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Experimental study of the formation of organosulfates from α-pinene oxidation. Part II: Time evolution and effect of particle acidity

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Abstract

The present work is an extensive laboratory study of organosulfate (OS) formation from the reaction of α-pinene oxidation products or proxies with acidified ammonium sulfate aerosols in three different acidity conditions ($(NH_4)_2SO_4$ 0.06 M; $(NH_4)_2SO_4/H_2SO_4$ 0.06 M/0.005 M; $(NH_4)_2SO_4/H_2SO_4$ 0.03 M/0.05 M). The kinetics of the reactions of α-pinene, α-pinene oxide, isopinocampheol, pinanediol and myrtenal with ammonium sulfate particles were studied using a quasi-static reactor. The reaction of α-pinene oxide with the highly acidic ammonium sulfate particles was determined to be 7, 10, 21 and 24 times faster than for isopinocampheol, α-pinene, pinanedial and myrtenal, respectively for an OS precursor concentration of 1 ppm and after 1h reaction time. The effective rate coefficients for OS formation from α-pinene oxide were determined to be two orders of magnitude higher in highly acidic conditions than for the two other acidity conditions. For α-pinene oxide reactions with highly acidic ammonium sulfate particles, OS formation was observed to increase linearly with (i) the time of reaction up to 400 minutes ($r^2 > 0.95$) and (ii) α-pinene oxide gas-phase concentration. However, OS formation from α-pinene oxide reactions with slightly acidic or pure ammonium sulfate particles was limited, with a plateau ($[OS]_{max} = 0.62 \pm 0.03$ µg) reached after around 15-20 minutes. Organosulfate dimers (*m/z* 401 and *m/z* 481) were detected not only with highly acidic particles but also with slightly acidic and pure ammonium sulfate particles, indicating that oligomerization processes do not require strong acidity conditions. Dehydration products of organosulfates (*m/z* 231 and *m/z* 383) were observed only under highly acidic conditions, indicating the key role of H_2SO_4 on the dehydration of organosulfates and the formation of olefins in the atmosphere. Finally, this kinetic study was completed with simulation chamber experiments in which mass concentration of organosulfates was shown to depend on the available sulfate amount present in the particle phase ($r^2 = 0.96$). In conclusion, this relative comparison between 5 organosulfate precursors shows that epoxide was the most efficient reactant to form organosulfates via heterogeneous gas-particle reactions and illustrates how gas-particle reactions may play an important role in OS formation and hence in the atmospheric fate of organic carbon. The kinetic data presented in this work provides strong support to organosulfate formation mechanisms proposed in the companion paper.

Introduction

Atmospheric particulate matter (PM) is known to play a key role in affecting climate change and air quality, leading to adverse health impact.[1–4] Atmospheric oxidation of biogenic volatile organic compounds (BVOCs) play a significant role in the formation of secondary organic aerosols (SOAs).[4] Biogenic secondary organic aerosols (BSOAs) contribute to a significant mass fraction of the fine particulate matter ($PM_{2.5}$) measured in several locations.[4] Despite ongoing improvements and the use of more sophisticated techniques, the insufficient knowledge of the composition of organic aerosol particles at the molecular level hinders a better understanding of the sources, formation and atmospheric processes of organic aerosol.[5]

Organosulfates (OSs) are ubiquitous in atmospheric aerosol particles and have been detected in ambient aerosols in various sites around the world.[6–21] OSs have been identified in laboratory experiments in the presence of acidified sulfate aerosol from various VOCs including isoprene,[6,22] monoterpenes, [6,7,22–24] sesquiterpenes,[25] polycyclic aromatic hydrocarbons,[8] or alkanes.[26] These studies have shown the key role of acidity in enhancing both SOA and OS formation. OSs may represent an important fraction of ambient organic aerosols, estimated to contribute up to 30 % of the PM_{10} organic mass.[22,27] Their highly oxygenated and sulfated chemical structure suggests that their presence may modify aerosol hygroscopicity leading to larger potential climate impact through formation of cloud condensation nuclei (CCN).[28] OS formation mechanisms have also been proposed in laboratory studies for oxidized BVOCs such as pinonaldehyde,[29] glyoxal,[30] α-pinene oxide,[23,24] β-pinene oxide,[23] isoprene epoxydiols (IEPOX),[31,32] or pinanediol.[24] During the last decade, a particular attention has been paid to epoxide compounds and related studies have highlighted that organosulfates are most likely formed from acid-catalysed reaction of epoxides with inorganic sulfate aerosol. [20,22,30–37] Few kinetic studies of organosulfate formation were conducted[33–35] and it was found experimentally in bulk aqueous solutions that epoxide reactions with sulfuric acid are kinetically favored over those of alcohols or aldehydes.[34,36,37] Kinetics studies of the aqueous-phase reactions of several monoterpenes epoxides (i.e. α-pinene oxide, β-pinene oxide, limonene oxide) have demonstrated that all of these epoxides will react more rapidly than isoprene epoxydiols in aqueous atmospheric particles, even under low-acidity conditions.[35,38] Some organosulfate formation pathways have been proposed in these studies, such as the esterification of hydroxyl or keto groups,[28,29] the acid-catalyzed ring-opening of epoxides,[23,34,36,39] radical-initiated processes in

aqueous aerosols,[40,41] or the nucleophilic substitution of organonitrates.[33] It is now crucial to gain further insights into mechanistic and kinetic processes describing OS formation.

In a recent companion study,[24] a new experimental approach has been described to perform simple and various experiments under controlled and repeatable conditions, to study heterogeneous processes at the gas-particle interface. Mechanisms describing organosulfate formation from α-pinene, α-pinene oxide, isopinocampheol , myrtenal and pinanediol have been proposed. Here, an extensive kinetic study of organosulfate formation from α-pinene oxide reactions with acidified ammonium sulfate aerosol was performed using a quasi-static reactor in quasi-dry conditions. These simplified experimental conditions were selected to specifically investigate the gas-surface reaction of a series of oxygenated VOCs with sulfate particles as a first step of the multiphasic process of reactive uptake. Kinetics information on heterogeneous formation of organosulfates was investigated, for the first time, with this approach in complement to previous studies focused on bulk reactions.[33–38,42] Effect of particle acidity on organosulfate formation is discussed. Complementary experiments in more atmospherically relevant conditions were performed in an atmospheric simulation chamber. In both experimental approaches, the gaseous phase was characterized by Proton Transfer Reactor - Time of Flight - Mass Spectrometer (PTR-TOF-MS). Organosulfate formation in the particle-phase was investigated by Liquid Chromatography combined with Electrospray Ionization (ESI) Mass Spectrometry (LC/ESI-MS) or with ESI High-Resolution – Time of Flight - Mass Spectrometry (LC/ESI-HR-QTOFMS) for structural elucidation. In this work, time evolutions of organosulfate formation from four other BVOCs (α-pinene, isopinocampheol, pinanediol and myrtenal) are also presented and compared.

Experimental section

Quasi-static reactor experiments

The experimental approach using a quasi-static reactor was developed to the study of heterogeneous processes at the gas-particle interface. The experimental set-up and procedure were described in detail and fully validated in the recent companion article.[24] With this set-up, heterogeneous reactions were investigated under pseudo-first order conditions, as demonstrated in each experiment by on-line monitoring of the gas phase composition

using PTR-TOF-MS. Briefly, experiments are based on the exposure of aerosols, deposited on a filter in a quasi-static reactor, to a continuous flow of a single volatile organic compound (VOC) under pseudo-first order conditions. VOC flow was generated by flushing nitrogen (N_2) into a bubbler of pure liquid compound. The VOC concentration (0.1 – 10 ppm) was then diluted in oxygen (O_2) and N_2, with a final O_2 concentration near 20 % of the mixture. O_2 (99.9990 % purity, Linde Gas SA) and N_2 (99.9990 % purity, Linde Gas SA) flows were controlled using mass flow controllers. Reactions were performed in complete darkness, at atmospheric pressure and ambient temperature (295 ± 2 K). The detailed experimental conditions are given in Table 1. Inorganic aerosols were generated by atomizing (using a TSI model 3075 through a diffusion dryer (TSI, model 3062)) an aqueous solution containing the seed aerosol constituents as presented in Table 1 and were collected on 47-mm PTFE filters (Millipore, Fluoropore™, 0.2 µm FG). The three different aerosol acidities were generated by varying the composition of the atomization solutions to investigate the effect of aerosol acidity on organosulfate formation. Prior to experiments, particles were further dried during an optimized 5 min-exposure to an orthogonal 1 L min^{-1} flow of nitrogen. The drying efficiency of the procedure was controlled by weighting the particles (on a filter). The drying step was considered to be achieved when the particle mass was checked to be stable within the instrumental uncertainty of a daily calibrated microbalance (i.e. 0,0001 g corresponding to 2-3 % of the total particle mass).

