subsequent sample contamination. The gas phase concentration of most species in the chamber was constant to within 5–10% over the time scales of each experiment. The notable exceptions are the oxygenated species which decreased by approximately 30% over this time. It is estimated that the uncertainty in the gas phase measurement is 20%.

2.3   Aerosol measurements

The aerosol composition, size, and number concentrations were quantified during the experiments with an Aerosol Mass Spectrometer (AMS) equipped with a quadrupole mass detector (Aerodyne Research Inc.), which has been described in previous publications (Allan et al., 2004; Jayne et al., 2000; Jimenez et al., 2003). In summary, particles are sampled through a critical orifice and aerodynamic lens system, which collimates the particles and accelerates them into the time of flight region. The velocity, related to the particle size, can be calculated from the time needed to reach a heated surface from a chopper located downstream of the inlet. Particles are then impacted and vaporized on the heated surface, ionized by electron impact (EI) and the resultant fragments carried into a quadrupole mass spectrometer for mass analysis. The AMS is capable of detecting single particle events for particles which contain sufficient mass (~300 nm NH_4NO_3) (Jayne et al., 2000). Initial aerosol diameters greater than 300 nm were deliberately chosen to take advantage of the efficient single particle

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detection in this size regime. The AMS was operated with a time resolution of 5 min, and sampled continuously for the length of each experiment (2.5–3 h).

3 Conclusions

Twenty-one experiments were performed under acidic particle conditions which were
5 controlled by varying the relative humidity within the chamber. A summary of the results of uptake for each experiment is given as an organic mass concentration ($\mu g\,m^{-3}$) in Table 2, representing the maximum organic mass observed. The organic and inorganic mass was calculated based on the algorithm of Allan et al. (2004). Organic material is added to the initial acidic seed particles in all cases, although to varying degrees, where
10 the maximum organic mass loading ranged from 1–546 $\mu g\,m^{-3}$ and corresponded to a maximum SO_4 seed mass of 47.7–137.2 $\mu g\,m^{-3}$. The time dependent mass loading curves were approximately the same for all compounds during this study and is given in Fig. 1 for a typical experiment. From Fig. 1 it is evident that the onset of organic uptake occurs very soon after the addition of the terpenoid species (denoted as t=0), and the
15 maximum in the organic mass was usually achieved within the first 20–50 min of each experiment. This suggests that the uptake mechanism is rather fast. However, the time dependent mass loading, although useful as an indicator of uptake, is complicated by particle wall losses and the ensuing decrease of total organic and inorganic mass from t=0. This obscurity is removed by normalizing the mass concentrations ($\mu g\,m^{-3}$) by the
20 number concentrations (cm^{-3}) of the approximately mono-disperse aerosols. The result is the mass on a per particle basis (g particle^{-1}), given in Table 2 and reported as the value at the end of each experiment. The time dependent normalized organic mass for selected experiments is shown in Fig. 2. The normalized organic mass at the end of each experiment was highly variable, ranging from 2.4×10^{-16}–5.31×10^{-13} g particle^{-1}
25 and was dependent upon relative humidity (RH); the largest uptake was observed under the lowest RH conditions (see next section). There was also a significant difference in the normalized organic mass between classes of biogenic compounds. The mass

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taken up for simple monoterpenes such as limonene, β-pinene and 3-carene under similarly acidic conditions was appreciably less than that of oxygenated monoterpenes or sesquiterpenes. This likely reflects the large differences between the vapor pressures of such compounds, and ultimately the accommodation of gases to the particle surface. Furthermore, the time dependent normalized mass curves in Fig. 2 typically exhibit a fast initial uptake followed by a slower increase in mass for the remainder of the experiments. This suggests the existence of multiple reactions/equilibria and is discussed further in the following sections.

3.1 Effect of relative humidity and acidity

Although experiments were conducted with acidic aerosols to varying degrees (Table 1), even aerosols with the weakest acidity contained substantial acidity (pH~−0.77), likely sufficient for acid catalysis to occur were it an important aspect of the reactions. Thus, the changes in uptake due to the changes in the aerosol acidity in these experiments were likely not large. In comparison, the effect of relative humidity (RH) is more pronounced. Significant differences in the magnitude of organic uptake were observed by varying the RH within the chamber, regardless of the species studied. These results are highlighted in Fig. 2. Increasing the RH from less than 5% (Fig. 2a) to 20–73% (Fig. 2b), and thus more realistic atmospheric RH conditions, reduced the normalized organic mass uptake, often by an order of magnitude, but still indicates that this process occurs under atmospheric conditions. The reduced uptake at increased RH (and thus increased aerosol liquid water content) also suggests that the solubility of the terpenoids plays an important role; the solubility of the hydrocarbons is typically small in water, but can be significantly enhanced in acidic solutions. Increasing the RH, thus increasing the water content of the particles, in the experiments likely has the effect of decreasing the terpenoid solubility and limiting the amount available for further reactive transformation in the particles which may be acid catalyzed. A secondary effect of increased RH is the dilution of acidity in the particles, although in these studies the particle acidities were not entirely controlled without changing the liquid water

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content, and thus this secondary effect could not be observed.

The importance of RH and solubility is also highlighted in several experiments where the RH was increased after reactive uptake had already occurred (Exp. 5, 9, 14 and 19), the results of which are shown in Fig. 3. The equivalent experiments utilizing 3-carene and β-pinene at fairly high RH from the start of each experiment are also shown in the figure for comparison. As illustrated in Fig. 3, increasing the RH after uptake has occurred immediately reduces the organic mass per particle in all cases. This is evidence that a type of equilibrium must exist between reaction products and the original terpenoid species. Increasing the RH, and hence the particle water content, likely decreases the solubility of the parent terpenoid and shifts the equilibrium from aerosol phase product (p) to gas-phase species (g) as depicted below.

$$\text{Terpene}_{(g)} \quad \leftrightarrows \text{Terpene}_{(l)} \leftrightarrows \quad \text{Reaction Product}_{(p)}$$
$$\downarrow$$
$$\text{Reaction Product}_{(p2)} \tag{1}$$

The reverse reaction in Eq. (1) above is obviously driven by the increase in particle water content. However, data clearly show that the reverse reaction in Eq. (1) is not complete, and as indicated by Eq. (1) that some of the dissolved terpenoids in particles probably end up in the reaction product ($p2$) which is not reversible. This is demonstrated by the clear difference in the aerosol organic mass uptake of experiments of different RH in Fig. 3. Experiments 8 (β-pinene, 54% RH) and 11 (3-carene, 73% RH) were conducted as high RH cases to show low organic uptake as a baseline. Experiments 5 (β-pinene) and 9 (3-carene) were conducted with RH which began low (3.3% and 2.4%, respectively), leading to high initial uptake. The RH was then increased (eventually >80%) approximately 150 min after the gas exposure of the particle and the initial uptake took place (Fig. 3). Although the organic mass decreased significantly in both cases upon the RH increase, it did not reach the low organic mass in the baseline experiments 8 and 11, respectively, at the same RH. The difference is represented by the arrows in Fig. 3, and implies that a portion of the uptake products, prior to the RH increase, is formed via irreversible reactions, likely in the liquid phase

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as shown in Eq. (1) (*p*2). It is likely, that these irreversible reactions occur continuously throughout the experiment but become increasingly important during the slow increase in organic mass observed for many experiments, after an initial steady state has almost been reached (Fig. 2). These irreversible reactions act to slowly shift the equilibrium of
5 Eq. (1) to the right. The nature of these reversible and irreversible products is discussed below.

