Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Decrease in sulfate aerosol light backscattering by reactive uptake of isoprene epoxydiols

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Materials and Methods

Aerosol and gas-phase IEPOX generation

IEPOX experiments:

Seed aerosol particles were generated with a constant output atomizer (TSI Inc, model 3076) containing an aqueous solution of ammonium sulfate of 0.06 M ($(NH_4)_2SO_4$ (solid), Sigma Aldrich > 99 %) and 0.12 M sulfuric acid (H_2SO_4 (aq) ChimiePlus 95-97 %) until the desired total steady state aerosol mass concentration was achieved. The pH of the atomized solution was determined using the thermodynamic model E-AIM II.[1] The concentration of the different ions was known and allowed to obtain the activity coefficient of H^+_{aq} and the moles of H^+_{aq}. From these values and using the equation proposed by Lin et al.,[2] the aerosol acidity is estimated to be 1.06. Before entering into the aerosol flow reactor (quartz tube of 182 cm length and 6.5 cm internal diameter), acidified ammonium sulfate (AAS) aerosols were dried using a diffusion dryer and size selected by a differential mobility analyzer (DMA, Electrostatic Classifier, TSI Inc, model 3080). The DMA was used with a sheath flow and a sample flow of 6 L/min with a size selection of 130 nm, without critical orifice. IEPOX vapor was produced by flowing ultra-high purity nitrogen (from 150 to 600 of standard cubic centimeters per minute (sccm)) into a solution of synthetized *trans-β*-IEPOX [4] dissolved into ethyl acetate (0.37 mg mL^{-1}) and stored in a glass bulb. The concentration of IEPOX was estimated from the vapor pressure of *β*-IEPOX (i.e., 0.456 Pa), as reported in the literature.[5]

Characterization:

For IEPOX experiments, the total particle number for each experiment was (5.98 ± 0.29) $x10^6$ particles per cubic centimeter corresponding to amass concentration of (3.45 ± 0.05) x 10^4 µg.m^{-3}, assuming a particle density of 1.77 g.cm^{-3}.[6]

Sampling and Extraction Method

The protocol has been described previously.[7] Briefly, half of each collected quartz fiber filter (PALL, 47 mm) was extracted twice with 6 mL of acetonitrile and agitated for 20 minutes with an orbital shaker at 1000 rpm.[7] The extracts were then filtered with a syringe filter (0.2 µm, Pall Acrodisc® PSF, with GHP membrane, hydrophilic polypropylene) to remove potential insoluble particles and blown dry under a gentle N_2 (g) stream at ambient

temperature. The residues were reconstituted in 1 mL of acetonitrile (Optima®LC/MS, Fischer Scientific) and were agitated during 5 minutes in an orbital shaker. Finally, the filter extracts were analyzed by ultra-high performance liquid chromatography (Dionex 3000, Thermo Scientific) using a Water Acquity HSS C_{18} column (1.8µL, 100 x 2.1mm) coupled with a Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific) equipped with an electrospray ionization (ESI) source operated in negative mode. The mobile phase used was constituted of (A) 0.1% formic acid in water (Optima® LC/MS, Fischer Scientific) and (B) 0.1% formic acid in acetonitrile (Optima® LC/MS, Fischer Scientific). Gradient elution was carried out by the A/B mixture at a total flow rate of 300 µL/min: 1% of B for 2 min, a linear gradient was used until 100% of B for 11 min, then 100% of B for 2 min and back to 1% of B in 0.1 min, and to end 1% of B for 6.9 min.

An internal standard, camphor sulfonic acid (CSA, *m/z* 231.0696), and an external standard, IEPOX-derived organosulfates (OS 216, *m/z* 215.0225), synthetized in house,[8] were used to determine the extraction efficiency and to quantify the organosulfates formed. A range of nine solutions was prepared from 2 to 200 µg/L. The correlation factor R^2 were equal to 0.99 and 0.98 for CSA and IEPOX-OSs, respectively. 5 µL was used of 10 000 µg/L CSA solution to spike the different samples filters during the experiments. Recovery was determined to be 90 ± 2% (1 std. dev.). Similarly, 5 µL was used of 13 000 µg/L IEPOX-OS was used to spike three blank filters and extraction efficiency was determined to be 100 ± 4% (1 std. dev.). All samples were analyzed twice.