Experiments were thus considered to be performed in quasi-dry conditions (RH < 1 ± 1 %). Meanwhile, it should be specified that a small residual amount of water may still be present in the particles, especially in the case of acidified particles due to the well-known strong hygroscopic properties of sulfuric acid.

Table 1. Experimental conditions of organosulfate formation in the quasi-static reactor for kinetic study. HA : highly acidic aerosols, SA : slightly acidic aerosols, NA : non-acidified aerosols

VOC	no. of experiment series	[VOC] (ppm)	Inorganic aerosol	Composition of atomized solution (M)	Acidity conditions	T (K)	Reaction time (min) (n experiments)
α-pinene oxide	R0	3.30 ± 0.1	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	295 ± 2	0-400 (n = 37)
α-pinene oxide	R1	1.00 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05		295 ± 2	0-200 (n = 8)
α-pinene oxide	R6	3.30 ± 0.1	$(NH_4)_2SO_4/H_2SO_4$	0.06/0.005	SA	295 ± 2	0-90 (n = 43)
α-pinene oxide	R7	1.65 ± 0.03	$(NH_4)_2SO_4/H_2SO_4$	0.06/0.005		295 ± 2	0-90 (n = 13)
α-pinene oxide	R8	0.82 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.06/0.005		295 ± 2	0-90 (n = 10)
α-pinene oxide	R9	0.33 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.06/0.005		295 ± 2	0-60 (n = 5)
α-pinene oxide	R10	3.30 ± 0.1	$(NH_4)_2SO_4$	0.06	NA	295 ± 2	0-60 (n = 16)
α-pinene	R2	1.00 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	295 ± 2	0-90 (n = 7)
isopinocampheol	R3	1.00 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	295 ± 2	0-90 (n = 7)
pinanediol	R4	1.00 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	295 ± 2	0-90 (n = 7)
myrtenal	R5	1.00 ± 0.02	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	295 ± 2	0-60 (n = 6)

After generation via aqueous solution atomization and drying using an aerosol diffusion dryer (TSI 3062), inorganic seed aerosols, deposited on a filter, were introduced in the reaction cell and exposed to the $VOC/O_2/N_2$ flow for a specific reaction time. The gas-phase constituents were monitored by PTR-TOF-MS (Kore Technology) all along the experiments. At the end of the reaction, the cell was purged with N_2 and aerosols were recovered, extracted and dissolved in 3 mL of acetonitrile (ACN) by sonification during 15 min in the presence of an internal standard, stored at - 18 °C and analyzed within 3 months.

Chamber experiments

Organosulfate formation from α-pinene oxide reactions was also studied in more atmospherically relevant conditions in the CESAM chamber (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber). The CESAM chamber was designed to study multiphasic atmospheric (photo-)chemistry and has been described in detail elsewhere.[43] Briefly, this facility consists of a cylindrical 4.2 m^3 double walled stainless steel chamber. Both temperature and relative humidity (RH) were measured with HMP234 Vaisala® humidity and temperature transmitter equipped with a capacitive thin film polymer sensor Humicap®. The circulation of

a cooling liquid at a suitable temperature regulated by a 10 kW thermostat (LAUDA, Integral T10000 W) was allowed to circulate between the double walls of the chamber in order to maintain the inner temperature during the experiment in the range (293 – 295) K between experiment, with a stability better that 1 K within the course of a single experiment (Table 1).

Experiments were carried out under dark conditions and at atmospheric pressure. Initial experimental conditions are described in Table 2. Between each experiment, the chamber was cleaned by maintaining a secondary vacuum ($\sim 6 \times 10^{-4}$ hPa) overnight. The chamber was then filled with synthetic air produced from a mixture of ~ 200 hPa of O_2 (Air Liquide, Alphagaz class 1) and ~ 800 hPa of N_2 generated from the evaporation of pressurized liquid nitrogen (Messer, purity > 99.995%). Inorganic seed aerosols were introduced into the chamber by atomizing (using a TSI model 3075 through a diffusion dryer (TSI, model 3062)) a solution containing the seed aerosol constituents presented in Table 2. Particle size distributions (20-980 nm diameter) were measured with a Scanning Mobility Particle Sizer (SMPS) composed of a TSI 3080 Differential Mobility Analyzer (DMA) and a TSI 3010 Condensation Particle Counter (CPC), assuming a particle density of 1 g cm^{-3}. Then, injection of α-pinene oxide (Sigma-Aldrich, 97 % purity) was performed by introducing a precisely known partial pressure of the compound (± 0.1 mbar) prepared in a bulb of known volume (V = 2.90516 L) from a frozen pure standard solution using a vacuum gas manifold. The bulb content was then immediately flushed with N_2 into the chamber. The concentration of α-pinene oxide was monitored using a Fourier-Transform Infrared Spectrometer (FTIR) from Bruker™ Tensor 37®. The total optical path length for the in-situ FTIR measurements was set to 192 m. In addition to FTIR, the gas-phase composition was also monitored by a PTR-TOF-MS from Kore Technology. Each reaction was studied for 3 hours. The mass concentration data from the experiments performed in the CESAM chamber were treated using a new algorithm developed recently by Lamkaddam et al.[44] The data could be corrected for both the dilution and the aerosol physical wall losses. These wall losses were corrected using a size dependent deposition rate coefficient parameterized using the model proposed by Lai and Nazaroff.[45]

Temporal profiles of organosulfate formation were investigated by collecting filters sampled every 25 min throughout the experiments (6 filters collected and labelled F_1-F_6). In parallel, organosulfate formation was also characterized by a filter sample collected over the entire time of the experiments (labelled F_{tot}). Aerosol

sampling was achieved by using 47-mm PTFE filters (Millipore, Fluoropore™, 0.2 µm FG). Before the VOC injection, inorganic seed aerosols were collected during 25 min onto a blank filter. The filter holders were installed downstream of an activated charcoal denuder, which was used to trap reactive gases and reduce positive sampling artefacts. The filter collection was performed at a flow rate of 3 L min^{-1}. The filters were extracted in 3 mL of ACN during 15 min of ultrasonic agitation and the final extracts were kept at -18°C and analyzed within 3 months.

Table 2. Summary of chamber experiment initial conditions; HA : highly acidic particles, SA : slightly acidic particles, NA : non-acidified particles

Experiment #	Hydrocarbon	Initial [VOC] (ppb)	Seed aerosol	Composition of atomized solution (M)	Acidity conditions	Initial seed particle mass (µg m^{-3})	T (K)	RH (%)
C1	α-pinene oxide	117	$(NH_4)_2SO_4/H_2SO_4$	0.03/0.05	HA	18.5	294 ± 1	< 1 ± 1
C4	α-pinene oxide	116	$(NH_4)_2SO_4/H_2SO_4$	0.003/0.005	HA	23	293 ± 1	< 1 ± 1
C7	α-pinene oxide	116	$(NH_4)_2SO_4/H_2SO_4$	0.06/0.005	SA	25	294 ± 1	< 1 ± 1
C8	α-pinene oxide	132	$(NH_4)_2SO_4$	0.06	NA	19	295 ± 1	< 1 ± 1

Sample preparation and analysis

The detailed extraction procedure and operating conditions of the analytical method have been previously described in the companion article[24] and hence, will only be presented briefly here.

