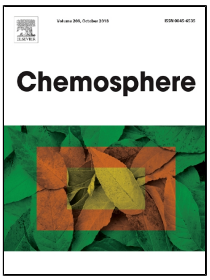
Radical oxidation of methyl vinyl ketone and methacrolein in aqueous droplets : characterization of organosulfates and atmospheric implications

Accepted Manuscript



Radical oxidation of methyl vinyl ketone and methacrolein in aqueous droplets: characterization of organosulfates and atmospheric implications

Paulina Wach, Grzegorz Spólnik, Krzysztof J. Rudziński, Krzysztof Skotak, Magda Claeys, Witold Danikiewicz, Rafał Szmigielski

PII:	S0045-6535(18)31679-5
DOI:	10.1016/j.chemosphere.2018.09.026
Reference:	CHEM 22106
To appear in:	*Chemosphere*
Received Date:	21 June 2018
Accepted Date:	04 September 2018

Please cite this article as: Paulina Wach, Grzegorz Spólnik, Krzysztof J. Rudziński, Krzysztof Skotak, Magda Claeys, Witold Danikiewicz, Rafał Szmigielski, Radical oxidation of methyl vinyl ketone and methacrolein in aqueous droplets: characterization of organosulfates and atmospheric implications, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.09.026

Radical oxidation of methyl vinyl ketone and methacrolein in aqueous droplets: characterization of organosulfates and atmospheric implications

Paulina Wach [a)]*, Grzegorz Spólnik [b)], Krzysztof J. Rudziński [a)], Krzysztof Skotak[c)], Magda Claeys [d)], Witold Danikiewicz [b)] and Rafał Szmigielski [a)]*

[a)] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

[b)] Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

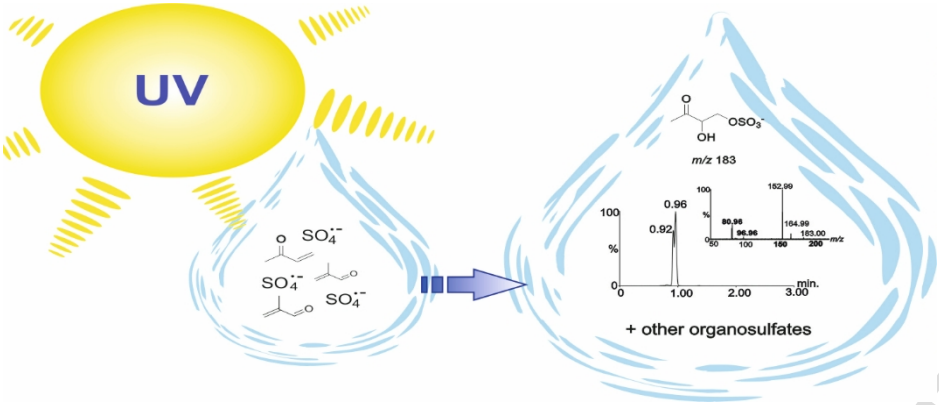
[c)] Institute of Environmental Protection-National Research Institute, ul. Krucza 5/11D, 00-548 Warszawa, Poland

[d)] Department of Pharmaceutical Sciences, University of Antwerp, BE 2610 Antwerp, Belgium

*Corresponding author:

Phone: +48 (22) 343 3402, e-mail: ralf@ichf.edu.pl pwach@ichf.edu.pl

Graphical Abstract



Abstract

In-cloud processing of volatile organic compounds is one of the significant routes leading to secondary organic aerosol (SOA) in the lower troposphere. In this study, we demonstrate that two atmospherically relevant α,β-unsaturated carbonyls, i.e., but-3-en-2-on (methyl vinyl ketone, MVK) and 2-methylopropenal (methacrolein, MACR), undergo sulfate radical-induced transformations in dilute aqueous systems under photochemical conditions to form organosulfates previously identified in ambient aerosols and SOA generated in smog chambers. The photooxidation was performed under sun irradiation in unbuffered aqueous solutions containing carbonyl precursors at a concentration of 0.2 mmol and peroxydisulfate as a source of sulfate radicals ($SO_4^{\bullet-}$) at a concentration of 0.95 mmol. UV-vis analysis of solutions showed the fast decay of unsaturated carbonyl precursors in the presence of sulfate radicals. The observation confirms the capacity of sulfate radicals to transform the organic compounds into SOA components in atmospheric waters. Detailed interpretation of high-resolution negative ion electrospray ionization tandem mass spectra allowed to assign molecular structures to multiple aqueous organosulfate products, including an abundant isoprene-derived organosulfate $C_4H_8SO_7$ detected at *m/z* 199. The results highlight the solar aqueous-phase reactions as a potentially significant route for biogenic SOA production in clouds at locations where isoprene oxidation occurs. A recent modelling study suggests that

such processes could likely contribute to 20-30 Tg year^{-1} production of SOA, referred to as aqSOA, which is a non-negligible addition to the still underestimated budget of atmospheric aerosol.

Highlights

- Methacrolein and methyl vinyl ketone form SOA in atmospheric waters
- This proceeds through SO_4 radical-mediated reactions to form organosulfates
- Structures of organosulfates formed were elucidated and in some cases revised
- An abundant isoprene-related organosulfate $C_4H_8SO_7$ (*m/z* 199) was detected
- Sunlight enhances the oxidative capacity of atmospheric waters

Keywords

secondary organic aerosol, aqueous photochemistry, organosulfates, sulfate radicals, methyl vinyl ketone, methacrolein

1. Introduction

Secondary organic aerosol (SOA) produced in the troposphere receives considerable attention for several reasons. First, it affects human life and health by triggering various lung and cardiovascular diseases. Second, it decreases visibility and destroys architectural monuments. Third, it impacts the Earth's climate through scattering and absorbing solar radiation and acting as cloud condensation nuclei (Bianchi et al., 2016).

Despite intensive laboratory and modelling studies, and field measurements with advanced analytical instrumentation and modelling, our understanding of the formation and growth of aerosol particles is still highly constrained (Hallquist et al., 2009; Nozière et al., 2015; Zhao et al., 2017).