3.2   Aerosol spectra, reaction mechanisms and reversibility

There is no doubt that the uptake of organic material in this study must have arisen from heterogeneous reactions subsequent to physical absorption and solubility. Firstly,
10 a pure physical absorption or adsorption to the aerosol phase, based on the theories of Pankow (Pankow, 1994), could not account for the amount of mass taken up in these experiments.   The high vapor pressures associated with these compounds preclude these physical processes from being a significant contributor, assuming that the species is not transformed to a low volatility product.   Secondly,
15 the observed aerosol mass spectra are consistent with heterogeneous products of low volatility.   Typical aerosol mass spectra for monoterpenes (limonene and 3-carene), oxygenated mono-terpene (geraniol), and sesquiterpene (β-caryophyllene) collected near the end of a given experiment are presented in Figs. 4a–c. A complete set of aerosol mass spectra for all the studied compounds can be found in
20 the supporting information (http://www.atmos-chem-phys-discuss.net/7/11973/2007/ acpd-7-11973-2007-supplement.pdf). Numerous m/z fragments appear in the spectra of Fig. 4 which are far greater than the molecular weight of the parent species (136 g/mol, 154 g/mol), despite the fact that the harsh ionization and heating of the AMS tends to result in smaller fragments.
25   There is evidence that more than one type of reaction mechanism was at play, leading to different types of reaction products, some of which are reversible in response to changes in RH that probably changed the aerosol water content, while others are not. A representation of possible pathways for the direct uptake of limonene and geraniol is

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given in Fig. 5. As noted previously (Liggio et al., 2007), the uptake of isoprene and α-pinene to acidic aerosols proceeds primarily via a cationic polymerization mechanism. Similarly, the uptake of the non-oxygenated monoterpenes and sesquiterpenes in the present study may also proceed via this route. As exemplified in Fig. 5 for the uptake of limonene by cationic polymerization, the initial protonation under acidic conditions can lead to complex polymeric structures such as (*B*) (Fig. 5), where polymers are terminated by H_2O (*C*) and may be further hydrated, either partially or fully (*D*). Fragments associated with this mechanism, observable in the mass spectrum, indicate that polymerization of at least 2 limonene units had occurred. Numerous other polymer orientations (too many to show), are possible from different combinations of ring cleavage and further polymerization. As a result of potential ring cleavage, and since all non-oxygenated monoterpenes have the same molecular weight ($C_{10}H_{16}$) and similar reactivity with respect to the olefin bonds present, they are expected to undergo similar polymerization reaction mechanisms, leading to similar mass spectra. This is evident in comparing the spectra of limonene (Fig. 4a), 3-carene (Fig. 4c), β-pinene (Fig. 2a – Supporting Information) and α-pinene (Liggio et al., 2007).

Although a similar mechanism is likely to occur for the non-oxygenated sesquiterpenes, the obtained spectrum (Fig. 4b) is largely skewed towards higher m/z fragments, reflecting the larger molecules of the sesquiterpenes with the additional C_5H_8 group compared to the terpenes. Nonetheless, as an example, the mass spectrum of β-caryophyllene products is again consistent with a cationic polymerization mechanism as illustrated in Fig. 3 – Supporting Information. Given that the parent m/z of β-caryophyllene is 204, the unusually large abundance of m/z 205 implies that initial protonation leading to a carbocation and hence further polymerization has occurred, while other polymer fragments are also observable in the mass spectrum.

3.3 Esterization in aerosols

However, oxygenated monoterpenes (or sesquiterpenes) may take an additional potential route to oligomerization products; the same conditions which foster cationic poly-

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merization are conducive to ester formation. A generalized mechanism for geraniol is presented in Fig. 5 to illustrate this point. In addition to carbocation formation from double bonds, protonation of the alcohol group on the geraniol molecule can also occur. This results in the attack of an electrophillic OH group as shown in Fig. 5 via an S_N2
mechanism leading to the ester product (*H*), which can be further hydrated partially or fully (*I*). Ester formation under these conditions (acidic and <150 C) is favored over the E_1 elimination (Wade, 2003) which would lead to a dehydration of the alcohol group. Attack of an electrophillic olefin at the same position via path (*b*) (*L*) may also occur and would lead to similar products as the reaction of non-oxygenated monoterpenes. The mass spectrum of geraniol products is in fact different than other monoterpenes (e.g. limonene, Fig. 4a), being slightly shifted to larger m/z. Fragments likely associated with organic ester compounds (Fig. 4 – Supporting Information) are observable in the mass spectrum of geraniol heterogeneous products (Fig. 4a).

In addition to organic esterization, inorganic esters may also arise as illustrated in the mechanisms for limonene and geraniol (Fig. 5). The mechanisms of Fig. 5, leading to organo-sulfates, are slightly different than reported previously for carbonyl containing species (Liggio and Li, 2006a). In this case, the addition of sulfuric acid to olefins can lead directly to organo-sulfates by attacking the olefinic bond (*E* and *K*); a reaction which is known to occur for most alkenes (Wade, 2003). This suggests that oxygenated secondary products are not necessary as a starting material, although sulfate ester formation involving the OH group of geraniol is certainly also possible (structure *M*, Fig. 5). Evidence for the existence of organosulfates in this study is based upon a decrease in the measured SO_4 per particle after the addition of the hydrocarbons, as shown in Fig. 6 for several experiments. A decrease in the measured SO_4 during the reactive uptake of a biogenic oxidation product (pinonaldehyde) has also been attributed to the formation of organosulfates previously (Liggio and Li, 2006a). This decrease in SO_4 was most evident in experiments at the lowest relative humidities which also resulted in the highest proton concentrations in the aerosols. Organosulfates may also form during less acidic experiments; however, the decrease in SO_4 is obscured by the uncertainty

in the SO_4 per particle measurement. For those experiments where a measurable decrease in SO_4 was observable (Exp. 1, 5, 9, 12, 14, 15, 16, 19, 21), the approximate fraction of the organic mass accounted for by organosulfates may be estimated assuming that the decrease in SO_4 must be accompanied by a corresponding increase in organic mass (Table 3). Although there are several uncertainties with this approach (Liggio and Li, 2006a), the estimated organosulfate fraction (3.4%±0.64–76.6%±60.3) nonetheless highlights the potential for a significant organosulfate contribution and is consistent with those previously reported during the uptake of pinonaldehyde. Currently, mass spectral evidence for any organosulfate products is not definitive given that most fragments derived would have the same nominal mass as any other heterogeneous reaction product fragment.

The proposed mechanisms are also consistent with the observed relationship between the normalized organic mass per particle and RH (Fig. 3). Typically, the addition of monomers to carbocations forming polymers, organic ester formation and the addition of sulfuric acid to alkenes are irreversible (at ambient temperatures), as depicted in Fig. 5. Conversely, protonation of olefins and subsequent hydration is relatively fast and entirely reversible (Wade, 2003). Consequently, it is likely that the irreversible reaction products of Fig. 3 are due to oligomerization or organosulfate formation, which is somewhat insensitive to increases in RH provided that sufficient acidity remains to catalyze reactions. Furthermore the rapid response to increases in RH (water content) is likely a result of the hydration of olefins and potentially the formation of the first generation hydrated terpenoid products depicted as F and J in Fig. 5. As noted above, the increase in the aqueous content of the aerosol would decrease the solubility of the terpenoid, thus shifting the equilibrium to the gas phase via Eq. (1). A comparison of the relative mass spectrum difference (difference before and after H_2O addition) with the relative spectrum at the end of a 3-carene experiment is given in Fig. 4c. The spectral difference represents the mass spectra of the organic material lost upon increasing the RH during experiment 9. This spectrum is clearly composed of low mass fragments, particularly when compared to the residual spectrum. This implies that a

volatile species is lost, possibly 3-carene from the reversibly formed hydrated 3-carene. The difference spectrum in Fig. 4c is similar to the NIST spectrum of 3-carene, with the only exception being m/z 43 which may be a result of increased fragmentation caused by the intense heating and ionization associated with the AMS. Similarly, low mass
5 fragments are also observed in the difference spectra of experiments 5, 14 and 19.

3.4 Quantitative results

3.4.1 Steady state partitioning

Under steady state conditions partitioning of gases to aerosols can be described by an effective partitioning coefficient ($K_{P,\mathrm{eff}}$):

$$10 \quad K_{p,\mathrm{eff}} = \frac{(C_p/C_{\mathrm{TSP}})}{C_g} \tag{2}$$

where C_p represents the total organic mass derived from the studied species, regardless of its current form ($\mu\mathrm{g\,m}^{-3}$), C_g represents the concentration of the species in the gas-phase ($\mu\mathrm{g\,m}^{-3}$) and C_{TSP} represents the total suspended particle mass ($\mu\mathrm{g\,m}^{-3}$). Estimated $K_{P,\mathrm{eff}}$ values during this study are given in Table 2. In most experiments a
15 relatively fast initial uptake is observed, which as described above is attributed to a fast reversible process; possibly hydration. Based on the fast rate of the initial uptake compared to the slow organic increase afterwards, $K_{P,\mathrm{eff}}$ can be approximated from the normalized organic mass after this initial period, assuming that a semi-steady state has been reached and irreversible liquid phase reactions do not control the overall organic
20 mass uptake at this point. Although a steady state may not always be entirely achieved during these experiments due to the presence of liquid phase irreversible reactions, the additional mass added beyond the initial uptake is usually quite small, and thus $K_{p,\mathrm{eff}}$ can be approximately determined. This estimation would only be applicable for the ambient atmosphere if a near steady state was actually achieved, similar to that

observed in these experiments. Whether this steady state in ambient particles is ever achieved is unclear. The TSP mass used in the calculation was determined as the sum of the inorganic and organic mass during the same period. Estimated $K_{p,\text{eff}}$ values are highly variable, ranging from 0.4×10^{-6}–$1.3\times10^{-3}\,\text{m}^3\,\mu\text{g}^{-1}$ depending on the
5 RH or acidity; with the highest values for any given species observed at the lowest RH and hence highest acidity. This is consistent with a reversible hydration mechanism. Furthermore, $K_{p,\text{eff}}$ for the oxygenated monoterpenes or sequiterpenes were often several orders of magnitude higher than those for simple non-oxygenated monoterpenes. This may reflect the lower vapour pressures associated with sesquiterpenes or the
10 increased solubility in acidic solution of oxygenated species. However, even the smallest $K_{p,\text{eff}}$ values (simple monoterpenes) are large when compared with other species which have experimental partition coefficients in a similar range (Chandramouli et al., 2003) yet significantly lower vapour pressure than those compounds studied here. This suggests that the fast initial uptake and approximate steady state is not purely a phys-
15 ical process. Although the applicability of the TSP in these experiments to that of the ambient atmosphere may be limited to situations where aerosol acidities are high, the calculated $K_{p,\text{eff}}$ values are a first step in assessing the importance of this process.