Uncertainty Estimates for IEPOX-OSs.

The determination of the uncertainties has already been described previously.[9,10] In brief, for both analytical standards, the different uncertainties taken into account are the volume, the mass used to prepare the solutions as well as the variability related to the mass spectrometer. The median has been taken to have a better representation of the uncertainties.

The uncertainty of CSA can be estimated as shown in eqn.1:

$$U_{CSA} = (\mu_{mv(CSA)}^2 + \mu_{Eff(CSA)}^2 + \mu_{s(CSA)}^2 + \mu_{L(CSA)}^2 + \mu_{R(CSA)}^2 + \mu_{d(CSA)}^2) \quad (1)$$

where,

$\mu_{mv(CSA)}$ = relative uncertainty on the volume and mass taken = 0.024;

$\mu_{Eff(CSA)}$ = relative uncertainty on the recuperation efficiency of CSA spike = 0.062;

$\mu_{s(CSA)}$ = relative uncertainty on the spike used to doped the sampling filters = 0.0004;

$\mu_{L(CSA)}$ = relative uncertainty on the linearity of the internal calibration curve = 0.024;

$\mu_{R(CSA)}$ = relative uncertainty on the analytical repetitively = 0.029;

$\mu_{d(CSA)}$ = relative uncertainty on the drift between two calibration = 0.024.

In the same way, the uncertainty using IEPOX-OS used to quantify the formation of organosulfates can be estimated as shown in eqn. 2:

$$U_{OS} = (\mu_{L(OS)}^2 + \mu_{R(OS)}^2 + \mu_{mv(OS)}^2 + \mu_{d(OS)}^2 + \mu_{Eff(OS)}^2) \quad (2)$$

where,

$\mu_{L(OS)}$ = relative uncertainty on the linearity of the internal calibration curve = 0.0661;

$\mu_{R(OS)}$ = relative uncertainty on the analytical repeatability= 0.017;

$\mu_{mv(OS)}$ = relative uncertainty on the volume and mass taken = 0.0094;

$\mu_{d(OS)}$ = relative standard uncertainty due to drift between two calibrations = 0.024;

$\mu_{Eff(OS)}$ = relative uncertainty on the recuperation efficiency of IEPOX-OSs spike = 0.012.

Combining UOS and UCSA and using the coverage factor k (equal to 2), [9,10] the total uncertainty can be estimated according to eqn.3:

$$U_{OS\ quantification} = 2 * (U_{OS} + U_{CSA})^{\frac{1}{2}} \quad (3)$$

$U_{OS\ quantification}$ = 22.2%

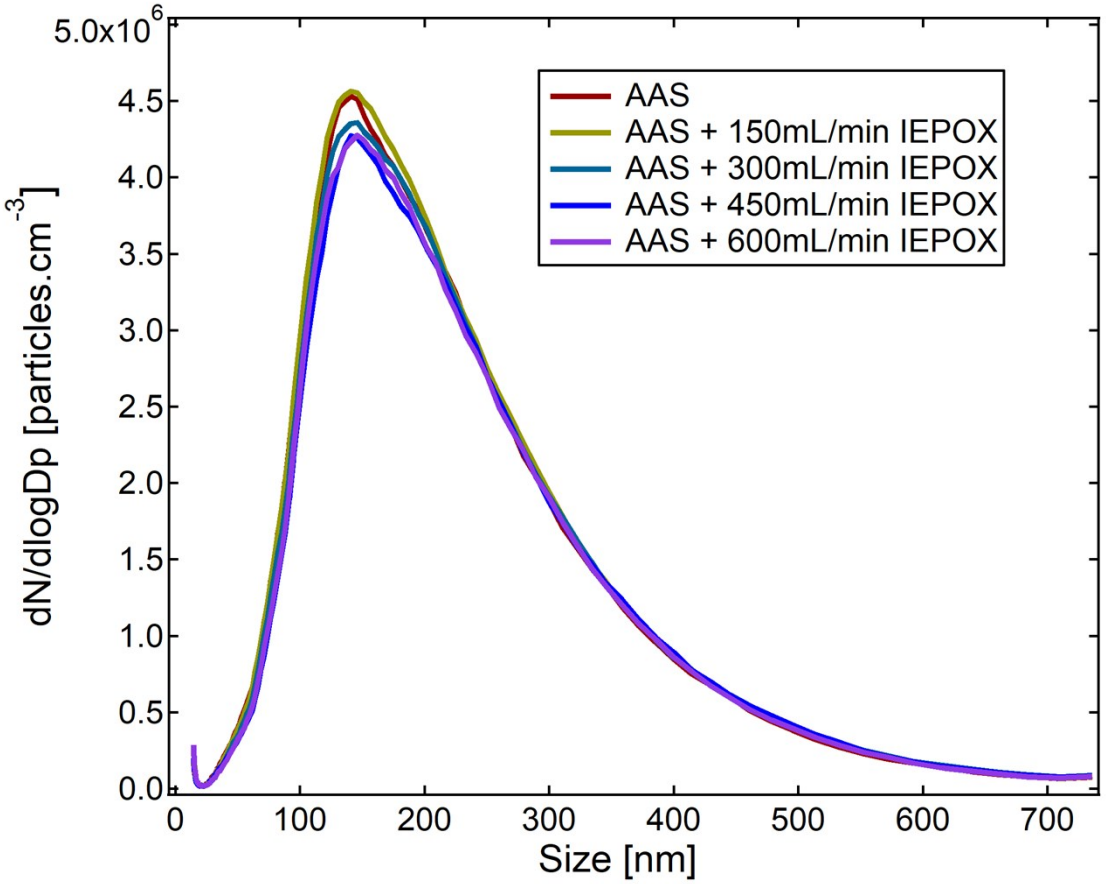

Figure S1. Size distributions of the reactive uptake of IEPOX in the presence of AAS particles for each experiment. The concentration of inorganic sulfate remained constant.

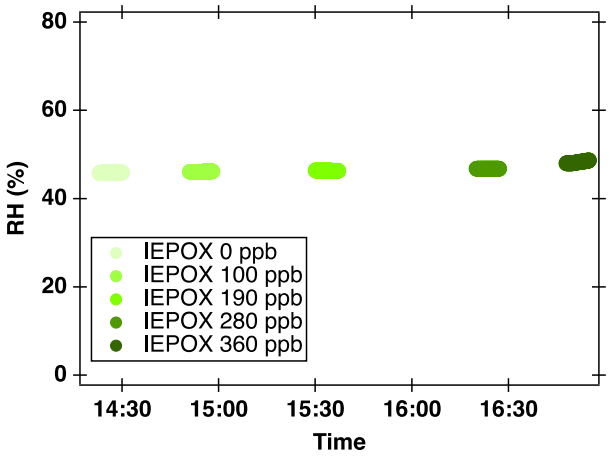

Figure S2. The Relative humidity (RH) was monitored during all our experiments and remained stable, i.e., ~ 49 ± 3 %.