The formation of SOA components from trace gases is fairly well characterized in respect to the most abundantly released biogenic hydrocarbons, including isoprene (2-methylbuta-1,3-dien, ISO), terpenes and sesquiterpenes. Isoprene is a key precursor of ambient SOA because of its emission rate which is highest of all non-methane hydrocarbons (Sindelarova et al., 2014) and its high reactivity due to two conjugated double bonds. In addition to SOA formation via gas-phase photooxidation of volatile precursors followed by gas-to-particle partitioning of its semi-volatile oxidation products and heterogeneous particle-bound processes (Hallquist et al., 2009), aqueous-phase organic reactions have been recently suggested to contribute to SOA (aqSOA). Yet, over the last few years another type of mechanism has been intensively investigated – atmospheric reactions occurring in aqueous media (Claeys et al., 2004; Rudziński et al., 2009; Liu et al., 2012; Schone et al., 2014; Szmigielski, 2016; Giorio et al., 2017). Aqueous-phase reactions of ISO and its gas-phase oxidation products, such as methyl vinyl ketone (MVK) or methacrolein (MACR), have been proposed as alternative routes to SOA formation. These include reactions taking place on the surface of water droplets or in the bulk of water solutions (Blando and Turpin, 2000; Kameel et al., 2014; Noziere, 2016; Szmigielski, 2016). So far, the role of MVK and MACR in these reactions has been largely neglected because of their low solubility in water (Henry

coefficients: H_{MACR} = 6.5 mol atm^{-1} and H_{MVK} = 41 mol atm^{-1}) (Leng et al., 2013). However, recent reports showed that both compounds are found in the aqueous phase at much higher concentrations than predicted from their Henry's coefficients (Schöne and Herrmann, 2014; Herrmann et al., 2015; McNeill, 2015). The concentrations of MACR and MVK measured in atmospheric waters ranged from 0.01 – 0.5 x 10^{-3} mmol L^{-1} and 0.05 – 2.2 x $^{-3}$ mmol L^{-1}, respectively (Van Pinxteren et al., 2005). Estimated global production of biogenic SOA in cloud water reaches 20-40 Tg $year^{-1}$, including the contribution from cloud processing of ISO and MVK as high as 2-3 Tg $year^{-1}$ (McNeill, 2015). "Other carbonyls originating from isoprene, including glyoxal, methylglyoxal, 2-methylglyceric acid and hydroxyacetone, also contribute to the organic aerosol mass through in-cloud processes" (Carlton et al., 2009; Ervens et al., 2011; Noziere, 2016). These processes are predominantly controlled by OH radicals, which are ubiquitous in the lower atmosphere (Monks, 2005). However, atmospheric water droplets can perfectly house reaction systems governed by other radical species (Herrmann et al., 2015). Of these, the sulfate radical anion ($SO_4^{\bullet -}$) plays an ample role since it has a great oxidation capacity (Ouyang et al., 2005) and the propensity to add to unsaturated olefins (Rudzinski, 2004; Rudziński et al., 2009; Liang et al., 2016).

Our previous studies (Rudzinski, 2004; Rudziński et al., 2009; Schöne and Herrmann, 2014; Rudzinski et al., 2016) along with reports from other laboratories (Nozière et al., 2010; Schindelka et al., 2013; Shalamzari et al., 2016) showed that the sulfate radical anions are a powerful driver for aqueous processing of isoprene and C_4-C_5 carbonyls leading to a series of organosulfates, which are relevant markers of the polar SOA fraction. In this study we focused on the molecular composition of aqSOA formed via sunlight-induced aqueous photochemistry of two water-soluble α,β-unsaturated carbonyls, i.e., MVK and MACR – as main products of isoprene oxidation in the atmosphere and potassium persulfate – as a simple precursor of aqueous sulfate radicals.

The experimental setup was intended to mimic natural atmospheric conditions as much as possible with a natural source of UV-vis wavelengths provided by sunlight and with

the use of diluted solutions of organic and inorganic species. To the best of our knowledge, such an approach has never been applied before. A key point of the study was to obtain insights into the chemistry taking place in the bulk aqueous phase in respect to the formation of SOA organosulfates. The progress of the aqueous-phase reactions of selected carbonyls with the sulfate radical anion was followed by UV-vis spectroscopy. Small molecular weight (MW) products were structurally characterized using ultra-high performance liquid chromatography combined with high resolution tandem mass spectrometry. The chemical composition of aqSOA samples obtained from laboratory experiments was compared with Diabla Gora ambient $PM_{2.5}$ (particles with diameters lower than 2.5 μm aerodynamic diameter) aerosol collected during the 2014 summer campaign in the north-eastern rural region in Poland (Masuria Province). This region is dominated by broad-leaf forests providing a local source of isoprene and isoprene-related oxidized volatile organic compounds, including MACR and MVK.

2. Materials and methods

2.1. Chemicals

High-purity water (18.2 MΩ·cm resistivity at 25 °C) used for the aqueous-phase experiments, reconstitution of aerosol extracts and preparation the LC mobile phase was obtained using a Milli-Q Advantage water purification system (Merck, Darmstadt, Germany). The following chemicals were used for the reactions without further purification: potassium persulfate, $K_2S_2O_8$, (pure, POCH, Poland), methyl vinyl ketone (99 %; Sigma Aldrich, St. Louis, MO 63103, USA), methacrolein (95 %; Sigma Aldrich). All solutions were prepared freshly before each experimental run.

2.2. Aqueous-phase

A series of sunlight-induced aqueous-phase experiments were performed using stock solutions of oxidized isoprene C_4 derivatives , i.e., methyl vinyl ketone (MVK) and methacrolein (MACR). Concentrations of carbonyl compounds were 0.19 mmol L^{-1}, while the inorganic potassium persulfate ($K_2S_2O_8$), the sulfate radical precursor (Kolthoff, 1951; C. von Sonntag, 1991), was 0.16 mmol L^{-1}. Reactions were conducted in the 1 mL quartz cuvettes, exposed to sun irradiation for 200 min during a summer day. All the experimental parameters, such as the decay of organic reactant, the ambient air temperature, and the light intensity were controlled every 30 min. The temperature of ambient air in close vicinity of the reaction vessels ranged from 298 to 303 K, while the sunlight intensity measured with an ILT 1400A radiometer (International Light Technologies) varied from 26.8 to 33.1 mW cm^2. UV-vis spectra were recorded with a Jasco V-570 spectrophotometer within the range of 200-300 nm (band width 0.1 nm, data pitch: 0.5 nm, scanning speed: 400 nm min^{-1}). As a baseline reference, Milli-Q water was used. The reference spectra for MAC and MVK were acquired with the same concentration levels, i.e., 0.19 mmol L^{-1}, and measurement parameters as stated above.

For comparison, dark experiments were performed following the same procedures as those for the runs. Stock solutions of carbonyl compounds and potassium persulfate were freshly prepared before each experiment and stored wrapped in aluminium foil. The UV-vis and negative ion electrospray mass spectra of aliquots were recorded immediately after sampling. Samples used for the mass spectral analyses were diluted with methanol (1:1; v/v).

2.3. Aerosol samples

Ambient $PM_{2.5}$ aerosol samples were collected in 24 hour periods during the summer campaign (July 26-31, 2014) in Diabla Gora, Poland, on 15 cm quartz fibre filters using a high-volume aerosol sampler (Digitel DHA-80, Switzerland). Diabla Gora is located in a rural site in the Borecka forest of the Masuria Province (54°07’29.52″N; 22°02’17.08″E).