3.4.2 Kinetics of uptake

Conversely, the rapid initial increases in the organic mass per particle (Fig. 2) may be
20 more appropriately described via uptake coefficients (γ). Uptake coefficients have been shown previously to be useful in assessing the importance of oligomer formation under kinetic control (Liggio et al., 2005), and are also presented in Table 2 for this study. The measured uptake coefficient is defined as the probability that a collision between a gas molecule and the aerosol surface will result in uptake, taking into account all aspects of
25 the uptake process including diffusion, mass accommodation, solubility and reactivity. These processes can be decoupled, and formulated as individual resistances (ignoring surface reactions) which sum to the overall uptake coefficient as shown in Eq. (3a) (Shi

et al., 1999),

$$\frac{1}{\gamma} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_b} \tag{3a}$$

where Γ_{diff} represents the effects of diffusion, α represents mass accommodation, and Γ_b accounts for solubility and liquid phase reactivity. Given the particle diameters and estimated diffusion coefficients for terpenoids, the resistance to mass transfer due to diffusion ($1/\Gamma_{diff}$) can be estimated in the manner described by Shi et al. (1999). The calculated diffusion resistance for these experiments was in the range of 0.86–1.45; significantly less than the smallest measured $1/\gamma$ below (10^4–10^7). Thus the $1/\Gamma_{diff}$ term can be effectively ignored and Eq. (3a) becomes:

$$\frac{1}{\gamma} \cong \frac{1}{\alpha} + \frac{1}{\Gamma_b} \tag{3b}$$

As noted previously, the mass uptake curves (Fig. 2) in most cases can be described by a fast initial uptake followed by a slower uptake region. Accordingly, uptake coefficients may be determined for both regions. In the initial phase of fast uptake, the resistance to mass transfer is either due to mass accommodation (α) or hydration reactions (encompassed within Γ_b), while other irreversible reaction are assumed to contribute little, at least initially. Acid catalyzed hydration of alkenes is invariably a first order process with the olefin protonation being the rate determining step (Chwang et al., 1977). First order rate constants for hydration of structurally similar compounds (in weaker acidic solutions) (Slebocka-Tilk et al., 1996) imply an olefin lifetime on the order of several seconds or less, with an effective steady state reached very quickly and favoring the protonated alkene. Given that the initial fast uptake phase takes as long as 20–40 min in some cases it is likely that the resistance to mass transfer is dominated by mass accommodation, i.e.

$$\left(\frac{1}{\gamma}\right)_{initial} \approx \frac{1}{\alpha} \tag{3c}$$

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This is also consistent with terpenoids having lower vapor pressures exhibiting a larger initial uptake, despite the fact that their reactivity with respect to hydration were likely similar. Thus, measured uptake coefficients in this region are more likely an estimation of the mass accommodation coefficient (α). The resistances to mass transfer for the second phase, characterized by a slow increase in the organic mass, is not so easily decoupled even though the curvature in Fig. 2 does indeed suggest that a change in the factors controlling the uptake has occurred, and thus Eq. (3b) still holds approximately true. Although this increase in organic mass is expected to be a result of irreversible reactions, it is not possible to determine if either of the $1/\alpha$ or $1/\Gamma_b$ resistance terms are controlling, or of similar magnitude. In principle, mass accommodation (α) could be reduced in this region as the surface characteristics of the particle change over time (become more organic). If α is not reduced, then the uptake coefficients calculated for this phase could represent Γ_b, controlled by reactivity. Uptake coefficients from the first phase as determined from Eq. (3c) ($\gamma_{initial} \approx \alpha$) are more likely applicable to freshly nucleated H_2SO_4 particles or pre-existing particles which have been freshly coated with H_2SO_4. On the other hand, uptake coefficients from the second region of Fig. 2 may be more applicable to aged aerosols.

Uptake coefficients are obtained by fitting a simple uptake model to the organic mass of both uptake region, as shown for several experiments in Fig. 7. The change in the normalized organic mass (m_{org}) added to an aerosol exposed to gaseous organic can be described by,

$$\frac{dm_{org}}{dt} = \gamma \pi a^2 <c> C_g \qquad (4)$$

where a, $<c>$ and C_g represent the particle radius, mean molecular speed, and gas phase concentration respectively. Since in these experiments the addition of organic mass to the aerosol results in a negligible increase in particle radius (<1%) from an initial seed diameter of greater than 300 nm, the radius is treated as a constant. Integration of Eq. (4) from $m=m_0$ to $m=m_{org}$ and $t=t_0$ to t where m_0 is the initial organic mass at the beginning of each uptake region and t_0 is the corresponding time, yields

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an equation representing the mass uptake as a function of time

$$M_{org} = kt + C \tag{5}$$

where $k = \gamma g \pi a^2 <c> C_g$ and $C = -kt_0 + m_0$. The uptake coefficient γ is derived from k assuming all other parameters are constant. The density of an appropriate H_2SO_4 so-
lution was used to estimate the mobility diameter and hence a in Eq. (4). For cases where a very high organic mass uptake is observed (Exp. 15 and 16), a similarly derived equation describing the uptake, but accounting for an increasing diameter, is fit to the mass data;

$$m_{org} = \left(\frac{jt - i}{h} \right)^3 - f \tag{6}$$

where $\quad j = \dfrac{3\gamma <c>}{4\rho} \quad i = \dfrac{3\gamma <c> C_g t_0}{4\rho} + 3\left(\dfrac{3m_0}{4\pi\rho} + a_0^3 \right)^{\frac{1}{3}} \quad h = 3\left(\dfrac{3}{4\pi\rho} \right)^{\frac{1}{3}} \quad f = \dfrac{4\pi\rho a_o^3}{3}$

where a_0 and ρ represent the initial seed aerosol radius and the density of the organic mass ($1.4\,\mathrm{g\,cm^{-3}}$). This uptake model has been described previously (Liggio and Li, 2006b). The uptake coefficient (γ) is obtained from the parameter j. For several experiments a slow increase in the organic mass per particle after the initial uptake phase is not observed, and thus uptake coefficients for this region were not determined. This may be a result of changes in RH caused by fluctuations in temperature (not controlled), which alters the aforementioned equilibrium and obscures a typically small irreversible uptake. It may also be the result of a drastically reduced mass accommodation coefficient (α) caused by significant initial uptake of organic mass in some cases.

The relative uncertainty in the k parameter of Eq. (5) or the j parameter of Eq. (6) derived from the fitting procedures ranged from 4 to 35%. This uncertainty, together with those associated with the assumed density, C_g and estimated mobility diameter, results in an overall uncertainty in the uptake coefficients γ approximately 52% (averaged over all γ). Another uncertainty is associated with potential for organosulfate formation. Given that for those experiments in Table 3 a decrease in SO_4 was observed,

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it is possible that a portion of this SO_4 loss was quantified as organic. Consequently, assuming a mass conservation, the total uptake of biogenic species and hence their uptake coefficients (and $K_{p,\text{eff}}$) may be somewhat lower than reported. Nonetheless, the derived uptake coefficients can serve as a useful first approximation for the overall importance of this process.