Uncertainty on the backscattered light intensity

The error bar affecting the backscattered intensity I_{bs} is only driven by statistical errors since our Pi-polarimeters exhibit negligible polarization and wavelength cross-talks[11]. The acquisition procedure and the calculation of the statistical error affecting I_{bs} are detailed in a previous publication[12]. In a few words, we followed the approach stated by M.I. Mishchenko,[13] which is necessary for quantitative evaluation of light scattering: any measurement of particles scattering consists in a two-stage procedure: the scattered intensity is first measured in the absence of the targeted particles as a background intensity $I_{bs,0}$, then in the presence of these particles as a total intensity $I_{bs} + I_{bs,0}$. Therefore, the targeted intensity I_{bs} backscattered by {AAS+IEPOX} is accurately measured by subtracting the contribution $I_{bs,0}$ of ambient laboratory aerosols to the total backscattered intensity $I_{bs} + I_{bs,0}$. To gain in accuracy, such an acquisition is repeated for different incident polarization states (labeled by the ψ-angle) and to reduce statistical errors, this measurement is repeated N-times per ψ-angle to get the value of I_{bs} plotted in Figure 3 as the resulting mean $\bar{I}_{bs}$ and standard deviation σ_{bs} of these N-files. Figure S3 plots $\bar{I}_{bs} = f(\psi)$ for successive IEPOX-concentrations at 355 and 532 nm wavelength.

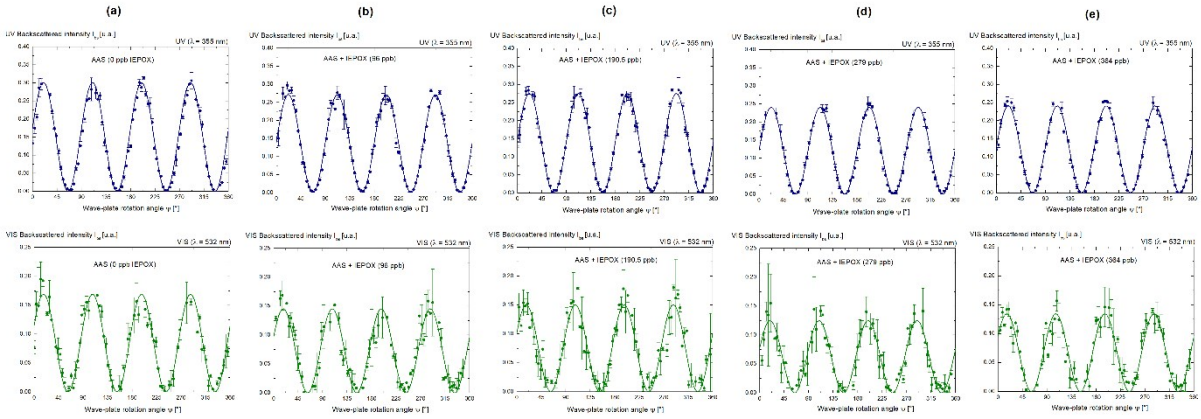

Figure S3. Detected light intensity I_{bs} backscattered by AAS + IEPOX: (a): 0 ppb IEPOX, (b): 109 ppb IEPOX, (c): 214 ppb IEPOX, (d): 313 ppb IEPOX, (e): 409 ppb IEPOX. Upper (resp. lower) panels respectively correspond to wavelength 355 nm (resp. 532 nm). Using the previously set-up published[11], to gain in accuracy, I_{bs} is recorded as a function of the orientation ψ of a wave-plate and to reduce statistical error bars, each data point results from measurement repeated N (= 5) times with corresponding mean and standard deviation.

Table S1: Compilation of the experimental results: (a) IEPOX backscattering experiments, (b) organosulfate quantification.

(a) IEPOX-OS backscattering

Experiment	1	2	3	4	5
IEPOX flow (mL/min)	0	150	300	450	600
IEPOX concentration (ppb)	0	109	214	313	409
$I_{s,M}/N_{tot}$ (UV)	1	0.93	0.98	0.895	0.885
$I_{s,M}/N_{tot}$ (VIS)	1	0.845	0.912	0.789	0.84

(b) IEPOX-OS extraction

Experiment 1					
IEPOX Flow (mL/min)	0	150	300	450	600
Mass OS *m/z* 215.0225 (µg)	0	0.45	1.63	2.87	10.05
Experiment 2					
IEPOX Flow (mL/min)	0	150	300	450	600
Mass OS *m/z* 215.0225 (µg)	0.26	1.7	2.63	5.14	8.67

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