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Ionic Strength Effect Triggers Brown Carbon Formation through Heterogeneous Ozone Processing of Ortho-Vanillin

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Abstract

Methoxyphenols are an important class of compounds emerging from biomass combustion, and their reactions with ozone and OH can generate secondary organic aerosols (SOA) in the atmosphere. Here we use a vertical wetted wall flow tube (VWWFT) reactor to assess the effect of ionic strength on the heterogeneous reaction of gas-phase ozone (O_3) with a liquid film of o-vanillin (o-VL) (2-hydroxy-3-methoxybenzaldehyde), as a proxy for methoxyphenols. At fixed pH = 5.6, which is representative of moderately acidic aerosol deliquescent particles, the uptake coefficients of O_3 (γ) on o-VL increases from $\gamma = (1.9 \pm 0.1) \times 10^{-7}$ in the absence of Na_2SO_4 to $\gamma = (3.5 \pm 0.1) \times 10^{-7}$ at $I = 0.3 \text{ mol L}^{-1}$, and then it decreases again. The addition of NO_3^- ions only slightly decreases the uptake coefficients of O_3 .

The Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) reveals that the formation of multi-core aromatic compounds is favored upon heterogeneous O_3 reaction with o-VL, in the presence of SO_4^{2-} and NO_3^- ions. The addition of NO_3^- ions favors the formation of nitrooxy (-ONO₂) or oxygenated nitrooxy group of organonitrates, which are potential components of brown carbon that can in turn affect both climate and air quality.

Introduction

Wood combustion and biomass burning generate significant amounts of methoxyphenols arising from the pyrolysis of lignin.^{1,2} The photochemical degradation of polycyclic aromatic hydrocarbons (PAHs), which are also released by biomass burning, is an important additional source of methoxyphenols.³ The methoxyphenols were found to account for about 45 % by mass of the total aerosol particles generated by wood-burning smoke.⁴ Therefore, methoxyphenols have been used as relatively stable tracers in the atmosphere, to assess the contribution of wood smoke to aerosol particles. Simpson et al. (2005)¹ detected methoxyphenols in the ng m^{-3} order, in ambient aerosol samples, with the most abundant compounds being vanillin, syringaldehyde, coniferylaldehyde, and sinapylaldehyde. For this reason, in this work we have chosen 2-hydroxy-3-methoxybenzaldehyde (ortho-vanillin, o-VL) as a proxy compound of methoxyphenols.^{5,6} The Henry's law coefficient of vanillin is relatively high ($4.56 \times 10^5 \text{ M atm}^{-1}$ at 298K)⁷, implying that aqueous-phase photochemical oxidation reactions represent an important o-VL transformation pathway, which could potentially initiate SOA formation in the atmosphere.⁸⁻¹⁰ The photodegradation and the reactions of methoxyphenols with atmospherically relevant oxidants, such as ozone (O_3), nitrate radicals (NO_3), chlorine atoms (Cl) and hydroxyl radicals (OH) have been extensively studied in the past.¹¹⁻¹⁷ A study of photooxidation of vanillin in the presence of nitrite (NO_2^-) at different pH values showed that nitrophenols are the major reaction products.¹⁸

The ionic strength (I) in cloud droplets varies between 7.5×10^{-5} and $7.5 \times 10^{-4} \text{ mol L}^{-1}$,¹⁹ while in marine aerosols it can reach values of up to 6 mol L^{-1} .²⁰ Moreover, aerosol particles in urban

atmosphere can reach $I = 18.6 \text{ mol L}^{-1}$,¹⁹ and haze particles can reach ionic strength values of up to 43 mol L^{-1} .²¹

For this reason, the rates of the photochemical degradation of organic constituents in clouds can differ substantially from those in aerosol deliquescent particles.²² However, our understanding of the ionic-strength effect on the photochemical degradation of organic compounds in aerosols is still in its infancy, compared to that for photooxidation in clouds. Recently, the photochemical degradation of two methoxyphenols, syringaldehyde and acetosyringone, has been investigated at low ionic strength values that are typical for cloud droplets.²³ The rates of degradation of syringaldehyde and acetosyringone were 1.5 and 3.5 times faster, respectively, in the presence of nitrate (NO_3^-) ions ($I = 2.3 \times 10^{-5} \text{ mol L}^{-1}$) than in sulfate (SO_4^{2-}) solutions ($I = 2 \times 10^{-4} \text{ mol L}^{-1}$).²³

At pH 3, which is relevant for acidic aerosol particles, a sharp increase has been observed for the uptake coefficients of O_3 on aqueous acetosyringone, from $\gamma = (1.39 \pm 0.38) \times 10^{-7}$ in the absence of salt to $\gamma = (1.17 \pm 0.01) \times 10^{-6}$ at $I = 0.9 \text{ mol L}^{-1}$, adjusted with Na_2SO_4 .²⁴