The derived uptake coefficients for both uptake regions (α or γ) were highly variable ($\alpha \approx 1\times10^{-7}$–$1\times10^{-4}$ and $\gamma \approx 1\times10^{-6}$–$2.5\times10^{-2}$) and are larger for low RH/high acidity experiments than those at higher RH. In all cases, α from the initial phase was at least an order of magnitude larger than γ of the slower uptake region, implying that uptake on fresh acidic aerosol coatings is considerably faster than on a more aged particles. Furthermore, uptake coefficients (α or γ) for oxygenated monoterpenes and sesquiterpenes were significantly larger than those for simple monoterpenes. Currently, there are no other measurements of reactive uptake coefficients or mass accommodation coefficients for these compounds on any surface type; however, the estimated coefficients for simple monoterpenes during the initial uptake are similar to those measured for the α-pinene oxidation product, pinonaldehyde, under otherwise similar conditions (Liggio and Li, 2006b), while γ of the slower uptake region are generally smaller than those of pinonaldehyde. The coefficients for oxygenated terpenes and sesquiterpenes are appreciably larger than those measured previously for pinonaldehyde, and somewhat larger than those of glyoxal on aerosols (Liggio et al., 2005), and other carbonyl species on sulfuric acid films (Iraci and Tolbert, 1997) or bulk solutions (Tolbert et al., 1993). The implications of these uptake coefficients and equilibrium partition coefficients to the ambient atmosphere are discussed in the next section.

3.5 Atmospheric significance

The current experiments suggest that biogenic species, particularly those with functional groups containing oxygen, can be taken up directly to acidic aerosols without the need for prior oxidation in the gas phase, resulting in a large variety of polymeric structures, organic esters and organosulfates. Given the vast array of unsaturated

species present in the atmosphere of both biogenic and anthropogenic origin, it is likely that such processes could contribute significantly to the atmospheric particle burden. The acidic nature of the aerosols in these experiments implies that these heterogeneous processes may be more relevant in the aerosols within power pant plumes,
5 from freshly nucleated H_2SO_4 particles, on pre-existing aerosols which H_2SO_4 has recently condensed, or in the free troposphere where particle acidity is expected to be high. Although the pH of aerosols in the lower troposphere has been reported as ∼3–5 (Hindman et al., 2006; Pszenny et al., 2004) significantly lower aerosol pH values (–2.4–0.2) in range of values used in this study (–1.5 – –0.77), have also been reported
10 on numerous occasions (Ferek et al., 1983; Li et al., 1997; Katoshevski, et al., 1999). This process may also be more important at night, when gas phase oxidant levels are low, and the competing gaseous oxidation of the hydrocarbons is less important or non-existent.

The irreversibility of some of the reactions, as observed by the residual organic after
15 increases in RH (Fig. 3) has implications for the ambient atmosphere. Since increasing the RH in this study did not reduce the organic mass completely, heterogeneous products formed irreversibly at the onset of H_2SO_4 nucleation, or where acidic particles exist, may remain present even if subsequent neutralization or hydration of aerosols occurred. This suggests that typical measured neutral aerosols could also contain a
20 significant amount of heterogeneous products from previous irreversible reactions as described here. Furthermore, equilibrium with water as demonstrated above may explain why attempts to quantify water soluble organic carbon (WSOC) as a measure of heterogeneous processing have been unsuccessful (Peltier et al., 2007); particularly since collection of aerosols in aqueous solvents would inadvertently shift the equilib-
25 rium, and since what large molecular weight irreversible polymers remain after this shift are likely insoluble in water.

The possibility that polymer formation is concentration dependent and enhanced at the high gas phase levels during this study cannot be completely ruled out. However as noted previously, the fast initial uptake and the apparent dependence upon vapour

pressure, make it more likely that mass accommodation is the controlling factor in this process. Also, significant organic uptake was nonetheless measured for several experiments performed under somewhat similar conditions but significantly lower gas-phase organic concentration. For example, experiments 1 and 2 utilizing limonene at significantly different gas-phase concentrations did not have a significant effect on the uptake. In addition, the uptake of gases was observed over a large range of gas phase concentrations spanning 80 ppb to 2.3 ppm. Previous studies of the oligomerization reactions of aldehydes (with a similar rate determining protonation step) in aerosols have also shown that there is no gas-phase concentration dependence for that process (Liggio and Li, 2006b).

The estimates of partitioning coefficients ($K_{P,\text{eff}}$) for monoterpenes and sesquiterpenes may be used to assess the potential for SOA formation via the near steady state processes observed in this study. Whether this steady state actually occurs in the atmosphere is not known. While the complexity of ambient aerosol processing may mean a steady state is never reached, and the applicability of these seed aerosols to the ambient atmosphere may be limited to situations where aerosol acidities are high, calculating $K_{p,\text{eff}}$ and applying it to the real atmosphere may be an instructive exercise, and a useful first step in understanding the importance of this process. Simple mono-terpenes (limonene, β-pinene and 3-carene), although more abundant in the atmosphere, had estimated $K_{p,\text{eff}}$ values significantly smaller (~ 0.4–35×10^6 m^3 μg^{-1}) than other oxygenated terpenes or sesquiterpenes, and did not vary significantly between species at higher RH (~ 1–3×10^6 m^3 μg^{-1}). They are also similar to the $K_{p,\text{eff}}$ values estimated for isoprene and a-pinene (Liggio et al., 2007). If it is assumed that other non-oxygenated monoterpenes behave similarly, the total equilibrium SOA due to direct uptake of monoterpenes is estimated as 3.5–25 ng m^{-3}, assuming ambient aerosol levels of 30 μg m^{-3} (of significant acidity). Ambient gaseous monoterpene levels are somewhat variable but are typically measured in the range of <0.1–2.5 ppb per species (Hakola et al., 2000; Harrison et al., 2001) depending upon location and hence a monoterpene total of 10 ppb was chosen for the above estimation. This SOA bur-

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den is somewhat small, yet it is comparable to measured isoprene oxidation products, such as methyltetrols, and other condensable biogenic species which have been measured in ambient aerosols (Böge et al., 2006; Li and Yu, 2005). Estimation of the SOA forming potential of oxygenated monoterpenes and sesquiterpenes via this process is somewhat more difficult. Although the equilibrium partition coefficients in this study are larger than those of monoterpenes, there are few reported typical ambient gas-phase concentrations for these species, due primarily to technical difficulties associated with their measurement and their very low ambient concentrations. Utilizing the average $K_{p,\text{eff}}$ for the high and low uptake experiments, and a total sesquiterpene/oxygenated terpene mixing ratio of 100 ppt, it is estimated that ∼0.6–25 ng m^{-3} of SOA may be formed at steady state. Under some circumstances mixing ratios significantly greater than 50 ppt for a single oxygenated monoterpene may be possible (Hakola et al., 2000), resulting in the potential for increased SOA mass via this steady state process.

A perhaps more realistic scenario is encountered if it is assumed that a steady state is not achieved, especially if ambient aerosols are intermittently exposed to condensing H$_2$SO$_4$ during their lifetime. In this case, the potential for SOA becomes more significant and can be estimated with the uptake coefficients of Table 2, by calculating a pseudo first order heterogeneous rate constant (k_{het}). This approach has been used on several occasions (Liggio and Li, 2006b; Liggio et al., 2005). Using the mass accommodation coefficient from the initial uptake region k_{het} values of 4.2×10^{-8}–5.1×10^{-6} s^{-1} (simple monoterpenes) and 2.4×10^{-7}–8.9×10^{-4} s^{-1} (oxygenated monoterpenes and sesquiterpenes) were estimated. Such large rate constants also imply that this process may compete as a sink for gas phase species, particularly at night, when low oxidant levels are present. Assuming the same gas phase concentrations as above, these estimates of heterogeneous formation rates may potentially result in 8.7 ng m^{-3}–1.1 μg m^{-3} of organic mass from non-oxygenated monoterpenes and 1.0 ng m^{-3}–2.7 μg m^{-3} from oxygenated monoterpenes and sesquiterpenes in a relatively short time (1 h). Such a particulate organic burden is highly significant. The equivalent estimates utilizing the uptake coefficient from the slower uptake phase

of these experiments resulted in k_{het} for monoterpenes of $4.4{\times}10^{-9}$–$1.3{\times}10^{-7}\,s^{-1}$ and $2.2{\times}10^{-8}$–$2.3{\times}10^{-6}\,s^{-1}$ for oxygenated monoterpenes and sesquiterpenes. These estimates may be more applicable for aged and mixed organic/inorganic aerosols. Although the heterogeneous lifetimes ($1/k_{het}$) associated with k_{het} in this case are too

5 long to be a significant loss mechanism for gas-phase species, they are not unimportant as a source of SOA. Accordingly, 3.6–$105\,ng\,m^{-3}$ of organic mass from monoterpenes and 0.3–$28.0\,ng\,m^{-3}$ from oxygenated monoterpenes and sesquiterpenes may be formed in 4 h. These estimates are highly dependent upon the particle-gas exposure time and the ambient levels of these species, but could result in persistent

10 oligomeric and organosulfate species in aerosols regardless of subsequent processing. Uptake coefficients reported here reflect the self reaction of one species in aerosols; given the vast array of unsaturated olefin containing compounds of natural and anthropogenic origin in the atmosphere, simultaneous uptake on aerosols may lead to mixed and complex oligomeric structures which have not been studied to this point. Nonethe-

15 less, reactive irreversible and reversible uptake of individual compounds is potentially an important contributor to SOA formation.