As described above, filter samples were extracted in 3 mL of acetonitrile (HPLC Grade, JT Baker) during 15 min of ultrasonic agitation. Then, extracts were filtered by centrifugation using PTFE filters (Ultrafree-MC, PTFE Membrane, 0.22 µm) and concentrated to about 50 µL under a gentle N_2 stream (99.995 % purity, Linde Gas SA) at 40 °C. Syringe standard (Octanoïc acid ^{13}C, Isotec, 99 %) was added to the samples for quantification of the internal standard before analysis. This double quantification allows the calculation of internal standard recovery yields and hence to check that internal standards, and therefore organosulfates, are not lost along the analytical workup procedures. Internal standard recovery yields were higher than 80 % for all samples analyzed in the present work. Filter extracts were analyzed by LC/ESI-MS and by HPLC(-)ESI-HR-QTOFMS. Chromatographic conditions and mass spectrometry parameters have already been presented

in the companion article.[24] All products were detected as their deprotonated ions (i.e. $[M - H]^-$). Camphor sulfonic acid (Sigma Aldrich 98 %) was used as an internal standard for quantification of organosulfates due to the lack of commercially available authentic standards for organosulfates. Although the use of surrogate compounds adds some uncertainty to the absolute quantification of OS, it does provide access to reliable information on relative variations and time-trends.[46] Analyses were carried out only if the conditions required for analysis (absence of contamination in the blank samples, sensitivity and response factors within 15 % of the optimized conditions) were fulfilled. Calibration solutions were injected before each analysis sequence and about every 10 samples to calculate the internal standard response factors. Organosulfate functional groups were identified by LC/ESI-HR-QTOFMS from their fragmentation ions SO_3^- (m/z = 79.9574), SO_4^- (m/z = 95.9523) or HSO_4^- (m/z = 96.9601).

Results and discussion

As shown in the companion article[24], the sum of organosulfates formed from α-pinene oxide was much higher than from the other VOCs studied under similar experimental conditions. Thus, kinetic experiments focused here primarily on the α-pinene oxide reaction. Temporal variations of organosulfate concentrations from other VOC experiments are also compared and discussed.

Organosulfate formation from α-pinene oxide – Quasi-static reactor experiments

Pseudo-first order conditions

The gas phase concentration of α-pinene oxide was checked to be constant by on-line monitoring using PTR-TOF-MS measurements along all experiments, demonstrating pseudo-first order kinetic conditions. Moreover, the total gas flow (dilution flow = 3.5 L min^{-1} and α-pinene oxide bubbler flow = 0.04 – 0.10 L min^{-1}) in the reaction cell was always higher than 3.5 L min^{-1}, leading to a VOC residence time in the reactor < 1 s, minimizing the VOC wall loss. Figure 1 presents the time monitoring of ions by PTR-TOF-MS at *m/z* 153 ($C_{10}H_{17}O^+$), 135 ($C_{10}H_{15}^+$) and 21 ($H_3{}^{21}O^+$) in two experiments ($t_{reaction}$ = 30 min) performed (a) in highly acidic conditions and (b) in slightly acidic conditions. As presented in Figure S1a, *m/z* 153 and *m/z* 135 are characteristic PTR-TOF-MS fragments of α-pinene oxide. Nonetheless, a change in the (*m/z* 153)/(*m/z* 135) ratio was observed when highly acidic aerosols were exposed to gaseous α-pinene oxide (Figure 1a). Alpha-pinene oxide isomerization reaction has already been evidenced in previous studies under acidic conditions, forming campholenic aldehyde.[23,47] The formation of campholenic aldehyde is highly suspected in this work but was not confirmed in the present experiments, both isomers (campholenic aldehyde and alpha-pinene oxide) having the same PTR-TOF-MS fragments under our experimental conditions (Figures S1a and S1b). Nonetheless, it is worth nothing that this different ratio is consistent with the observed different ion distribution for campholenic aldehyde, as shown in Figure S1. Under slightly acidic or neutral conditions, a change in the (*m/z* 153) / (*m/z* 135) ratio was never observed, suggesting that the isomerization reaction is catalyzed under acidic conditions.

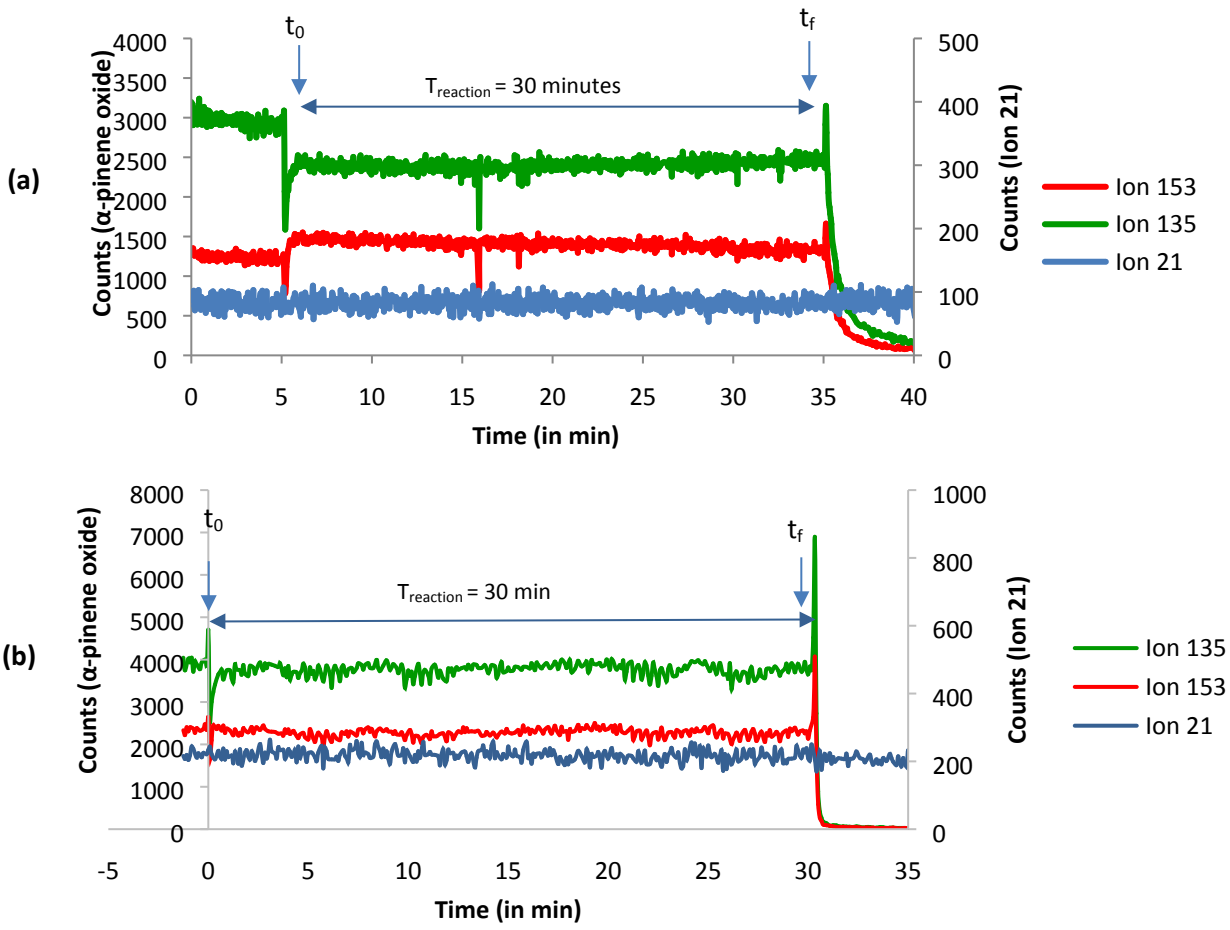


Figure 1. Typical evolution of *m/z* 153, *m/z* 135 and *m/z* 21 ($H_3{}^{18}O^+$) ions by PTR-TOF-MS during an experiment in quasi-static reactor between α-pinene oxide (3.30 ppm) and ammonium sulfate aerosol under (a) highly acidic conditions and under (b) slightly acidic conditions – t_0 is the time when the VOC flow was introduced in the reaction cell and t_f was the time when the VOC flow was stopped.

Organosulfate formation

Overall, 132 experiments were performed in the present work to study the heterogeneous organosulfate formation from α-pinene oxide under three different acidic conditions. Various α-pinene oxide concentration levels (0.3-3.3 ppm) were tested for reaction times ranging from 0 to 400 min. As shown in the companion article,[24] more than 15 organosulfate (OS) products, including organosulfate dimers (DiOS) and trimers (TriOS) were formed from α-pinene oxide under highly acidic conditions. The chromatograms and MS/MS fragmentation patterns allowing the identification of the organosulfates formed from α-pinene oxide are fully described and discussed in light of previous studies in the companion article.[24] Table 3 summarizes the mass

of organosulfates detected in these experiments. As an example, the OS masses detected in these experiments after 1 hour of reaction are also presented in Table 3.