The sampling site is surrounded by lakes and dense broad-leaf forest stands providing an important local source for isoprene emission and formation of isoprene-derived carbonyls. The Diabla Gora station is a reference station for measuring clean air masses and monitoring air pollution according to the European Monitoring Evaluation Policy. After sample collection, filters were wrapped in a prebaked aluminum foil and stored at −20 °C until further analysis. The filter extracts were prepared as follows: two 1 cm^2 punches were cut from each selected quartz fibre filter and were extracted 3 times with 10 mL of methanol using a PSU-20i orbital shaker (Biosan, Poland) for 10 min. The extracts were combined and concentrated to 1 mL using a Büchi rotary evaporator (35 °C, reduced pressure), filtered through a 0.2 µm Teflon filter, and evaporated to dryness with a gentle stream of nitrogen. The obtained dry residues were reconstituted in 140 µL of methanol/water (1:1; v/v) and used for further analyses.

2.4. *High resolution LC/MS analysis*

Products of aqueous-phase reactions and extracts of ambient $PM_{2.5}$ aerosol were screened using a high resolution Synapt G2-S HDMS (Waters, Poland) mass spectrometer. The instrument was equipped with an electrospray ion source and a quadrupole – time-of-flight mass analyzer. Measurements were carried out in the negative ion mode with a sampling cone voltage of 20 V, a capillary voltage of 3 kV and a FWHM (full-width-at-half-maximum) mass resolving power of 20 000. The MS unit was coupled with a Waters UHPLC ACQUITY UPLC I-Class system (Waters, Poland), equipped with an ACQUITY UPLC HSS T3 column (1.8 µm, 2.1 x 100 mm). The applied mobile phases consisted of 20 mmol ammonium acetate (A) and methanol (B). The gradient elution program was as follows: the concentration of eluent A was kept at 100% for the first 3 min with a flow rate 0.35 mL/min. During the next 5 min eluent B was increased to 100% and was kept at this level for 2 min. For the last 3 min eluent B was decreased to 0%. The data processing and the instrument control were done using a MassLynx V4.1 software package (Waters, Poland).

3. Results and discussion

3.1. Formation of organosulfates

Based on 2009 (Hallquist et al., 2009), 2011 (Ervens et al., 2011) and 2015 (Nozière et al., 2015) review papers, aqSOA samples containing organosulfates can be produced in a laboratory framework through in-cloud chemistry under dark and/or solar conditions. In the dark mode two atmospherically relevant pathways have been suggested: (1) addition of the sulfate radicals onto an unsaturated C=C bond of the precursor (Szmigielski, 2016; Kwong et al., 2018), (2) nucleophilic addition of the sulfate anion onto an isoprene-derived epoxy ring (Darer et al., 2011; Nguyen et al., 2014). In contrast, solar approaches have entailed (1) UV irradiation of concentrated solutions of ammonium sulfate and the organic precursor (Nozière et al., 2010), (2) laser photolysis of concentrated solutions containing sulfate peroxide and carbonyl precursors (Schindelka et al., 2013). In either case radicals formed (e.g., OH, SO_4) add onto biogenic olefins to spur further transformations. We have decided to perform the solar experiment as close to the natural environment as possible, by using sun irradiation to generate sulfate radicals in diluted solutions of organic precursors. In case of both selected precursors, our mimicking experiments revealed the formation of a variety of products, including atmospherically-relevant organosulfates.

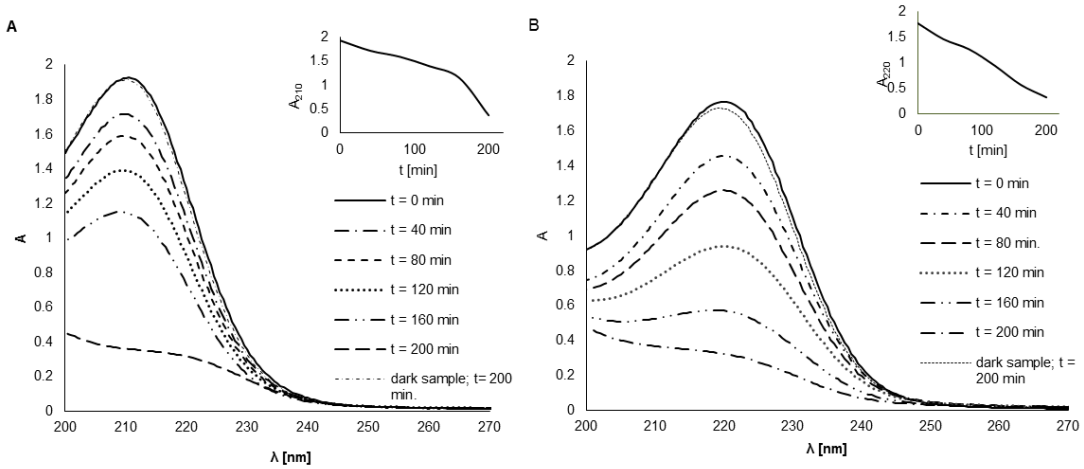
3.2. UV-vis observations of MVK and MACR decay

The decay of organic compounds (MVK, MACR) during each experiment, were monitored using UV-vis spectroscopy. The results obtained under irradiation were compared with those recorded for dark conditions to exclude any chemical artefacts. For methyl vinyl ketone and methacrolein the maxima of absorption were measured in a shortwave UV range – intense absorption bands are located at the wavelengths of *ca*. 210 nm (MVK), and *ca.* 220 nm

245 (MACR), respectively, which correspond to the π→ π* transition. The presence of these
246 bands suggest the existence of MACR and MVK in their carbonyl forms in aqueous solutions,
247 which are in line with an earlier study (Renard et al., 2015).

248 The irreversible loss of MVK and MACR during the photooxidation experiment (Fig.1)
249 suggests the occurrence of chemical processes leading to an array of novel products.

250



251

252 **Fig.1** Decay of UV absorption bands for A) methyl vinyl ketone (λ_{max} 210 nm) and B)
253 methacrolein (λ_{max} 220 nm) during the aqueous-phase reaction with sulfate radicals
254 (experimental conditions: mean temperature 300 K, mean light intensity 31.5 mW cm^2).
255 Insets show maxima of the absorption bands in function of time.

256

257 We can observe that the UV spectra of the first sample (t = 0 min) after the addition of
258 potassium persulfate (before exposure to sun light) and for the dark sample (dark sample; t =
259 200 min) are comparable within an experimental measurement. When exposed to sun
260 irradiation, there is a gradual loss of absorption until a reaction time of 160 min, after which
261 we can observe the greatest loss of absorption band for MVK. After 200 min of sun exposure
262 MVK is completely consumed. The difference between the sun-irradiated sample and that
263 kept in a dark environment is obvious, indicating that natural occurring UV light significantly

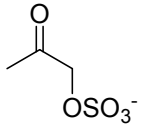
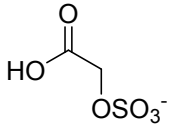
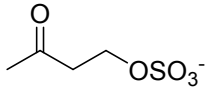
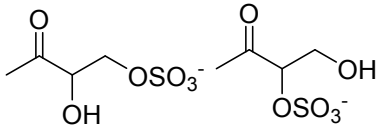
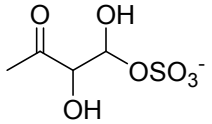
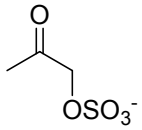
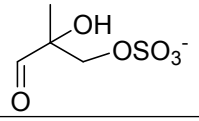
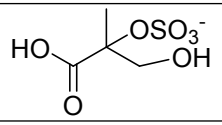
accelerates the decrease of organic precursor due to the effective radical formation *via* photolysis.