References

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A

20 generalized method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909–922, 2004.

Böge, O., Miao, Y., Plewka, A., and Herrmann, H.: Formation of secondary organic particle phase compounds from isoprene gas-phase oxidation products: An aerosol chamber and field study, Atmos. Environ., 40, 2501–2509, 2006.

25 Chandramouli, B., Jang, M., and Kamens Richard, M.: Gas-particle partitioning of semivolatile organic compounds (SOCs) on mixtures of aerosols in a smog chamber, Environ. Sci. Technol., 37, 18, 4113–4121, 2003.

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Chwang, W. K., Nowlan, V. J., and Tidwell, T. T.: Reactivity of Cyclic and Acyclic Olefinic Hydrocarbons in Acid-Catalyzed Hydration, J. Am. Chem. Soc., 99, 22, 7233–7238, 1977.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system H-NH4-Na-SO4-NO3-Cl-H2O at 298.15 K, J. Phys. Chem., 102A, 2155–2171, 1998.

Eldering, A., and Cass, G.R.:Source-oriented model for air pollutant effects on visibility, J. Geophys. Res., 101(D14), 19 343–19 369, 1996.

Ferek, R. J., Lazrus, A. L., Haagenson, P. L., and Winchester, J. W.: Strong and weak acidity of aerosols collected over the northeastern United States, Environ. Sci. Technol., 17, 315–324, 1983.

Goldberg, M. S., Burnett, R. T., Valois, M.-F., Flegel, K., Bailar Iii, J. C., Brook, J., Vincent, R., and Radon, K.: Associations between ambient air pollution and daily mortality among persons with congestive heart failure, Environ. Res., 91, 1, 8–20, 2003.

Hakola, H., Laurila, T., Rinne, J., and Puhto, K.: The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site, Atmos. Environ., 34, 4971–4982, 2000.

Hannigan, M. P., Cass, G. R., Penmann, B. W., Crespi, C. L., Lafleur, A. L., Busby Jr., W. F., Thilly, W. G., and Simoneit, B. R. T.: Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a human cell mutagenicity assay, Environ. Sci. Technol., 32, 22, 3502–3514, 1998.

Harrison, D., Hunter, M. C., Lewis, A. C., Seakins, P. W., Bonsang, B., Gros, V., Kanakidou, M., Touaty, M., Kavouras, I., Mihalopoulos, N., Stephanou, E., Alves, C., Nunes, T., and Pio, C.: Ambient isoprene and monoterpene concentrations in a Greek (Abies Borisii-regis) forest. Reconciliation with emissions measurements and efects on measured OH concentrations, Atmos. Environ., 35, 4699–4711, 2001.

Hastings, W. P., Koehler, C. A., Bailey, E. L., and De Haan, D. O.: Secondary Organic Aerosol Formation by Glyoxal Hydration and Oligomer Formation: Humidity Effects and Equilibrium Shifts during Analysis, Environ. Sci. Technol., 39, 8728–8735, 2005.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, L18809, doi:10.1029/2005GL023831, 2005.

Hindman, E. E., Borys, R. D., Lowenthal, D. H., and Phillip, N.: Long-term, wintertime aerosol, cloud and precipitation measurements in the northern Colorado Rocky Mountains, Atmos. Res., 82, 194–202, 2006.

Hoffmann, T.: Adsorptive preconcentration technique including oxidant scavenging for the mea-

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surement of reactive natural hydrocarbons in ambient air, Fres. J. Anal. Chem., 351, 41–47, 1995.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H.: Formation of organic aerosols from the oxidation of biogenic hydrocarbons, J. Atmos. Chem., 26, 189–222, 1997.

Iinuma, Y., Müller, C., Böge, O., Gnauk, T., and Herrmann, H.: The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions, Atmos. Environ., 41, 27, 5571–5583, September 2007.

Iraci, L. T. and Tolbert, M. A.: Heterogeneous interaction of formaldehyde with cold sulfuric acid: implications for the upper troposphere and lower stratosphere, J. Geophys. Res., 102(D13), 16 099–16 107, 1997.

Jang, M., Carroll, B., Chandramouli, B., and Kamens Richard, M.: Particle growth by acid-catalyzed heterogeneous reactions of organic carbonyls on preexisting aerosols, Environ. Sci. Technol., 37, 17, 3828–3837, 2003.

Jang, M. and Kamens, R.: Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, Environ. Sci. Technol., 35, 24, 4758-4766, 2001.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, Aerosol Sci. Technol., 33, 1–2, 49–70, 2000.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res., 108(D7), 8425, doi:10.1029/2001JD001213, 2003.

Katoshevski, D., Nenes, A., and Seinfeld, J. H.: A study of processes that govern the maintenance of aerosols in the marine boundary layer, J. Aerosol Sci., 30, 4, 503–532, 1999.

Kavouras, I. G., Mihalopoulos, N., and Stephanou, E. G.: Secondary organic aerosol formation vs primary organic aerosol emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests, Environ. Sci. Technol., 33, 7, 1028–1037, 1999.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary Organic Aerosol Formation from Isoprene Photooxidation, Environ. Sci. Technol., 40, 6, 1869–1877, 2006.

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Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res., 110, D23207, doi:10.1029/2005JD006004, 2005.

Li, S.-M., Macdonald, A. M., Strapp, J. W., Lee, Y. N., and Zhou, X. L.: Chemical and physical characterizations of atmospheric aerosols over southern California, J. Geophys. Res., 102(D17), 21 341–21 353, 1997.

Li, Y.-C. and Yu, J. Z.: Simultaneous Determination of Mono- and Dicarboxylic Acids, ö-Oxocarboxylic Acids, Midchain Ketocarboxylic Acids, and Aldehydes in Atmospheric Aerosol Samples, Environ. Sci. Technol., 39, 7616–7624, 2005.

Liggio, J. and Li, S.-M.: Organosulfate formation during the uptake of Pinonaldehyde on Acidic Sulfate Aerosols, Geophys. Res. Lett., 33, L13808, doi:10.1029/2006GL026079, 2006a.

Liggio, J. and Li, S.-M.: Reactive Uptake of Pinonaldehyde on Acidic Aerosols, J. Geophys. Res., 111, D24303, doi:10.1029/2005JD006978, 2006b.

Liggio, J., Li, S.-M., Brook, J. R., and Mihele, C.: Direct polymerization of isoprene and α-pinene on acidic aerosols, Geophys. Res. Lett., 34, L05814, doi:10.1029/2006GL028468, 2007.

Liggio, J., Mclaren, R., and Li, S.-M.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res., 110, D10304, doi:10.1029/2004JD005113, 2005.

Limbeck, A., Kulmala, M., and Puxbaum, H.: secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, Geophys. Res. Lett., 30(19), 1996, doi:10.1029/2003GL017738, 2003.

Noziere, B. and Riemer, D. D.: The chemical processing of gas-phase carbonyl compounds by sulfuric acid aerosols: 2,4-pentandione, Atmos. Environ., 37, 841–851, 2003.

Pankow, J. F.: An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, Atmos. Environ., 28, 2, 189–193, 1994.

Peltier, R. E., Sullivan, A. P., Weber, R. J., Wollny, A. G., Holloway, J. S., Brock, C. A., Gouw, J. A. D., and Atlas, E. L.: No evidence for acid-catalyzed secondary organic aerosol formation in power plant plumes over metropolitan Atlanta, Georgia, Geophys. Res. Lett., 112, D10S18, doi:10.1029/2006JD007515, 2007.

Pilinis, C., Pandis, S. N., and Seinfeld, J. H.: Sensitivity of direct climate forcing by atmospheric aerosols to aerosol size and composition, J. Geophys. Res., 100(D9), 18, 739–754, 1995.

Pszenny, A. A. P., Moldanova', J., Keene, W. C., Sander, R., Maben, J. R., Martinez, M., Crutzen, P. J., Perner, D., and Prinn, R. G.: Halogen cycling and aerosol pH in the Hawaiian

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marine boundary layer, Atmos. Chem. Phys., 4, 147–168, 2004,
http://www.atmos-chem-phys.net/4/147/2004/.

Shi, Q., Davidovits, P., Jayne, J. T., Worsnop, D. R., and Kolb, C. E.: Uptake of gas-phase ammonia. 1. Uptake by aqueous surfaces as a function of pH, J. Phys. Chem., 103, 8812–8823, 1999.

Slebocka-Tilk, H. and Brown, R. S.: Acid-Catalyzed Hydration of anti-sesquinorbornene, J. Org. Chem., 61, 8079–8082, 1996.