In all conditions, the two main organosulfates *m/z* 249 (i.e. OS 249 (1) and OS 249 (2)) have already been reported in some previous laboratory studies.[22,23,48] Note that these two compounds were not detected in a previous study in bulk aqueous solution by Bleier and Elrod (2013)[38] who detected a single organosulfate formed from the ring opening of α-pinene oxide using ^{1}H and ^{13}C NMR characterization. Both OS 249 (1) and OS 249 (2) were also reported from various ambient aerosol analyses.[14,22,46,47] However, a very recent study based on the comparison of possible α-hydroxy OS products formed from pinanediol and α-pinene oxide to two regioisomers synthesized authentic standards evidenced that the compounds detected in a set of 18 ambient samples were not formed through SN2 reactions of α-pinene oxide with H_2O or H_2SO_4[49] yielding to the conclusion that epoxides may not be the precursors of ambient bicyclic organosulfates.

In this work, the OS 249 monomers as well as the organosulfate dimers (*m/z* 401, OS 401 and *m/z* 481, OS 481) were also detected under "slightly acidic" and "non-acidified" conditions, indicating that oligomerization processes do not require strong acidity conditions. Dehydration products of OS 249 (*m/z* 231, MW 232) and OS 401 (*m/z* 383, MW 384) were observed only under highly acidic conditions, indicating the key role of H_2SO_4 as both a strong acid and a strong hygroscopic reactant, on the dehydration of organosulfates and the formation of olefins in the atmosphere. Particle-phase dehydration of cyclic[50] and non-cyclic[51] hemiacetal compounds as well as organosulfates[29] was already observed to occur and lead to the formation of olefins in the presence of highly acidic or sulfuric acid particles. Consistently, this reaction was shown to be favored under low relative humidity conditions[51]. Hemiacetals or organosulfates dehydration products are unsaturated and hence more reactive towards atmospheric oxidants such as OH radicals, NO_3 radicals, or O_3. Dehydration may thus affect in very specific (i.e. highly acidic and quasi-dry) conditions both the oxidation state and the reactivity of aerosols in the atmosphere. No organosulfate trimer was observed under slightly acidic conditions or with non-acidified ammonium sulfate aerosols. Table S1 presents the molecular structures proposed for the products identified in α-pinene oxide experiments, performed under different aerosol acidities (Table 3).[24] The total organosulfate mass formed under highly acidic conditions was two orders of magnitude more abundant than those obtained under slightly acidic or neutral conditions. For the highly acidic aerosols, water may still

be present due to the highly hygroscopic nature of H_2SO_4[52] allowing H^+ to drive the reaction. This emphasizes the key role of H^+ ions in organosulfate formation in the atmosphere. Nonetheless, organosulfate formation did occur with non-acidified ammonium sulfate aerosols ($(NH_4)_2SO_4$ at 0.06 M) showing that acidity from NH_4^+ is sufficient to allow ring-opening of epoxide, in agreement with what was previously reported by Nguyen et al.[32]

Table 3. Organosulfate masses (in ng) quantified in quasi-static reactor experiments from α-pinene oxide (3.3 ppm) using camphor sulfonic acid as an internal standard; HA : highly acidic particles, SA : slightly acidic particles, NA : non-acidified particles.

Detected organosulfates	Highly acidic condition (HA) [a] (in ng) (R0)	Slightly acidic condition (SA) [b] (in ng) (R6)	Non-acidified condition (NA) [c] (in ng) (R10)
OS 231	0 – 1700 (190 ± 60)[d]	-	-
OS 249 (1)	0 – 50 480 (14 110 ± 200)[d]	0 – 740 (740)[d]	0 – 605 (511)[d]
OS 249 (2)	0 – 64 150 (8255 ± 910)[d]	0 – 1 430 (1430)[d]	0 – 570 (790)[d]
Σ DiOS 401	0 – 26 660 (5350 ± 1870)[d]	0 – 200 (59)[d]	0 – 60 (24)[d]
Σ DiOS 481	0 – 19 410 (3550 ± 120)[d]	0 – 20 (8)[d]	0 – 5 (2)[d]

[a] Reaction time: 0 – 400 min; [b] Reaction time: 0 – 90 min; [c] Reaction time: 0 – 60 min; [d]Mass of organosulfates detected after 60 min of reaction (for R0, n = 3; for R6 and R10, n = 1)

OS 249 (1) and OS 249 (2) were the two main organosulfates present at approximatively the same concentrations under highly acidic conditions, contrary to previous observations in chamber experiments by Iinuma et al.[23], where OS 249 (2) was the only main product. In their study, the authors suggested that the dominance of the secondary carbon-substituted organosulfate indicates that sulfation reactions compete with isomerization reactions leading to campholenic aldehyde and hence to a third *m/z* 249 organosulfate, identified as campholenol hydrogen sulfate (Figure S2). Previously, Liggio et al.[29] had also observed organosulfate formation from the reactive uptake of pinonaldehyde on acidic sulfate particles and proposed a formation mechanism via the protonation of the carbonyl group followed by the nucleophilic attack of HSO_4^-. Under our experimental conditions and as discussed previously, campholenic aldehyde was highly suspected to be formed in the gas phase (according to PTR-TOF-MS measurements). However, the continuous renewal of the gas phase in the flow reactor cell may prevent from campholenic aldehyde accumulation in the flow reactor cell and hence limit the occurrence of the gas-surface formation of a third *m/z* 249 organosulfate which was not detected in quasi-static reactor experiments. This is also in good agreement with the results reported by Iinuma

et al.[23] who have shown that the reaction yield of heterogeneous organosulfate formation from aldehydes may be low.

Temporal profiles of organosulfate formation

Organosulfate temporal profiles are presented in the following section. These profiles were found to strongly depend on the particle acidity.

"Highly acidic" (HA) conditions

37 experiments (R0, Table 1) and 8 experiments (R1, Table 1) were carried out with 3.3 ppm and 1.0 ppm of α-pinene oxide respectively, to describe the kinetics of organosulfate formation from α-pinene oxide. Under highly acidic conditions, the concentrations increase linearly, with reaction time for all observed products, and may be described by the equation (1).

$$[\boldsymbol{OS}] = \boldsymbol{k_{eff}} \times \boldsymbol{t} \quad (1)$$

As an example, Figure 1 presents the temporal profiles of OS 249 (2) organosulfate formation. The experimental data points were fitted using a linear regression ($r^2 > 0.99$), showing that the reaction rate was constant over the reaction time. As presented previously, the concentration of α-pinene oxide was constant under our experimental conditions. The first step of the organosulfate formation is supposed to be the protonation of the epoxide as presented in Figure S2. Thus, if this protonation is considered as the rate limiting step, a simple kinetic equation can be proposed in a first approach:

$$\boldsymbol{v} = \boldsymbol{k'}[\boldsymbol{APO}][\boldsymbol{H}^+] = \frac{\boldsymbol{d}[\boldsymbol{OS}]}{\boldsymbol{dt}} \quad (2)$$

with k' = the rate coefficient (in cm^3 $molecule^{-1}$ s^{-1}) of the protonation of α-pinene oxide. As observed in the experiments, the OS formation rate shows that both reactants are in constant (stationary) concentrations under our experimental conditions, allowing Equation (2) to be reduced to (3):

$$\frac{\boldsymbol{d}[\boldsymbol{OS}]}{\boldsymbol{dt}} = \boldsymbol{k_{eff}} \quad (3)$$

With k_{eff} = k' [APO] $[H]^+$ (in molecule cm^{-3} s^{-1})

From this kinetic behavior, as demonstrated by the linear plots of the reaction product formation shown in Figure 2a, it is assumed that H^+ was also present in excess. More, the k_{eff} values are shown to vary linearly with α-pinene oxide concentrations (Figure 2b). This result is well described by the kinetic equation presented previously, where k_{eff} is proportional to the α-pinene oxide concentration under our experimental conditions. As it can be seen in Figure S3a, the effective rate coefficient determined for OS 249 (1) formed concomitantly to OS 249 (2) from the same set of experiments was found to vary between each of the 7 series of experiments performed with 3.3 ppm of α-pinene oxide. Linear fit slopes varied daily from 0.13 to 0.34 ($r^2 > 0.95$ for 6 series of experiments). During their preparation, particles were thoroughly dried prior to reaction allowing experiments to be carried out under quasi-dry conditions in the quasi-static reactor. Nonetheless, as explained previously, it cannot be excluded that the particle water content may have varied daily within the uncertainties of the balance used for the particle mass control (2-3 % of the particle mass). This small residual amount of water in the particles seems to have a critical role in OS 249 (1) formation pathway. Further investigation would be very useful to gain insight on this issue.