A similar situation was obtained for aqueous photooxidation of methacrolein in the presence of potassium persulfate (Fig. 1 B), where after 200 min reaction time a difference between the sun-irradiated sample and the dark one is clearly observable – most of the olefin is consumed considering the intensity of absorption band for unreacted MACR. In contrast to MVK, methacrolein was consumed evenly during the reaction.

3.4. Chemical characterization of products from aqueous photooxidation of MVK

The analyses of organosulfates formed during the irradiation of the aqueous solution containing methyl vinyl ketone and potassium persulfate were targeted to low-MW C_3-C_4 products. The mass spectrometric data for detected organosulfates in both aqueous-phase reactions and ambient $PM_{2.5}$ extracts along with suggested structures are summarized in Table 1. All of the listed organosulfates were reported in the literature as products of reactions conducted with use of different modes of sulfate radicals formation (Nozière et al., 2010; Schindelka et al., 2013).

281 *Table 1. Detected organosulfates from aqueous SOA and ambient $PM_{2.5}$ extracts along with their proposed structures.*

Organic precursor	$[M - H]^-$	Error [mDa]	Formula	No. of isomers	Aqueous-phase reaction	Ambient sample	Suggested structure
MVK	152.9859	+ 0.1	$C_3H_5O_5S$	1	present	present	
MVK	154.9652	+ 0.2	$C_2H_3O_6S$	1	present	present	
MVK	167.0018	+ 0.4	$C_4H_7O_5S$	1	present	not	
MVK	182.9958	- 0.5	$C_4H_7O_6S$	2	present	one isomer is present (on the left)	
MVK	198.9911	- 0.1	$C_4H_7O_7S$	1	present	not	
MACR	152.9857	-0.1	$C_3H_5O_5S$	1	present	present	
MACR	182.9962	-0.1	$C_4H_7O_6S$	1	present	not	
MACR	198.9939	+1.5	$C_4H_7O_7S$	1	present	present	

MW 154, 156 and 168 organosulfates

The MW 154 organosulfate detected in both $PM_{2.5}$ ambient aerosol and aqSOA from MVK appeared as a single peak in the chromatographic analysis, which indicates the simple molecular structure of hydroxyacetone sulfate. Our finding is in line with earlier reports from ambient and laboratory experiments and could be rationalized by the SO_4 radical addition to the MVK unsaturated bond (Safi Shalamzari et al., 2013; Schindelka et al., 2013). The appearance of the MW 156 organosulfate in ambient $PM_{2.5}$ aerosol and in the aqueous-phase experiment as a single chromatographic peak points to a further oxidation product. For MW 156 organosulfate the structure of sulfated glycolic acid (Table 1) is suggested, which is likely formed *via* the reactive uptake of glyoxal on ammonium sulfate seed aerosol under irradiated conditions (Safi Shalamzari et al., 2013). However, the underlying photochemical mechanism is not clear. Here, we propose that the MW 156 organosulfate forms from MVK as a result of the addition of the hydroxyl radical to the earlier-formed hydroxyacetone sulfate in the aqueous-phase. In the case of the MW 168 organosulfate the results obtained are different – although such a product is formed during the reaction; however, its retention time does not correspond to the MW 168 organosulfate reported elsewhere for $PM_{2.5}$ ambient samples (Schindelka et al., 2013), suggesting the MVK reaction channel has no significance towards its formation in the atmosphere. However, the MW 168 organosulfate has recently been reported in Arctic aerosol (Hansen et al., 2014) and suggested by earlier studies to originate from methacrolein based on smog chamber measurements of the photochemical oxidation of isoprene in the presence of acidic sulfate aerosol (Surratt et al., 2007; Szmigielski et al., 2007).

MW 184 organosulfate

During the irradiation of MVK solutions we could observe the appearance of two isomeric products, which elute from the LC column at 0.92 and 0.96 min, respectively (Fig. 2 B).

Accurate mass measurements allowed the assignment of these products as the MVK-related organosulfate with the MW 184 ($C_4H_7O_6S$; measured mass: 182.9965; error: 0.2 mDa).