Steinbacher, M., Dommen, J., Ammann, C., Spirig, C., Neftel, A., and Prevot, A. S. H.: Performance characteristics of a proton-transfer-reaction mass spectrometer (PTR-MS) derived from laboratory and field measurement, Int. J. Mass Spectrom., 239, 117–128, 2004.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for Organosulfates in Secondary Organic Aerosol, Environ. Sci. Technol., 41, 2, 517–527, 2007.

Tolbert, M. A., Pfaff, J., Jayaweera, I., and Prather, M. J.: Uptake of formaldehyde by sulfuric acid solutions: Impact on stratospheric ozone, J. Geophys. Res., 98(D2), 2957–2962, 1993.

Wade, L. G.: Organic chemistry, Prentice Hall, Upper Saddle River, Englewood Cliffs, N. J., 2003.

Table 1. Initial gas and aerosol parameters associated with each experiment.

Exp.#	Species	[Gas]^a (ppm)	RH (%)	Initial Seed Aerosol Composition (moles kg^{-1})^b	Initial Aerosol pH	Initial Diam. (nm) ($\pm\sigma$)^c
Monoterpenes						
1	Limonene	2.3	1.6	H$^+$=33.2 HSO$_4^-$=34.1 SO$_4^{2-}$=0.82 NH$_4^+$=2.5	−1.52	463 (4.6)
2	Limonene	0.40	3.1	H$^+$=28.0 HSO$_4^-$=28.1 SO$_4^{2-}$=1.0 NH$_4^+$=2.1	−1.45	482 (2.0)
3	Limonene	1.1	18.8	H$^+$=15.8 HSO$_4^-$=13.6 SO$_4^{2-}$=1.7 NH$_4^+$=1.1	−1.19	517 (3.4)
4	Limonene	1.4	45.8	H$^+$=10.0 HSO$_4^-$=6.8 SO$_4^{2-}$=1.9 NH$_4^+$=0.63	−1.0	527 (4.2)
5	β−pinene	1.8	3.3	H$^+$=27.5 HSO$_4^-$=27.5 SO$_4^{2-}$=1.0 NH$_4^+$=2.1	−1.43	468 (2.5)
6	β−pinene	1.8	17.1	H$^+$=16.4 HSO$_4^-$=14.3 SO$_4^{2-}$=1.6 NH$_4^+$=1.15	−1.21	515 (3.9)
7	β−pinene	1.8	24.2	H$^+$=14.3 HSO$_4^-$=11.7 SO$_4^{2-}$=1.8 NH$_4^+$=1.0	−1.16	476 (2.9)
8	β−pinene	1.8	54.2	H$^+$=8.7 HSO$_4^-$=5.5 SO$_4^{2-}$=1.9 NH$_4^+$=0.53	−0.94	503 (3.6)
9	3-Carene	1.0	2.4	H$^+$=29.7 HSO$_4^-$=30.1 SO$_4^{2-}$=0.93 NH$_4^+$=2.2	−1.47	498 (3.5)
10	3-Carene	1.1	40.0	H$^+$=11.0 HSO$_4^-$=7.9 SO$_4^{2-}$=1.9 NH$_4^+$=0.71	−1.04	491 (4.4)
11	3-Carene	1.0	73.0	H$^+$=5.9 HSO$_4^-$=3.3 SO$_4^{2-}$=1.5 NH$_4^+$=0.35	−0.77	491 (2.7)
12	Linalool	0.08	1.4	H$^+$=34.3 HSO$_4^-$=35.4 SO$_4^{2-}$=0.79 NH$_4^+$=2.6	−1.54	464 (4.8)
13	Linalool	0.42	47.5	H$^+$=9.7 HSO$_4^-$=6.5 SO$_4^{2-}$=1.9 NH$_4^+$=0.61	−0.99	517 (5.0)
14	Geraniol	0.03	2.1	H$^+$=30.8 HSO$_4^-$=31.4 SO$_4^{2-}$=0.88 NH$_4^+$=2.3	−1.49	506 (5.4)
Sesquiterpenes						
15	β−Caryophyllene	0.15	1.4	H$^+$=34.2 HSO$_4^-$=35.2 SO$_4^{2-}$=0.78 NH$_4^+$=2.6	−1.53	473 (6.8)
16	β−Caryophyllene	0.10	1.8	H$^+$=32.3 HSO$_4^-$=33.1 SO$_4^{2-}$=0.84 NH$_4^+$=2.5	−1.51	486 (4.4)
17	β−Caryophyllene	0.19	18.8	H$^+$ = 15.8 HSO$_4^-$ = 13.5 SO$_4^{2-}$ = 1.7 NH$_4^+$ = 1.1	−1.20	517 (3.1)
18	β−Caryophyllene	0.20	55.5	H$^+$=8.5 HSO$_4^-$=5.4 SO$_4^{2-}$=1.8 NH$_4^+$=0.52	−0.93	523 (4.3)
19	α−Humullene	0.12	1.4	H$^+$=34.3 HSO$_4^-$=35.4 SO$_4^{2-}$=0.79 NH$_4^+$=2.6	−1.54	488 (6.3)
20	α−Humullene	0.30	66.5	H$^+$=6.9 HSO$_4^-$=4.0 SO$_4^{2-}$=1.7 NH$_4^+$=0.41	−0.84	498 (3.0)
21	Nerolidol	0.64	2.5	H$^+$=29.5 HSO$_4^-$=29.9 SO$_4^{2-}$=0.93 NH$_4^+$=2.2	−1.47	511 (7.0)

^{a} Mean of the measurements during the experiment.
^{b} Based on equilibrium thermodynamic calculation (Clegg et al., 1998).
^{c} Initial mean vacuum aerodynamic diameter as measured by the Q-AMS.

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Table 2. Measured organic mass uptake and calculated uptake parameters.

Exp No.	Gas Phase Species	Org Mass[a] ($\mu g\,m^{-3}$)	SO$_4$ Mass[a] ($\mu g\,m^{-3}$)	Org/part.[b] (g)×10^{16} (±σ)	SO$_4$/part[c] (g)×10^{16} (±σ)	$K_{p,eff}$[d] (m$^3\mu g^{-1}$)×10^6 (±σ)	α[e] ×10^5 (±σ)	γ[f] ×10^7 (±σ)
1	Limonene	5.0	60.6	41.3 (4.6)	377.6 (20.0)	4.3 (1.1)	2.6 (1.3)	6.6 (3.0)
2	Limonene	4.9	137.2	25.0 (4.1)	678.8 (24.0)	12.3 (7.5)	5.4 (2.4)	36.5 (16.6)
3	Limonene	1.25	76.8	5.0 (3.5)	447.6 (32.7)	1.5 (1.0)	0.9 (0.6)	–
4	Limonene	1.0	49.0	2.4 (4.7)	661.9 (33.0)	0.61 (1.0)	–	–
5	β−pinene	9.7	116.8	81.5 (9.0)	589.3 (16.6)	8.7 (1.4)	4.1 (1.9)	45.5 (20.4)
6	β−pinene	1.29	51.6	11.5 (2.0)	427.1 (28.3)	2.0 (0.57)	0.30 (0.16)	0.87 (0.49)
7	β−pinene	0.77	77.7	3.2 (1.3)	371.4 (27.2)	0.4 (0.13)	0.11 (0.07)	1.1 (0.56)
8	β−pinene	1.2	60.0	7.4 (1.8)	301.8 (18.1)	1.4 (0.4)	0.12 (0.06)	1.1 (0.53)
9	3-Carene	23.6	100.2	91.7 (5.5)	408.0 (21.0)	35.5 (6.2)	12.6 (5.8)	–
10	3-Carene	2.8	47.7	7.3 (5.8)	387.0 (26.4)	2.9 (2.0)	1.6 (0.9)	–
11	3-Carene	2.6	94.0	5.4 (1.7)	281.0 (18.0)	2.7 (1.2)	0.28 (0.16)	1.1 (0.50)
12	Linalool	63.3	59.7	456.8 (26.5)	476.8 (20.4)	1161 (282)	881 (403)	–
13	Linalool	0.99	57.9	6.4 (4.1)	421.2 (25.4)	4.3 (1.6)	0.71 (0.38)	4.4 (2.0)
14	Geraniol	21.9	80.8	104.4 (7.3)	345.8 (32.4)	1260 (216)	435 (196)	255.7 (198)
15	β−Caryophyllene	546	79.6	5305 (289)	316.2 (11.8)	761.8 (130)	2568 (1600)	739 (432)
16	β−Caryophyllene	69.4	65.0	849.1 (61.8)	388.7 (15.9)	774.1 (150)	422 (212)	980 (550)
17	β−Caryophyllene	7.6	79.1	49.0 (3.6)	369.6 (25.1)	58.1 (9.6)	12 (6.5)	41.7 (18.7)
18	β−Caryophyllene	1.5	77.4	8.7 (3.1)	437.5 (23.8)	10.5 (2.1)	1.1 (0.55)	6.0 (2.9)
19	α−Humulene	114.8	70.1	1393 (89.0)	452.3 (30.6)	810.3 (144.9)	535 (247)	–
20	α−Humulene	1.1	72.7	4.9 (1.1)	351.5 (11.9)	1.8 (0.7)	–	8.7 (3.9)
21	Nerolidol	13.7	52.6	82.7 (7.4)	417.8 (27.1)	34.2 (6.7)	17.3 (10)	–

[a] Maximum mass as measured by the Q-AMS, neglecting particle wall losses.