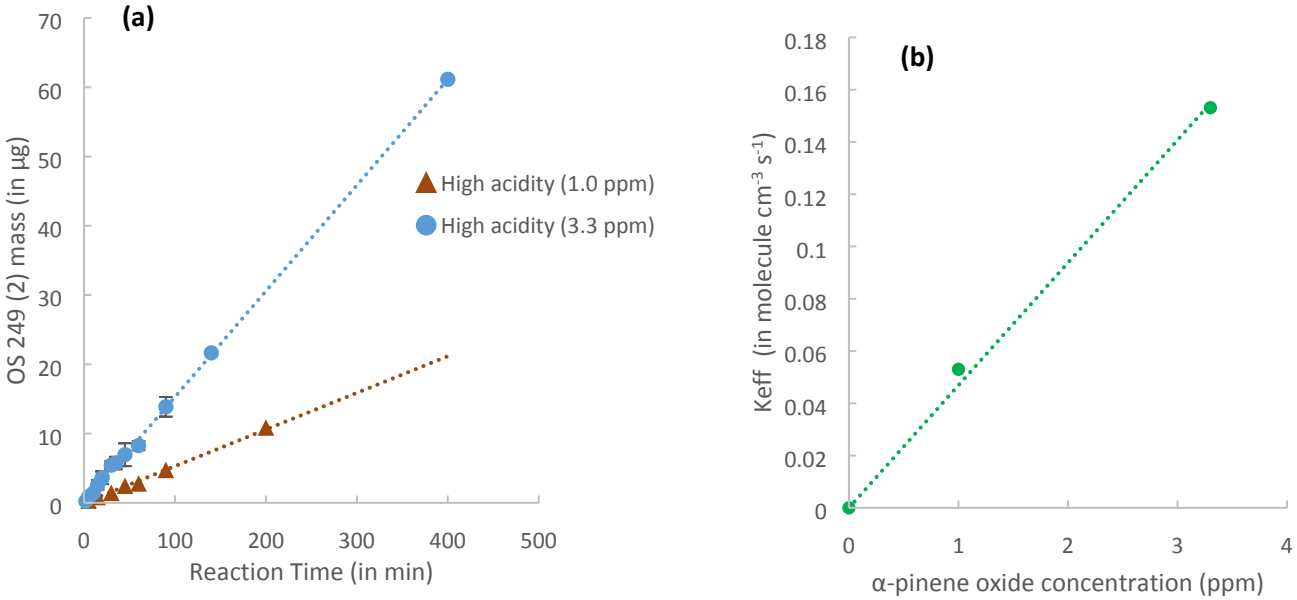


Figure 2. (a)Temporal profiles of *m/z* 249 (2) organosulfate formation under highly acidic conditions, (b) Keff values in function of α-pinene oxide concentrations

The temporal profiles of *m/z* 401 and *m/z* 481 organosulfate dimers are shown in Figures S3c and S3d. First, the oligomerization processes start very rapidly (within the first minutes of reaction) since organosulfate dimers were detected in the particle phase after only 2 minutes of reaction. As presented in Figure 3, the concentration of the sum of *m/z* 401 organosulfate dimers is highly correlated to that of OS 249 (1) ($r^2 = 0.92$). In the proposed mechanism (see the companion article and Figure S2), the main *m/z* 401 organosulfate (TR 21.3 min, representing from 65 to 80 % of the total concentration of ∑DiOS 401) is assumed to be formed via the addition of OS 249 (2) on a tertiary carbocation intermediate (in the red dashed box, Figure S2), formed from the protonation of α-pinene oxide. This tertiary carbocation intermediate, also directly involved in the formation of OS 249 (1), is assumed to be highly sensitive to the presence of water. Thus, the high correlation between concentrations of OS 249 (1) and the sum of *m/z* 401 organosulfate dimers from day to day (Figure S3) firmly supports the proposed mechanism in the companion article.[24]

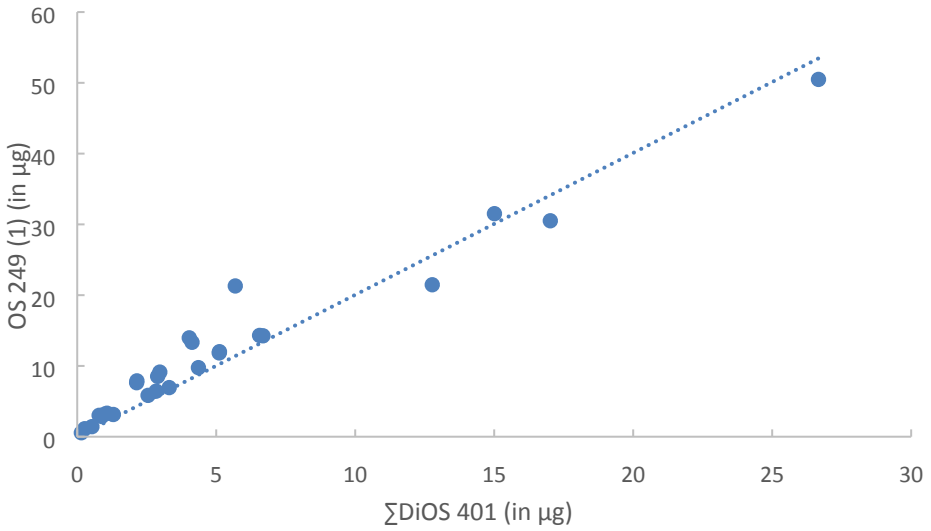


Figure 3. Correlation between OS 249 (1) formation and ∑DiOS 401 formation from α-pinene oxide under highly acidic conditions.

Nonetheless, when α-pinene oxide concentration was decreased from 3.3 ppm to 1.0 ppm, the effective reaction rate coefficients for OS 249 (1) and for ∑diOS 401 were estimated to be from (2.5 to 6.2) and (2.5 to 7.1) times lower, respectively. This suggests that the proposed kinetic model (as described in equation (2)) may also be valid for OS 249 (1) and diOS 401. Interestingly, *m/z* 481 DiOS were formed in approximatively the same concentrations in experiments performed with 1.0 ppm and 3.3 ppm of α-pinene oxide (Figure S3c), illustrating

that the effective rate for the formation of these products does not depend on α-pinene oxide concentration in the gaseous phase.

"Slightly acidic" (SA) and "non-acidified" (NA) conditions

In total, 71 experiments were carried out at various α-pinene oxide concentrations: 3.30 ppm (n = 43), 1.65 ppm (n = 13), 0.82 ppm (n = 10) and 0.33 ppm (n = 5) to gain further insights on the kinetics of organosulfate formation under slightly acidic conditions. As presented in Table 1, 16 experiments were also performed in this work in the presence of non-acidified ammonium sulfate aerosols. High variability of DiOS temporal profiles was observed due to levels near the detection limit and they are therefore not presented. Figure 4 summarizes the temporal profiles of OS 249 (1) obtained under "slightly acidic" and "non-acidified" conditions. The experimental variability of the data points describing the OS 249 (1) formation is in agreement with the results presented above and may be tentatively explained as proposed by the variation of the residual amount of water in the particles. The experiments carried out with 3.3 ppm of α-pinene oxide show that the formation of OS is limited under low acidity conditions, with a plateau reached ($[OS]_{max}$ = 0.62 µg) after around 15-20 minutes. The value of the plateau represents the OS maximum concentration formed under our experimental conditions. OS 249 (2) mass reached up to 1.4 µg (Table 3), a plateau value higher than for OS 249 (1) (contrary to the results obtained in highly acidic conditions), evidencing that acidity is a key parameter not only for global kinetics but also for the mechanistic pathways leading to organosulfate formation.