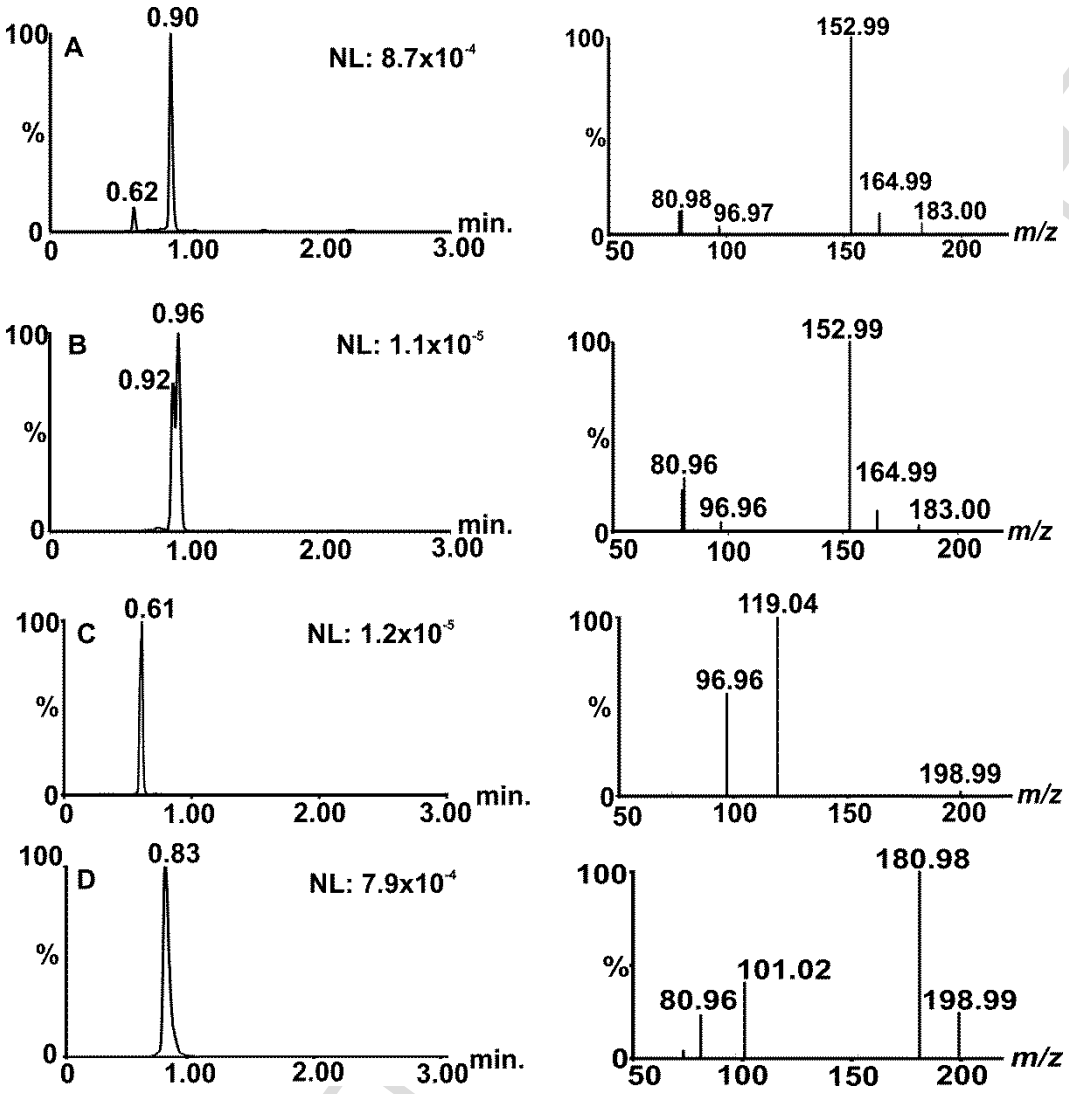
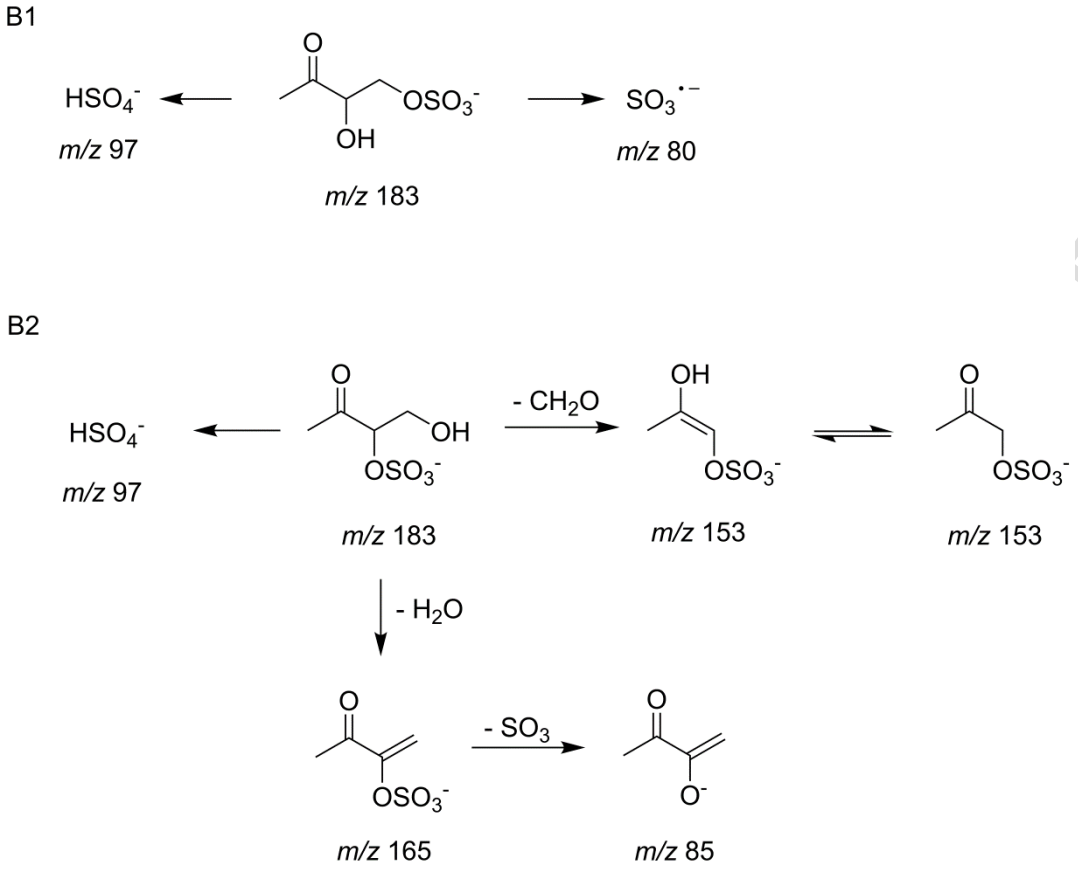


Fig. 2. Extracted ion chromatograms along with negative ion electrospray product ion spectra recorded for: A) *m/z* 183 ion in the fine ambient $PM_{2.5}$ aerosol sample; B) *m/z* 183 ion in the MVK aqueous sample (the product ion spectrum for the RT 0.92 min isomer is not shown); C) *m/z* 199 ion in the ambient $PM_{2.5}$ aerosol sample; D) *m/z* 199 ion in the MVK aqueous sample.

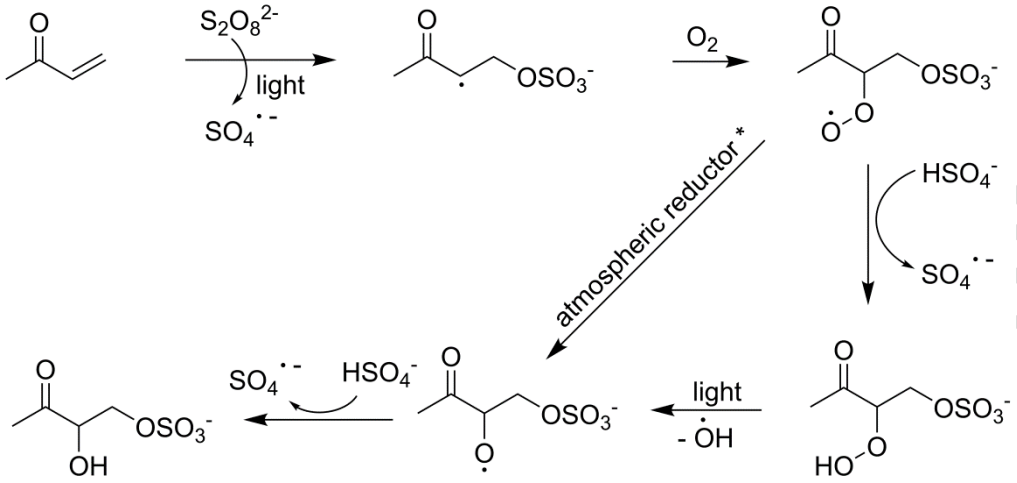
The presence of the two weakly resolved peaks in the chromatographic profile points to positional isomers, which could differ by the position of the sulfate group in the molecule. Although the MW 184 organosulfate has been reported in earlier studies (Surratt et al., 2006; Schindelka et al., 2013; Shalamzari et al., 2016), the separation and structural differentiation of its isomers failed due to a poor chromatographic resolution. The *m/z* 183 product ion mass spectrum recorded for the major RT 0.96 min isomer revealed a *m/z* 183 → *m/z* 153 transition, corresponding to the neutral loss of CH_2O (formaldehyde), which points to the presence of a terminal primary OH group (Scheme 1 B2). Interestingly, the same fragmentation behavior was not evidenced for the RT 0.92 min isomer (spectra not shown), which suggests the presence of a sulfated primary OH group and a secondary OH group in the MVK-retained backbone (Scheme 1 B1). A detailed discussion of the issue was reported elsewhere (Safi Shalamzari et al., 2013; Szmigielski, 2016; Spolnik et al., 2018). The comparison of LC-MS data for ambient $PM_{2.5}$ aerosol and laboratory-generated aqSOA revealed that the later-eluting isomer (RT 0.96 min) of the MW 184 organosulfate produced from the laboratory experiment is present in ambient $PM_{2.5}$ aerosol (RT 0.90 min) as indicated by its chromatographic and mass spectral properties. The reason for the difference in the retention times could be in very different chemical composition of matrices in the two samples.