[b] Organic mass normalized by AMS number concentration, near the end of the experiment (mean over the last 30 min).

[c] Sulfate mass normalized by AMS number concentration at the end of the experiment, where no decrease in sulfate mass was observed. Where a decrease in SO$_4$ per particle was observed a value prior to gas phase addition is reported.

[d] Assuming a near steady state was reached at the end of the initial fast uptake.

[e] Assuming uptake is controlled by mass accommodation in the fast initial phase (i.e.: $\gamma \approx \alpha$).

[f] Calculated from the slow increase in organic mass after an initial fast uptake. A slow increase in organic mass per particle was not always observed (refer to text).

Table 3. Inorganic to organosulfate conversion during biogenic gas uptake experiments.

Exp No.	Species	Oxygenated or Pure Hydrocarbon	Fraction SO_4 Conversion (%) ($\pm\sigma$)	Fraction of Organic (%)($\pm\sigma$)
1	Limonene	Pure hydrocarbon	9.5 (7.3)	76.6 (60.3)
5	β–pinene	Pure hydrocarbon	12.5 (6.3)	73.6 (37.0)
9	3-Carene	Pure hydrocarbon	10.6 (8.4)	43.2 (34.1)
12	Linalool	Oxygenated hydrocarbon	45.6 (12.3)	46.1 (12.5)
14	Geraniol	Oxygenated hydrocarbon	17.3 (11.4)	54.3 (35.6)
15	β–Caryophyllene	Pure hydrocarbon	57.1 (11.0)	3.4 (0.64)
16	β–Caryophyllene	Pure hydrocarbon	29.5 (12.2)	12.2 (5.0)
19	α–Humullene	Pure hydrocarbon	37.8 (9.5)	12.5 (3.1)
21	Nerolidol	Oxygenated hydrocarbon	12.9 (8.7)	74.6 (51.0)

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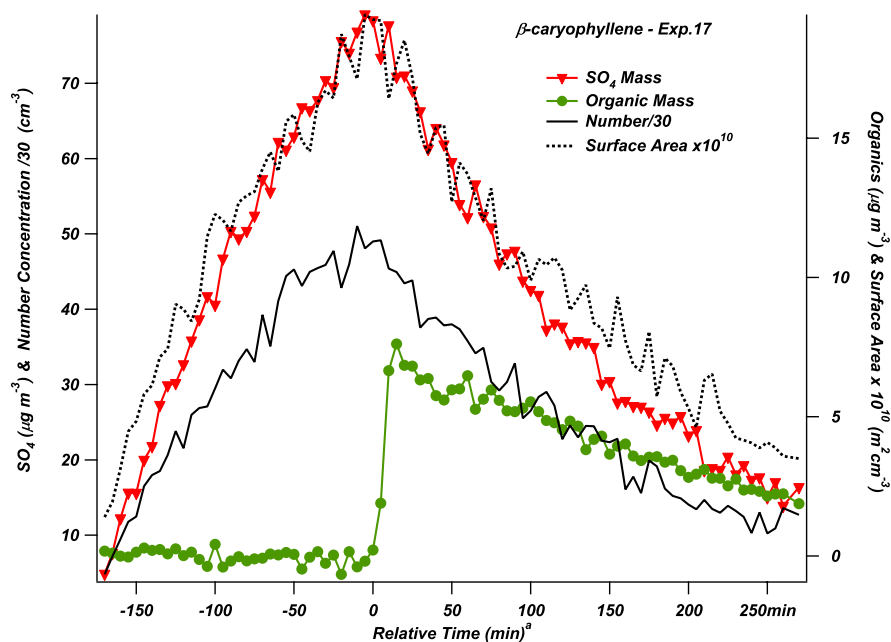
Fig. 1. Example of the time dependent mass loading curves (SO_4 and Organics), particle number concentration and total surface area for the uptake of biogenic species. Time=0 indicates the injection of the olefin into the chamber.

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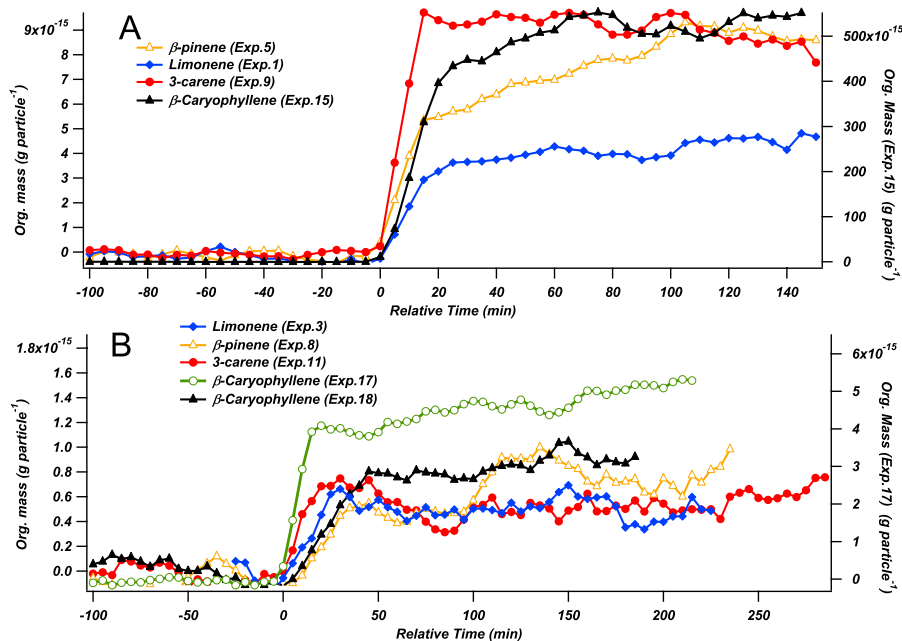
Fig. 2. Time dependent normalized organic mass (per particle) for selected experiments.