As OS formation was not limited with highly acidic particles, the plateau observed here with slightly acidic or non-acidified particles was not attributed to the presence of a very viscous organic phase or to phase-separated aerosols[53] but rather to the amount of protons available for reactions. A simple kinetics approach was proposed to model the formation of OS 249 (1): data points were fitted using a first order exponential function, defined as follows:

$$[OS](t) = [OS]_{max} \times (1 - e^{-k't}) \quad (4)$$

where [OS](t) is the organosulfate concentration formed on the particles, $[OS]_{max}$ the maximum organosulfate concentration and k' the pseudo-first order rate coefficient of the reaction. The fitting parameters are extracted from the Figure 4. Note that experiments performed at lower VOC concentrations could not be fitted using the

same parameter values, either because of the experimental variability of the data points or because the kinetic model is not appropriate. As a matter of fact, the plateau could also result from an equilibrium between organosulfate formation and reverse reaction or dimer formation. Further experiments will be needed to gain further insights on the kinetics of heterogeneous formation of organosulfate from α-pinene oxide, especially as a function of aerosol surface area.

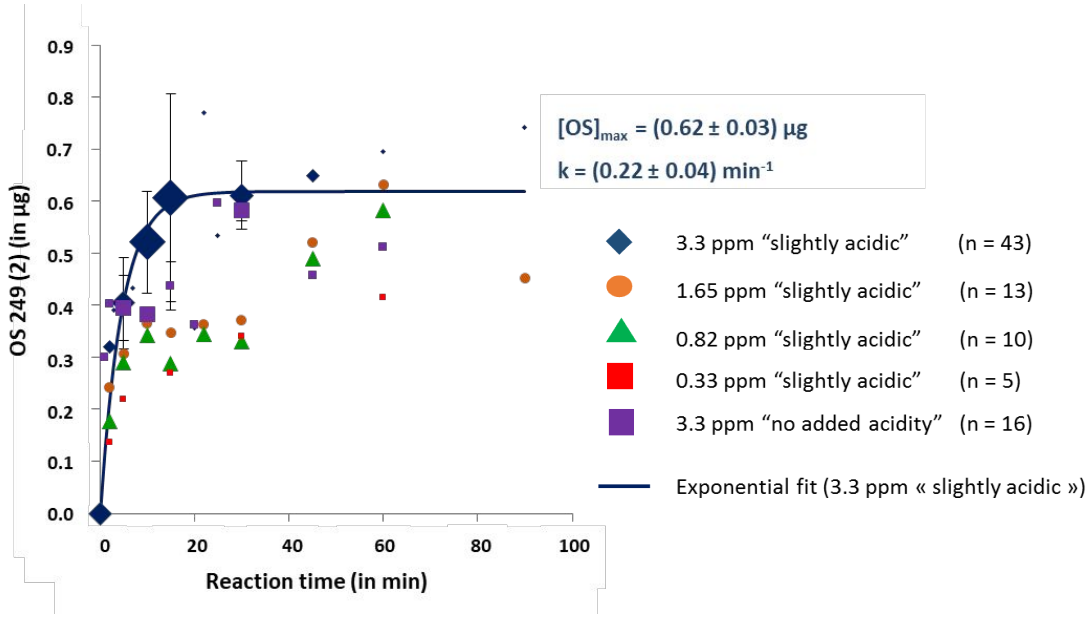


Figure 4. Temporal mass profiles of OS 249 (1) obtained in slightly acidic conditions and in the presence of sulfate ammonium aerosols - The size of data represents the number of experiments (ranging from 1 to 11)

Finally, the time profiles of organosulfate formation in "slightly acidic" or "no-added acidity" conditions were very similar, probably because of the low concentration of sulfuric acid in the "slightly acidic" conditions. This strongly suggests that in both conditions, the protonation of α-pinene oxide to form the first intermediate occurs mostly via reaction with NH_4^+, in agreement with Nguyen et al.[32] It would be interesting to carry out further experiments by varying the amount of NH_4^+ to firmly support the role of this ion.

In complement to these measurements in the quasi-static reactor, some experiments were carried out in atmospheric simulation chamber.

Organosulfate formation from α-pinene oxide – chamber experiments

Gas phase

Depending on experimental conditions, a decrease of about 10 to 50 % of α-pinene oxide concentration in 60 minutes was measured in the CESAM chamber, with or without particles. This unusually fast wall loss (even for an oxygenated compound) was attributed to isomerization processes on the metallic wall surface. PTR-TOF-MS data measurements displayed a decrease of the *m/z* 135 fragment signal as well as an increase at *m/z* 153. Thus, formation of campholenic aldehyde or other isomerization products of α-pinene oxide were assumed to occur in CESAM. Previous studies have reported the isomerization of α-pinene oxide using Fe-supported catalysts[54] and CESAM stainless steel wall might play a role in this particular reaction. However, α-pinene oxide was found to be stable in CESAM chamber under humid conditions (RH = 20 % and RH = 50 %)[24], highlighting that the α-pinene oxide loss was influenced by the presence of condensable species such as water. Note that cyclohexene oxide (Sigma Aldrich, 98 %) was found to be stable in the CESAM chamber, showing that wall loss was specific to α-pinene oxide, corroborating that this loss was likely due to isomerization. It is worth noting that the α-pinene oxide loss to the CESAM chamber walls cannot be explained by memory effects from prior experiments conducted in the presence of acidic sulfate aerosol because the chamber walls were manually cleaned with purified water and ethanol and by maintaining a secondary vacuum ($\sim 6 \times 10^{-4}$ hPa) overnight.

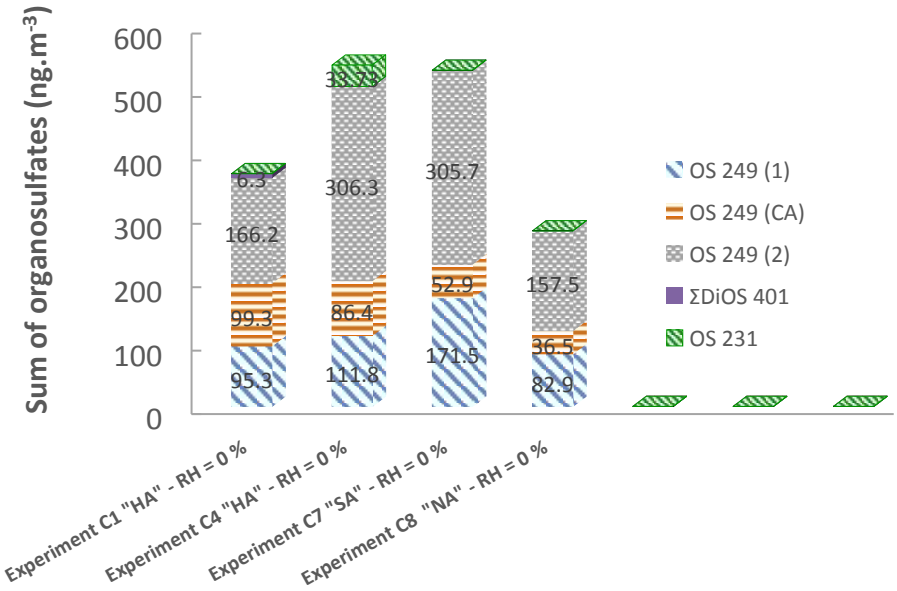
The amount of α-pinene oxide which reacted on particles was roughly inferred from the total amount of organosulfate formed in the chamber. From this calculation and the concentration of α-pinene oxide measured in the gas-phase, it could be estimated that about 0.05 % of the initial gaseous α-pinene oxide had reacted on particles. It was thus considered that regardless of the wall loss, gaseous α-pinene oxide was present in a large excess during the experiments in CESAM and hence that OS formation occurred under pseudo-first order conditions.

Organosulfate formation

Figure 5a summarizes organosulfate concentrations (in ng m^{-3}) measured in the aerosol phase obtained in CESAM when α-pinene oxide was introduced in the presence of sulfated aerosols. No clear increase of the particle mass concentration was observed in the experiments with an initial seed aerosol mass of about 20 µg

m^{-3}, regardless of the aerosol acidity conditions (experiments C1, C7 and C8). Considering the wide size distribution of the seed particles in these 3 experiments, the uncertainty associated to the measurements of particle mass concentration using SMPS (about 1 μg m^{-3}) hindered to detect any aerosol mass growth related to organosulfate formation (Figure 5a). However, in experiment C4, the aqueous solution containing the seed aerosol constituents was diluted by a factor 10, resulting in the introduction of smaller particles in the chamber. Under these specific experimental conditions, a clear increase of about 3 μg m^{-3} in the particle mass concentration was observed (Figure S4) along the experiment, suggesting that α-pinene oxide may be an effective organosulfate precursor especially in region area dominated by trees which largely emit monoterpenes. It is worth noting that OS 249 have been observed in many regions of the world[14,15,22,23,46], suggesting that OS formation from α-pinene oxide occurs under ambient conditions, although their exact structures were recently discussed[49].