Scheme 1. Postulated fragmentation pathways of the MW 184 organosulfate originating from MVK aqueous : B1) early-eluting isomer with the retention time 0.92 min and B2) late-eluting isomer with the retention time of 0.96 min.

A possible reaction pathway for the formation of the MW184 organosulfate from MVK is presented in Scheme 2. Sulfate radicals that form by the homolytic dissociation of peroxydisulfate add to the C=C double bond of methyl vinyl ketone to form a distonic ion with negative charge located on the sulfate group and the radical on the carbon atom. Then, an oxygen molecule, dissolved in the aqueous solution adds to the radical center giving rise to a peroxy radical. In a further reaction, the latter abstracts a hydrogen atom from a bisulfate ion, which is ubiquitous in experimental solutions and turns into the hydroperoxide. Under solar light irradiation, hydroperoxide can dissociate into OH and alkoxy radical, which then can abstract hydrogen from bisulfate anion and turn into the MW 184 product. On the other hand, in atmospheric waters a peroxy → alkoxy radical transition can be pursued by other

dissolved species, such as ubiquitous S(IV) species, e.g., sulfite anions (Townsend et al., 2012); however, the issue would require further laboratory studies.



m/z 183 OS

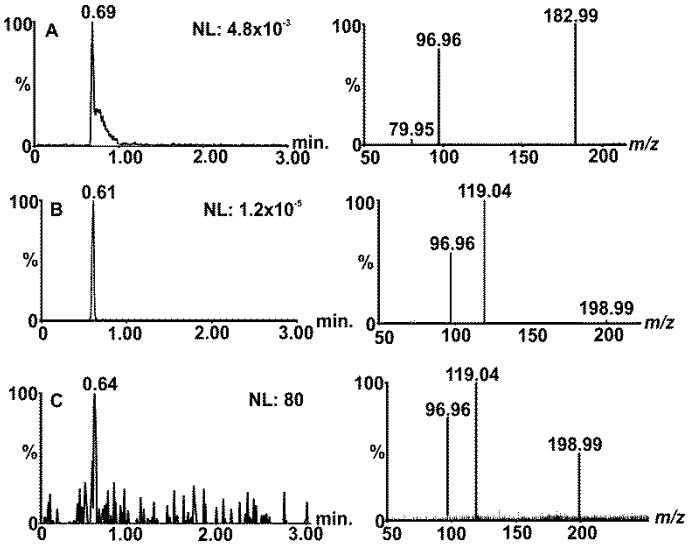
Scheme 2. A tentative reaction mechanism explaining the formation of the MW 184 organosulfate from aqueous of MVK. (* Any atmospherically-relevant red-ox system, e.g., HSO_3^-/SO_3^{2-} -> HSO_4^-/SO_4^{2-})

MW 200 organosulfate

The MW 200 organosulfate originating from the aqueous-phase oxidation of MVK reveals an abundant product at the retention time of 0.83 min ($C_4H_7O_7S$; measured mass: 198.9901; error: -1.1 mDa), although neither the retention time nor the product ion spectrum are reflected in the MW 200 trace component of ambient $PM_{2.5}$ aerosol (Fig. 2 C, D). The presence of a MW 200 organosulfate originating from MVK in ambient fine aerosol was reported earlier (Schindelka et al., 2013); however, our results do not support the latter conclusion.

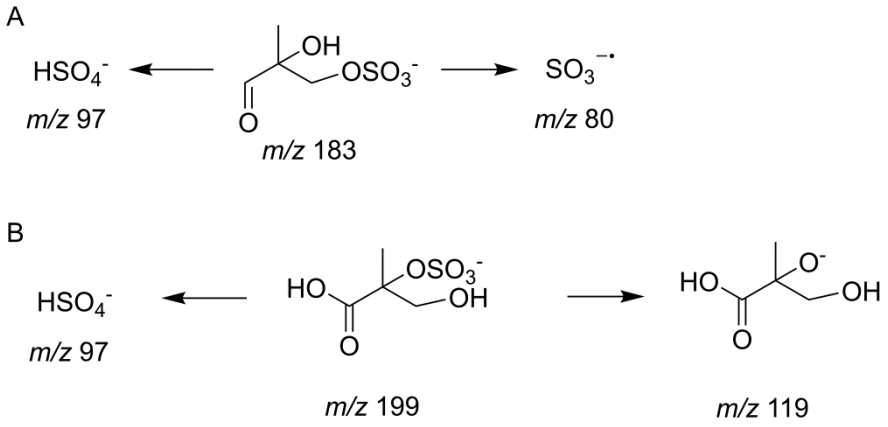
3.5. Chemical characterization of products from aqueous of MACR

375 The chemical characterization of MACR oxidation was targeted to C_3-C_4 organosulfates with
376 the main detected products are listed in Table 1. The MW 154 organosulfate bears the same
377 structural signature as that previously described for MVK.
378



379

380 **Fig. 3.** Extracted ion chromatograms and product ion spectra of: A) *m/z* 183 ion obtained
381 through aqueous of MACR; B) *m/z* 199 in ambient $PM_{2.5}$ aerosol; C) *m/z* 199 obtained
382 through aqueous of MACR.
383
384 *MW 184 organosulfate*
385
386 The aqueous-phase reaction of MACR with the sulfate radicals leads to the formation of a
387 MW 184 organosulfate (Fig. 3 A). In contrast to MVK, the MACR-derived organosulfate with
388 the MW 184 was previously observed in ambient $PM_{2.5}$ aerosol (e.g., Schindelka et al.,
389 2013). Taking into consideration the fragmentation properties, it can be assumed that the
390 position of the sulfate group is terminal since no characteristic neutral loss of formaldehyde
391 (30 Da) is observed. The proposed fragmentation pathways are presented in Scheme 3 A.
392
393



394

395 **Scheme 3.** Proposed fragmentation channels for MACR-derived organosulfates A) the MW

396 184 and B) the MW 200 formed via aqueous reactions.