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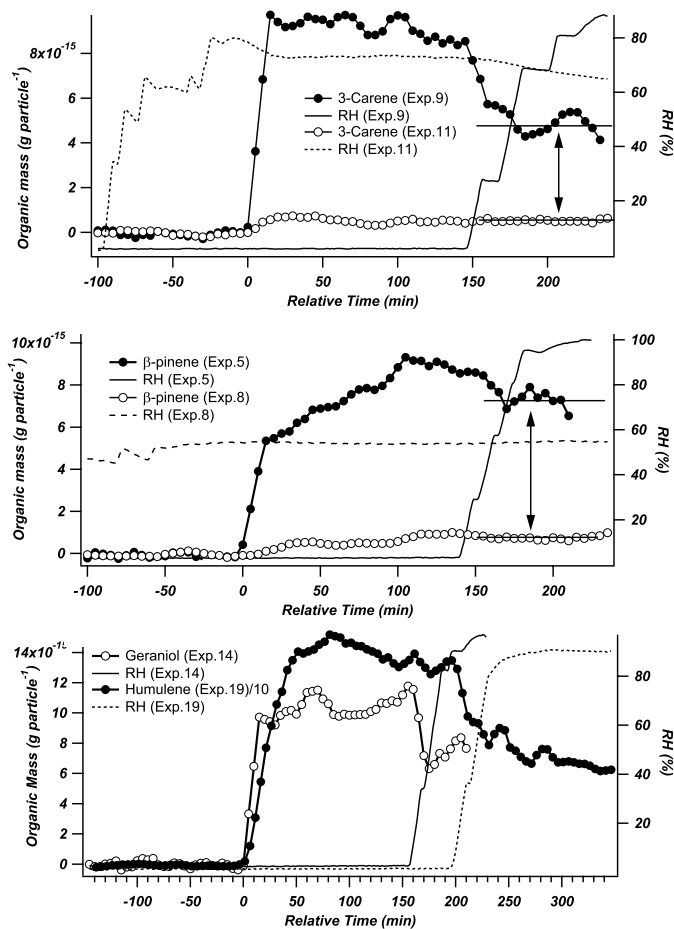
Fig. 3. Effect of increasing RH after initial uptake on the per particle normalized organic mass for selected experiments.
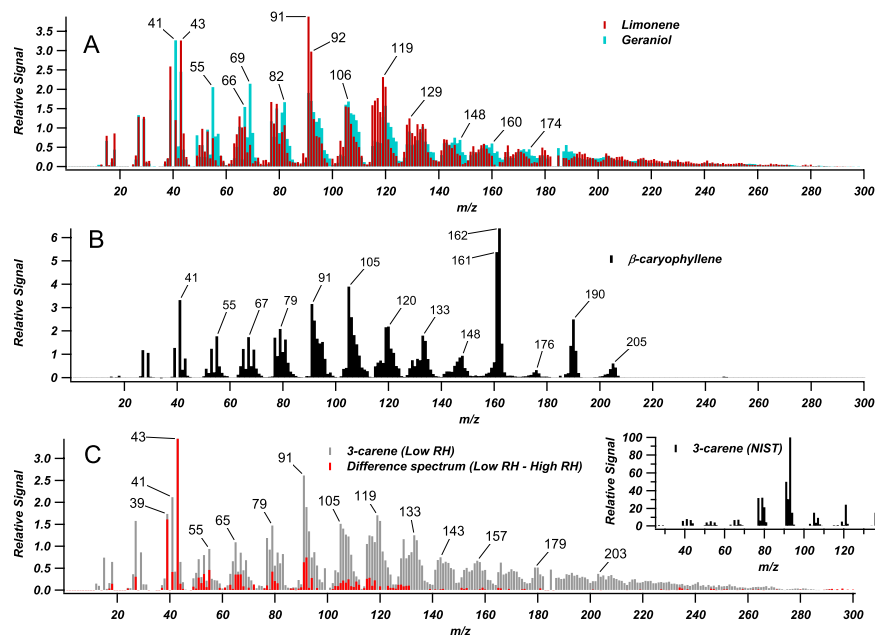
Fig. 4. Aerosol mass spectra for monoterpenes uptake products of limonene (A), β–caryophyllene (B), oxygenated monoterpene geraniol (A), collected near the end of a given experiment. Aerosol spectra for 3-carene products of experiment 9, where RH was increased and the relative spectra of the mass spectral difference (Low RH – High RH) (C). NIST EI mass spectra of pure 3-carene.

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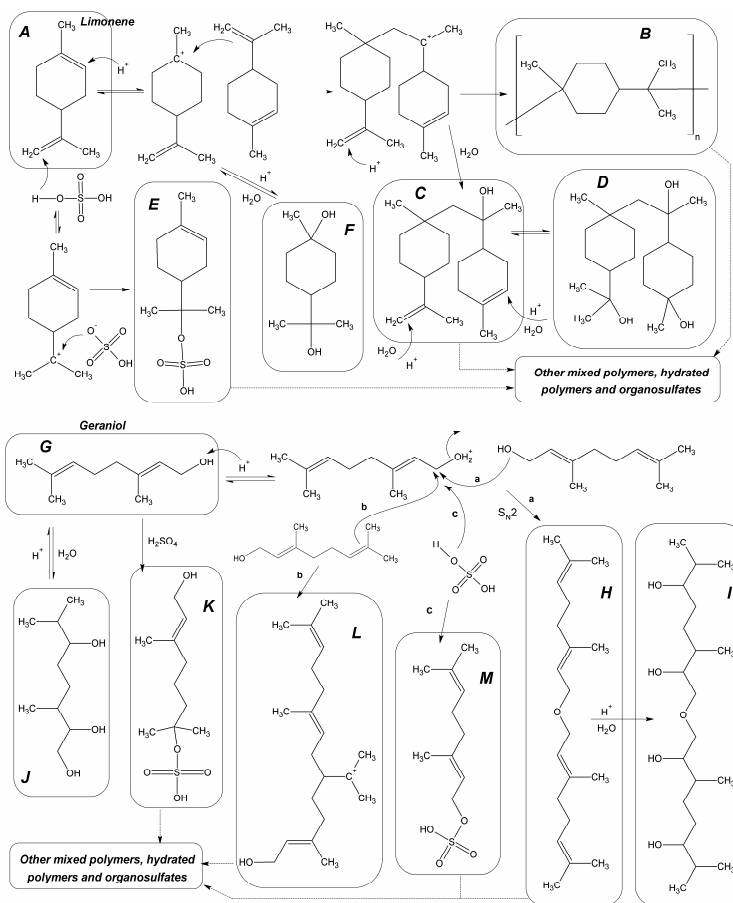
Fig. 5. Potential mechanism leading to heterogeneous products of limonene and geraniol.
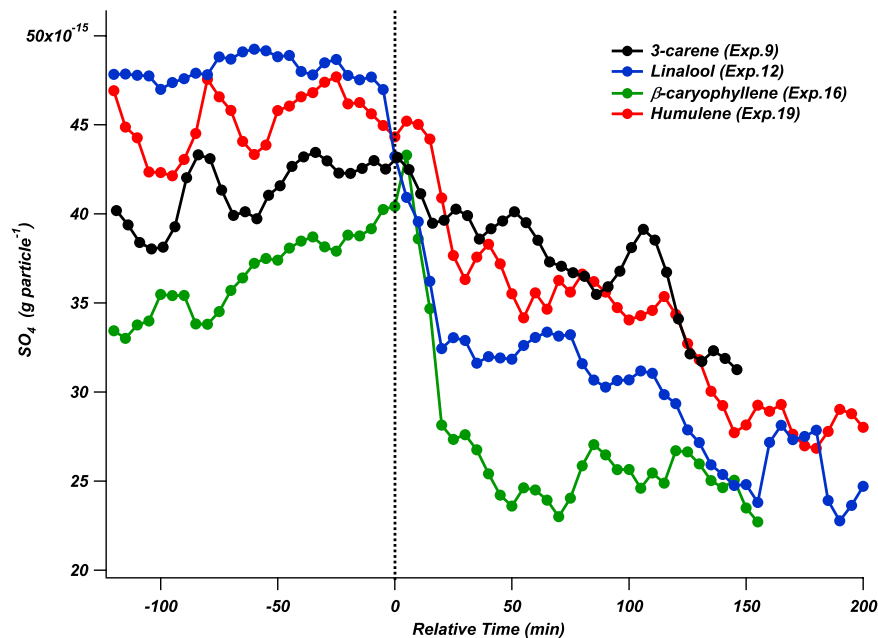
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Fig. 6. Decrease in the AMS measured SO_4 (per particle) after the addition of the biogenic gas (time=0) for selected experiments, suggesting the formation of organosulfates.

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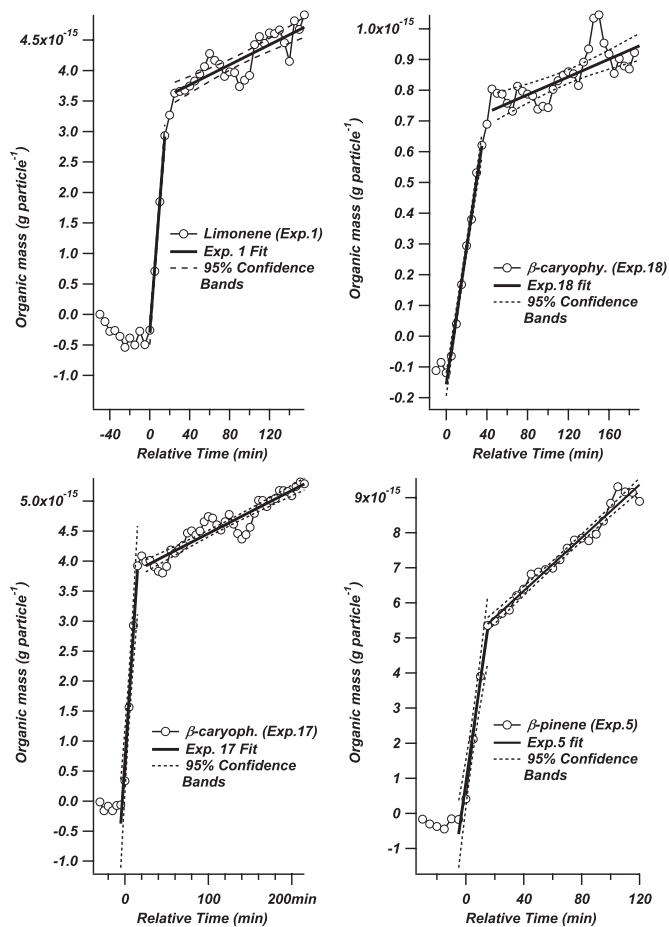
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Fig. 7. Selected fits of uptake model to the organic mass per particle for the initial uptake phase and subsequent slow increase. Fit parameters were used to determine uptake coefficients.