(5a)



(5b)

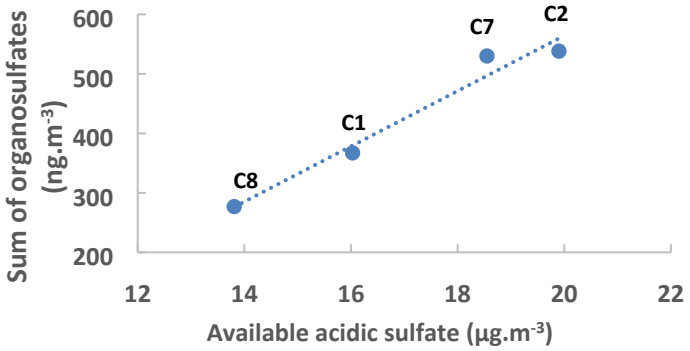


Figure 5. (a) Sum of organosulfates and (b) organosulfate mass concentrations as a function of the available acidic sulfate concentration in the particle phase for α-pinene oxide experiments in the CESAM chamber

Interestingly, organosulfate concentrations are of the same order of magnitude in all experiments performed without water vapor injection, independently of the presence of acidified sulfate aerosols (Figure 5a), contrary to the results obtained from quasi-static reactor experiments or in previous works.[6,39] As previously shown for monoterpene oxides in chamber[23] and bulk solution[34] experiments, formation yields of organosulfates were shown to depend on the available sulfate concentration. In agreement with these studies, Figure 5b displays the relationship between the total OS concentration and the sulfate aerosol concentration, highlighting the importance of the available surface area in heterogeneous reactions. Further investigation involving total aerosol surface area and condensation sink did not allow us to provide a straightforward relationship with OS formation amounts.

It is also worth noting that the concentration of OS 249 (CA) from campholenic aldehyde was increased when increasing the particle acidity. As reported in Figure 5a, the concentration of this organosulfate (99 ng m^{-3} for C1 and 86.4 ng m^{-3} for C4) is more important under highly acidic conditions than under slightly (53 ng m^{-3} for C7) or non-acidified ones (37 ng m^{-3}), suggesting that α-pinene oxide isomerization is favored under acidic conditions. Moreover, the OS 249 (1)/OS 249 (CA) concentration ratio was decreased with increasing acidity (HA: 1.0 (C1) and 0.8 (C4); SA: 0.3 (C7); NA: 0.4 (C8)), suggesting the competition for the tertiary carbocation intermediate between isomerization and HSO_4^- attack, as proposed in the formation mechanism (Figure S2). An example of temporal profiles of organosulfate formation in CESAM is presented in Figure S5. In the 4 experiments, organosulfates were formed rapidly in the first few minutes and reached a threshold value independently of the particle acidity, suggesting that the available aerosol surface area is a key parameter in these heterogeneous processes. Temporal variations were similar for all other experiments, showing no effects of acidity on the dynamics of organosulfate formation under these experimental conditions.

Organosulfate formation from other precursors - comparison of temporal variations

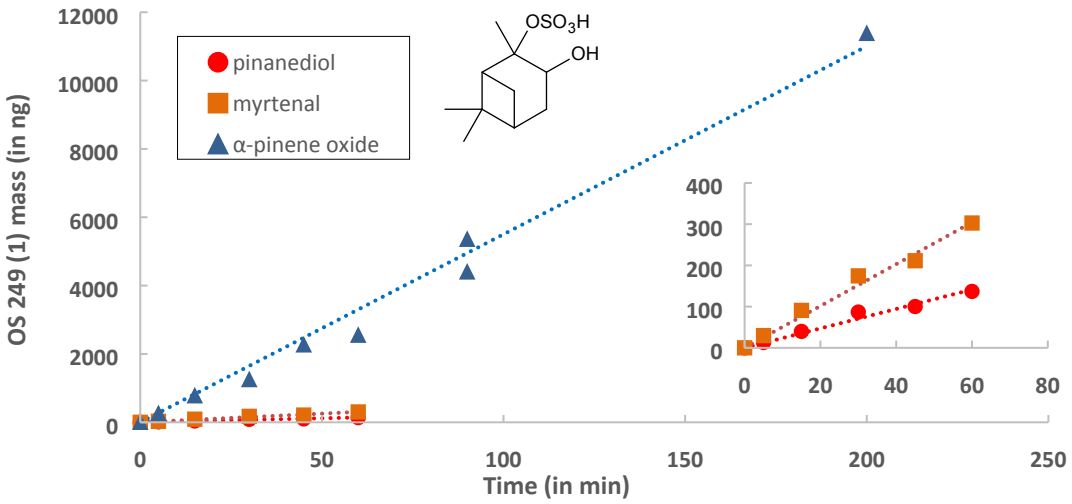
As shown in the companion article, organosulfates are also formed from other precursors. Their formation kinetics was studied, as for α-pinene oxide, under pseudo-first order conditions. During all experiments, the gas concentration of each VOC was checked to be constant in the reaction cell by on-line monitoring using PTR-TOF-MS. Their temporal profiles derived from quasi-static reactor experiments are presented and discussed below.

Organosulfates *m/z* 249

Figure 6 presents the temporal mass variations of OS 249 (1) and OS 249 (2), the two main products formed from experiments between highly acidic sulfate aerosols and α-pinene oxide, pinanediol or myrtenal ([VOC] = 1.0 ppm). Similarly, to the case of α-pinene oxide reaction, experimental data points issued from pinanediol and myrtenal could be nicely fitted with a linear regression. Although such temporal profiles only provide preliminary information on organosulfate formation kinetics, it is relevant to compare in a first approach the slopes of the linear fits to determine organosulfate formation rates. The apparent rate coefficient k_{eff}(α-pinene oxide) is 11 and 23 times larger than k_{eff}(myrtenal) and k_{eff}(pinanediol) for OS 249 (1), respectively. Similarly,

k_{eff}(α-pinene oxide) is 14 times higher than k_{eff}(pinanediol) for OS 249 (2). Note that the formation of OS 249 (2) was very limited for myrtenal with respect to OS 249 (1). This study provides quantitative results showing that epoxides are favored reactants to form organosulfates via heterogeneous gas-particle reactions, in agreement with previous studies.[24,34,36,55]

6(a)



6(b)

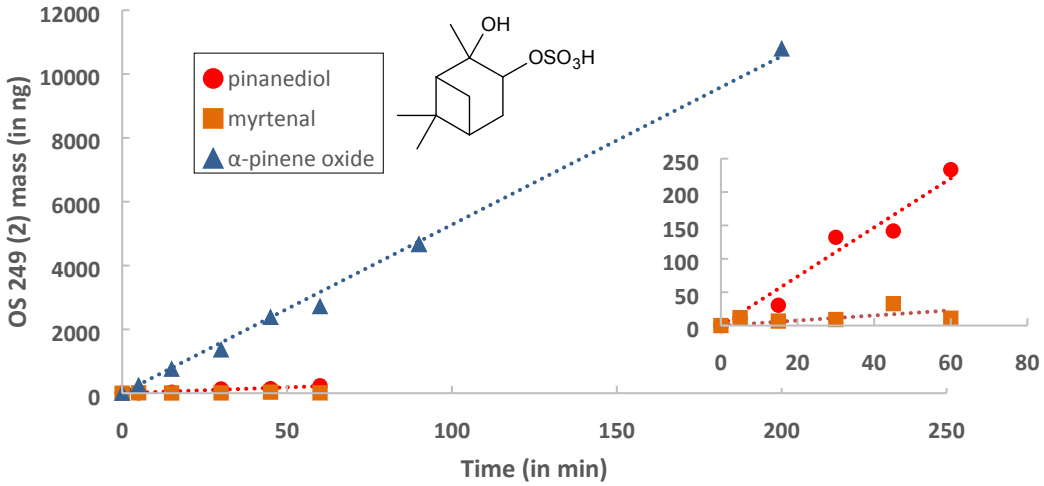


Figure 6. Temporal mass variations of OS 249 (1) (6a) and OS 249 (2) (6b) from reactions between acidified ammonium sulfate particles $(NH_4)_2SO_4/H_2SO_4$ (0.03/0.05 M) and α-pinene oxide, myrtenal or pinanediol (1.0 ppm)

Organosulfates *m/z* 233

The organosulfate m/z 233 formation pathways from α-pinene and isopinocampheol were already presented in the companion article.[24] Figure 7 presents the temporal mass variations of the two main *m/z* 233 organosulfates formed from α-pinene and isopinocampheol reactions under highly acidic conditions. Contrary to the *m/z* 249 organosulfates, the kinetic models for OS 233 (1) and OS 233 (2) formations appear different according to the studied precursor. Experimental data points from isopinocampheol experiments could also be fitted using a linear regression. The values of k_{eff} are of the same order of magnitude than k_{eff}(pinanediol) or k_{eff}(myrtenal) for both organosulfates. This was not the case for the reaction with α-pinene, where a plateau was reached for both OS 233 after about 15 min.