397

398 *MW 200 organosulfate*

399

400 The MW 200 organosulfate has been reported in previous laboratory experiments (Nozière et

401 al., 2010; Schindelka et al., 2013). The analysis of ambient $PM_{2.5}$ aerosol reveals the MW

402 200 organosulfate as a single peak ($C_4H_7O_7S$; measured mass 198.9915, error: 0.3 mDa)

403 eluting at RT 0.61 min (Fig. 3 B). The aqueous-phase reaction gives rise to the MACR-

404 derived organosulfate featuring a similar retention time (RT. 0.64 min) and an identical

405 fragmentation profile ($C_4H_7O_7S$; measured mass 198.9927; error: 1.5 mDa) as that detected

406 in ambient $PM_{2.5}$ aerosol (Fig. 3 B, C). A detailed analysis of the extracted ion chromatogram

407 (*m/z* 199) at a void time region along with the product ion spectrum led us to postulate a

408 structure bearing a carboxylic acid moiety, a hydroxymethyl moiety and sulfate group located

409 at the tertiary hydroxyl group. Although the fragmentation profile is not very informative (Fig.

410 3 B, C) we can conclude that an easy formation of the bisulfate ion at *m/z* 97 (HSO_4^-)

411 requires access to the proton at the vicinal carbon atom (Scheme 3 B). If the sulfate group

412 was located at the terminal carbon, this fragmentation route would be less likely to occur

413 (Attygalle et al., 2001). As in case of the MVK-related MW184 OS differences are observed

414 for the retention times between the ambient $PM_{2.5}$ sample and the aqSOA sample. In the

415 $PM_{2.5}$ sample the peak elutes slightly earlier, which most probably indicates different matrix
416 comparing to aqSOA from laboratory experiment.
417
418 ## 4. Conclusions
419
420 We showed that two atmospherically relevant α, β-unsaturated carbonyls, but-3-en-2-on
421 (methyl vinyl ketone, MVK) and prop-2-en-1-on (methacrolein, MACR)
422 undergo transformations induced by sulfate radicals in dilute aqueous systems under solar
423 irradiation to form the organosulfates that were previously identified in ambient aerosols and
424 in smog chamber-generated SOA. A detailed interpretation of negative ion electrospray mass
425 spectra along with accurate mass measurements allowed for the molecular characterization
426 of several organosulfates: MWs 154 ($C_3H_5O_5S$), 156 ($C_2H_3O_6S$), 168 ($C_4H_7O_5S$), 184
427 ($C_4H_7O_6S$) and 200 ($C_4H_7O_7S$) that were products of MVK oxidation; and MWs 154
428 ($C_3H_5O_5S$), 184 ($C_4H_7O_6S$) and 200 ($C_4H_7O_7S$) that were products of MACR oxidation. The
429 interpretation of MS^2 mass spectra recorded for MVK-derived organosulfate (MW 184) let us
430 revise its molecular structure. Kinetic analysis based on UV-spectra showed that both MACR
431 and MVK oxidations were fast processes. Therefore, we suggest that photooxidation of
432 MACR and MVK induced by radicals can likely take place in atmospheric waters and lead to
433 formation of aqSOA. Atmospheric waters, which take the form of clouds, rain, fog and dew,
434 offer an ubiquitous environment hosting radical precursors such as SO_2 and H_2O_2. Irradiated
435 by sun, they become a chemical reactor potentially capable of transforming atmosphere
436 organic components into oxidized and functionalized products that contribute to the aqSOA
437 formation. Revealing the molecular identity and structure of these products, and the
438 mechanisms of their formation enables the construction of more accurate models for
439 predicting SOA formation in the atmosphere and its implication on climate change. A recent
440 modelling study showed that aqueous-phase processes can likely contribute to 20-30 Tg
441 $year^{-1}$ production of aqSOA, which is a substantial fraction in the still underestimated budget
442 of atmospheric aerosol (McNeill, 2015). On the other hand, detailed understanding of the

SOA composition helps to track and eventually reduce or eliminate the sources of SOA precursors. Atmospheric transformation of MACR and MVK into aqueous organosulfates is expected in regions with considerable emission of isoprene such as deciduous woodlands or rain forests. The indispensable precursors of sulfate radicals include natural and anthropogenic sulfur dioxide and, according to some researchers (e.g., Nozière et al., 2010), inorganic sulfates, which are ubiquities components of atmospheric aerosol.

Acknowledgments

The research was partially supported by the funding from the Polish National Science Centre (grant Nr OPUS8-2014/15/B/ST10/04276).

References

Attygalle, A.B., Garcia-Rubio, S., Ta, J., Meinwald, J., 2001. Collisionally-induced dissociation mass spectra of organic sulfate anions. J. Chem. Soc.Perkin Trans. 2. 498-506.

Bianchi, F., Tröstl, J., Junninen, H., Frege, C., Henne, S., Hoyle, C.R., Molteni, U., Herrmann, E., Adamov, A., Bukowiecki, N., Chen, X., Duplissy, J., Gysel, M., Hutterli, M., Kangasluoma, J., Kontkanen, J., Kürten, A., Manninen, H. E., Münch, S., Peräkylä, O., Petäjä, T., Rondo, L., Williamson, C., Weingartner, E., Curtius, J., Worsnop, D. R., Kulmala, M., Dommen, J., Baltensperger, U., 2016. New particle formation in the free troposphere: A question of chemistry and timing. Science 352, 1109-1112.

Blando, J.D., Turpin, B.J., 2000. Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. Atmos. Environ. 34, 1623-1632.

von Sonntag, C.S., Schuchmann, H. P., 1991. The elucidation of peroxyl radical reactions in aqueous solution with the help of radiation-chemical methods. Angew. Chem., Int. Ed. Engl. 30, 1229-1253.

Carlton, A.G., Wiedinmyer, C., Kroll, J. H., 2009. A review of Secondary Organic Aerosol (SOA) formation from isoprene. Atmos. Chem. Phys. 9, 4987-5005.

Claeys, M., Bim, G., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., Maenhaut, W., 2004. Formation of Secondary Organic Aerosols through photooxidation of isoprene. Science 303, 1173-1176.

Darer, A.I., Cole-Filipiak, N. C., O'Connor, A. E., Elrod, M. J., 2011. Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates. Environ. Sci. Technol. 45, 1895-1902.

Ervens, B., Turpin, B. J., Weber, R. J., 2011. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. Atmos. Chem. Phys. 11, 11069-11102.

Giorio, C., Monod, A., Bregonzio-Rozier, L., DeWitt, H. L., Cazaunau, M., Temime-Roussel, B., Gratien, A., Michoud, V., Pangui, E., Ravier, S., Zielinski, A. T., Tapparo, A., Vermeylen, R., Claeys, M., Voisin, D., Kalberer, M., Doussin, J.-F., 2017. Cloud processing of Secondary Organic Aerosol from isoprene and methacrolein photooxidation. J. Phys. Chem. A. 121, 7641–7654.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmos. Chem. Phys. 9, 5155-5236.

Hansen, A.M.K., Kristensen, K., Nguyen, Q. T., Zare, A., Cozzi, F., Nøjgaard, J. K., Skov, H., Brandt, J., Christensen, J. H., Ström, J., Tunved, P., Krejci, R., Glasius, M., 2014. Organosulfates and organic acids in Arctic aerosols: speciation, annual variation and concentration levels. Atmos. Chem. Phys. 14, 7807-7823.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., Otto, T., 2015. Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase. Chem. Rev. 115, 4259-4334.

Kameel, F.R., Riboni, F., Hoffmann, M. R., Enami, S., Colussi, A. J., 2014. Fenton oxidation of gaseous isoprene on aqueous surfaces. J. Phys. Chem. C. 118, 29151-29158.

Kolthoff, I.M.; Miller, I.K., 1951. The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. J. Am. Chem. Soc. 73, 3055-3059.

Kwong, K.C., Chim, M. M., Davies, J. F., Wilson, K. R., Chan, M. N., 2018. Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate. Atmos. Chem. Phys. 18, 2809-2820.

Leng, C., Kish, J. D., Kelley, J., Mach, M., Hiltner, J., Zhang, Y., Liu, Y., 2013. Temperature-dependent Henry's Law constants of atmospheric organics of biogenic origin. J. Phys. Chem. A. 117, 10359-10367.

Liang, C.S., Duan, F. K., He, K. B., Ma, Y. L., 2016. Review on recent progress in observations, source identifications and countermeasures of PM2.5. Environ. Int. 86, 150-170.

Liu, Y., Monod, A., Tritscher, T., Praplan, A. P., DeCarlo, P. F., Temime-Roussel, B., Quivet, E., Marchand, N., Dommen, J., Baltensperger, U., 2012. Aqueous phase processing of secondary organic aerosol from isoprene photooxidation. Atmos. Chem. Phys. 12, 5879-5895.

McNeill, V.F., 2015. Aqueous organic chemistry in the atmosphere: sources and chemical processing of organic aerosols. Environ. Sci. Technol. 49, 1237-1244.

Monks, P.S., 2005. Gas-phase radical chemistry in the troposphere. Chem. Soc. Rev. 34, 376-395.

Nguyen, T.B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O., Seinfeld, J. H., 2014. Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds. Atmos. Chem. Phys. 14, 3497-3510.

Noziere, B., 2016. Don't forget the surface. Science 351, 1396-1397.

Nozière, B., Ekström, S., Alsberg, T., Holmström, S., 2010. Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols. Geophys. Res. Let. 37, L05806, doi:10.1029/2009GL041683.

Nozière, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgić, I., Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., Wisthaler, A., 2015. The molecular identification of organic compounds in the atmosphere: state of the art and challenges. Chem. Rev. 115, 3919-3983.

Ouyang, B., Fang, H. J., Zhu, C. Z., Dong, W. B., Hou, H. Q., 2005. Reactions between the SO4 center dot- radical and some common anions in atmospheric aqueous droplets. J. Environ. Sci. China 17, 786-788.

Renard, P., Siekmann, F., Salque, G., Demelas, C., Coulomb, B., Vassalo, L., Ravier, S., Temime-Roussel, B., Voisin, D., Monod, A., 2015. Aqueous-phase oligomerization of methyl vinyl ketone through photooxidation - Part 1: Aging processes of oligomers. Atmos. Chem. Phys. 15, 21-35.

Rudzinski, K.J., 2004. Degradation of isoprene in the presence of sulphoxy radical anions. J. Atmos. Chem. 48, 191-216.

Rudziński, K.J., Gmachowski, L., Kuznietsova, I., 2009. Reactions of isoprene and sulphoxy radical-anions – a possible source of atmospheric organosulphites and organosulphates. Atmos. Chem. Phys. 9, 2129-2140.

Rudzinski, K.J., Szmigielski, R., Kuznietsova, I., Wach, P., Staszek, D., 2016. Aqueous-phase story of isoprene - A mini-review and reaction with HONO. Atmos. Environ. 130, 163-171.

Safi Shalamzari, M., Ryabtsova, O., Kahnt, A., Vermeylen, R., Hérent, M.-F., Quetin-Leclercq, J., Van der Veken, P., Maenhaut, W., Claeys, M., 2013. Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene. Rapid Comm. Mass Spectrom. 27, 784-794.

Schindelka, J., Iinuma, Y., Hoffmann, D., Herrmann, H., 2013. Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols. Faraday Discuss. 165, 237-259.

Schöne, L., Herrmann, H., 2014. Kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solutions. Atmos. Chem. Phys. 14, 4503-4514.

Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K. J., Szmigielski, R., Herrmann, H., 2014. Atmospheric aqueous phase radical chemistry of the isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid -kinetics and product studies. Phys. Chem. Chem. Phys. 16, 6257-6272.

Shalamzari, M.S., Vermeylen, R., Blockhuys, F., Kleindienst, T. E., Lewandowski, M., Szmigielski, R., Rudzinski, K. J., Spólnik, G., Danikiewicz, W., Maenhaut, W., Claeys, M., 2016. Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-E-pentenal, 2-E-hexenal, and 3-Z-hexenal. Atmos. Chem. Phys. 16, 7135-7148.

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., Muller, J. F., Kuhn, U., Stefani, P., Knorr, W., 2014. Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. Atmos. Chem. Phys. 14, 9317-9341.

Spolnik, G., Wach, P., Rudzinski, K. J., Skotak, K., Danikiewicz, W., Szmigielski, R., 2018. Improved UHPLC-MS/MS methods for analysis of isoprene-derived organosulfates. Anal. Chem. 90, 3416-3423.

Surratt, J.D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., Seinfeld, J. H., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. J. Phys. Chem. A. 110, 9665-9690.

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., Seinfeld, J. H., 2007. Evidence for organosulfates in secondary organic aerosol. Environ. Sci. Technol. 41, 517-527.

Szmigielski, R., 2016. Evidence for C_5 organosulfur secondary organic aerosol components from in-cloud processing of isoprene: Role of reactive SO_4 and SO_3 radicals. Atmos. Environ. 130, 14-22.

Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., Claeys, M., 2007. Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry. J. Mass Spectrom. 42, 101-116.

Townsend, T.M., Allanic, A., Noonan, C., Sodeau, J. R., 2012. Characterization of sulfurous acid, sulfite, and bisulfite aerosol systems. J. Phys. Chem. A. 116, 4035-4046.

van Pinxteren, D., Plewka, A., Hofmann, D., Mueller, K., Kramberger, H., Svrcina, B., Baechmann, K., Jaeschke, W., Mertes,S., Collett, J. L., Herrmann, H. 2005. Schmuecke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): Organic compounds. Atmos. Environ., 39, 4305–4320.

Zhao, H., Jiang, X., Du, L., 2017. Contribution of methane sulfonic acid to new particle formation in the atmosphere. Chemosphere 174, 689-699.

Highlights

- Methacrolein and methyl vinyl ketone form SOA in atmospheric waters
- This proceeds through SO_4 radical-mediated reactions to form organosulfates
- Structures of organosulfates formed were elucidated and in some cases revised
- An abundant isoprene-related organosulfate $C_4H_8SO_7$ (*m/z* 199) was detected
- Sunlight enhances the oxidative capacity of atmospheric waters