Experimental data points were fitted using a first order exponential function to provide a first quantitative insight into this reaction. The results highlight here two different formation behaviors, in agreement with the proposed mechanism (see the companion article).[24] The sulfation of α-pinene occurs via the addition of sulfate on the C-C double bond whereas the sulfation of isopinocampheol occurs via the nucleophilic substitution of the hydroxyl functional group by the bisulfate anion. Therefore, in the first case, the initial step is the addition of a proton on the C-C double bond whereas it is a nucleophilic attack of the leaving group, for isopinocampheol reaction. Finally, temporal mass variations of OS 233 (3) from isopinocampheol is proposed in Figure S6. This compound was formed in the first few minutes and seemed to decrease afterwards but no clear trend was evidenced in its formation. Since this compound was not positively identified, further information on its formation pathway cannot be proposed.

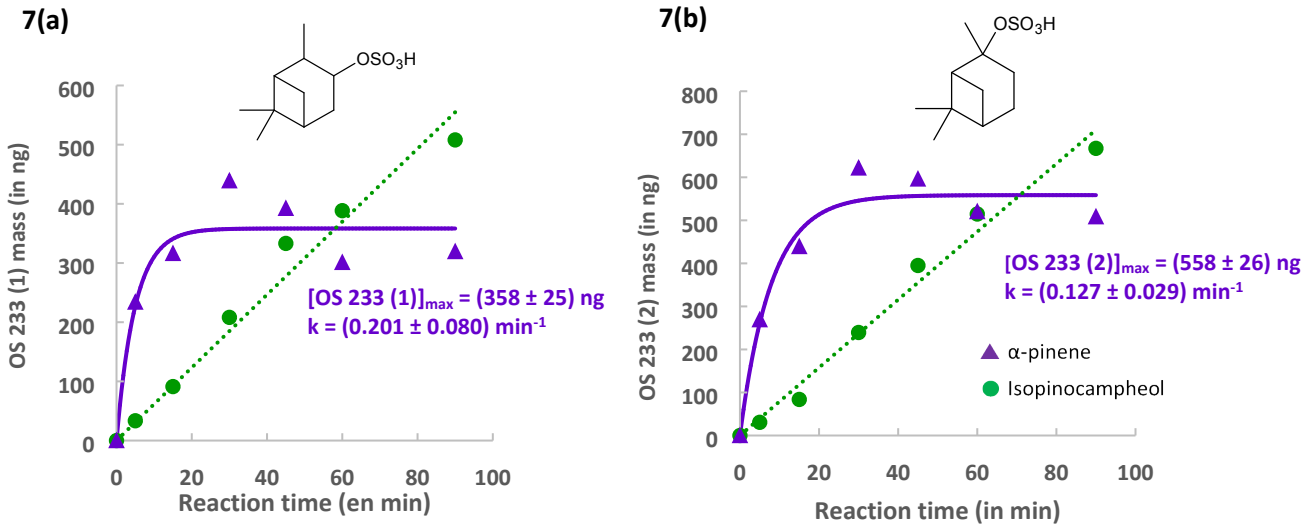


Figure 7. Temporal mass variations of OS 233 (1) (7a) and OS 233 (2) (7b) from experiments between acidic sulfated aerosols $(NH_4)_2SO_4/H_2SO_4$ (0.03/0.05 M) and α-pinene or isopinocampheol

Conclusion

In the present study, α-pinene oxide has been identified as the most efficient precursor of α-pinene-derived organosulfates observed in field studies.[14,22,23,28,45] The amount of organosulfates formed in quasi-static reactor experiments was found to increase notably with higher aerosol acidity. It was also found that the mass concentrations of organosulfates depend on the available sulfate in the aerosol phase in chamber experiments, in agreement with previous studies.[23,55] In this work, the oligomerization processes was observed under both

low and high acidic conditions. This suggests that the formation of organosulfate dimers from α-pinene oxide may contribute to SOA composition in the atmosphere on a large aerosol pH range and more specifically where highly acidic aerosols (pH < 1) have been reported.[56–58]. These results also provide some new organosulfate structures to be looked for in field studies, especially in environments where monoterpenes are the predominant BVOCs.

This study also presents an extensive laboratory investigation of organosulfate formation from oxidation products of α-pinene or proxies, with ammonium sulfate model aerosols. Temporal variations of organosulfate concentrations, for the reactions of α-pinene, α-pinene oxide, isopinocampheol, pinanediol and myrtenal are presented and discussed for the first time. For all precursors, except for α-pinene under highly acidic conditions, organosulfate formation was found to be linear with reaction time, showing that all reactants were present in a large excess. Effective rate coefficients for OS formation were determined to be one or two orders of magnitude higher for α-pinene oxide than for the 4 other precursors. Although some recent studies[38,49] still question the exact OS carbon backbone structures and formation mechanisms highlighting the need of further investigations, this work allows to conclude that epoxides appears as a favored reactant to form organosulfates via heterogeneous gas-particle reactions under our experimental conditions.

As a future work, it would be interesting to use this methodology to compare the apparent rate coefficient of OS formation from IEPOX and α-pinene oxide, and then assess their contribution to OS formation under similar conditions. In the presence of slightly acidic or non-acidified ammonium sulfate aerosols, the amounts of organosulfates were much lower than those obtained under highly acidic conditions, showing that ammonium ions may be involved in OS formation via a slightly different mechanism, also depending on the aerosol acidity and the RH/aerosol water content. The complementary study in CESAM chamber have shown the OS formation under more realistic conditions and have given first kinetic description of the studied mechanistic pathways. The experiments performed in the CESAM chamber were designed to allow us to confront the mechanistic and kinetic results on OS formation obtained in a quasi-static reactor to experimental data determined for specific and selected chemical systems in more realistic conditions (e.g. using suspended aerosol instead of deposited on a filter). Hence, both experimental approaches were highly complementary and fruitfully associated in this work. Although the present study provides highly robust and relevant new

knowledge on heterogeneous OS formation, the kinetic data are yet "experimental condition"-dependent and thus cannot be directly implemented in an atmospheric chemistry box-model to evaluate the contribution of α-pinene oxide to OS formation in the atmosphere. Therefore, further experiments more specifically focused on OS formation from α-pinene oxide are needed to extend our experimental approach relying in the fruitful association of quasi-static reactor and atmospheric simulation chamber to a wider range of experimental conditions (i.e. α-pinene oxide concentrations, RH, acidity and sulfate concentration…). This should then achieve the complete kinetic parametrization of this complex gas-surface reaction and allow the implementation of OS heterogeneous formation in atmospheric chemical models. Nevertheless, this study already illustrates how gas-particle reactions may play an important role in OS formation and hence in the atmospheric fate of organic carbon.[53,59]

ASSOCIATED CONTENT

Supporting Information.

Figure S1 presents the mass spectra from PTR-TOF-MS for α-pinene oxide and campholenic aldehyde. Figure S2 displays the proposed organosulfate formation mechanism from α-pinene oxide. Figure S3 presents the temporal mass profiles of m/z 249 (1), m/z 401 and m/z 481 organosulfate formation in the particulate phase. Figure S4 shows the aerosol particle concentration in the CESAM chamber measured during the C4 experiment. Figure S5 presents the temporal variations of OS 249 (1), OS 249 (2) and OS 249 (CA) from α-pinene oxide under non-acidified sulfate conditions in the CESAM chamber. Figure S6 presents the temporal mass profile of OS 233 (3) from experiments between acidic sulfated aerosols $(NH_4)_2SO_4/H_2SO_4$ (0.03/0.05 M) and isopinocampheol. Table S1 shows the structure of the organosulfates detected in α-pinene oxide experiments. The Supporting Information is available free of charge on the ACS Publications website http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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