In this study, we use a vertical wetted wall flow tube (VWWFT) reactor to investigate the influence of sulfate and nitrate ions on the heterogeneous reactions of O_3 with o-VL, in the dark and under light irradiation ($320 \text{ nm} < \lambda < 400 \text{ nm}$), at pH 5.6 that corresponds to moderately acidic aerosol particles. Indeed, there are lately more and more studies showing that the pH values of aerosol particles under hazy and foggy conditions in China are higher compared to pH values of aerosols in Europe and the USA^{21,25-27}. The combined experimental and field results provided convincing evidence that the pH value of aerosol particles is sufficiently high to promote SO_2 oxidation by NO_2 under polluted conditions in China.²⁶ A pH range of 4.7–6.9 was estimated in winter fog in Beijing²⁷. Cheng et al (2016)²¹ have shown that the aqueous S(IV) concentrations

increase decrease? by two orders of magnitude through S(IV)-NO₂ reaction when the solution pH increases from 4 to 5.4–6.2. Shi et al (2017)²⁵ defined a moderately polluted region (3 < pH < 6), where secondary nitrate and sulfate were the most abundant water soluble (WS) ions²⁵. The oligomeric species formed during the heterogeneous reactions of O₃ with o-VL were assessed by means of Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). The formation of oxygenated aliphatic CHO compounds and multi-core aromatics were observed upon heterogeneous reaction of gas-phase ozone with o-VL in a dilute aqueous phase corresponding to cloud droplets, while the addition of NO₃⁻ ions typical of aerosol deliquescent particles favored the formation of organonitrates, which represent typical brown carbon components.

2 Experimental

2.1 Experimental set-up

The heterogeneous reaction between gas-phase O_3 and a 1mm-thin aqueous layer containing either o-VL, or a mixture of o-VL with SO_4^{2-} or NO_3^- at different concentrations was investigated using a VWVFT connected to an O_3 analyzer. The details of this experimental set-up have been provided in our previous papers.^{24,28} The flow tube is 80-cm long, with an internal diameter (d) = 0.9 cm. Gaseous ozone was generated by a commercial ozone generator (UVP, LLC Upland). The generated ozone was introduced into the vertically aligned flow tube by a movable glass injector^{24,28}, and the ozone concentrations were measured online at the exit of the flow tube by an ozone analyzer (Thermo Scientific Model 49i, USA).

A thermostated bath (Lauda, RC Germany) was used to maintain a constant temperature in the flow tube (298 K (\pm 0.02) K). Aqueous solutions of o-VL ($[o\text{-VL}] = 1 \times 10^{-5}$ mol L⁻¹) (Sigma-Aldrich, 98.5%), or mixtures of o-VL with Na_2SO_4 (Sigma Aldrich, \geq 99.0%) or $NaNO_3$ (Sigma Aldrich, \geq 99.0%) were prepared with ultra-pure water (Sartorius 18 M Ω , H₂O-MM-UV-T, Germany). The experiments related to the dependence of the uptake coefficients on the o-VL concentrations (Figure 1, see below) were performed at the following concentrations of o-VL: 1×10^{-5} , 3×10^{-5} , 4.5×10^{-5} , and 1×10^{-4} mol L⁻¹. The pH values of the o-VL solutions were measured by a pH meter (Mettler Toledo). Adding different concentrations of Na_2SO_4 to an aqueous solution containing o-VL alters its pH (see Table S2). To simulate the pH of clouds and moderately acidic particles, pH was adjusted to 5.6 by drop-wise addition of a prepared 1M solution of HCl. Then, the freshly prepared solution was continuously pumped (5 mL min⁻¹) by

peristaltic pump (LabV1/MC4, SHENCHEN, China) into the flow tube. A laminar flow of the liquid film was established, with Reynolds number lower than 10 ($Re = 0.2$).²⁴

Solid phase extraction (SPE) was used on the o-VL liquid samples containing NaNO_3 and Na_2SO_4 to eliminate the salt prior to FT-ICR MS analysis. A liquid sample with volume of 3 mL was added to the SPE cartridges (Oasis WAX, 150mg, 6cc, 30 μm , Waters, U.S.A). The cartridges were activated by sequential flushing using 3 mL acetone (3 times), methanol, and 2.5% ammonium hydroxide (NH_4OH) dissolved in methanol, respectively. After activation, they were cleaned by 5 mL Ultrapure water (18.2 $\text{M}\Omega$ cm, SARTORIUS, Germany), and air dried. Then, the cartridges were eluted 3 times with 3 mL of NH_4OH in methanol (2.5%). Finally, the effluents were rinsed with methanol and collected in 10mL glass vials. During this procedure, some product compounds can be lost.²⁹⁻³¹

Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

Immediately after the SPE procedure, the liquid samples were collected and analyzed by a solariX XR FT-ICR MS instrument (Bruker Daltonik GmbH, Bremen, Germany), which comprises a refrigerated, 9.4 T actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and a Paracell analyzer cell.^{28,32} The samples were ionized by an electrospray ionization (ESI) ion source (Bruker Daltonik GmbH, Bremen, Germany) in the negative ion mode. The mass range was set to m/z 150 – 1000, and ion accumulation time to 0.65 s.²⁸ The mass spectra were calibrated externally with arginine clusters in negative ion mode, using a linear calibration. A total of 64 continuous 4M data FT-ICR transients were co-added to increase the signal-to-noise ratio and dynamic range.²⁸ To improve the molecular formula assignment accuracy, the final spectrum was internally recalibrated with typical O_2 class species peaks using quadratic calibration in DataAnalysis 4.4 (Bruker Daltonics).³⁰ A typical mass-

resolving power ($m/\Delta m_{50\%}$, where $\Delta m_{50\%}$ is the mass spectral peak full width at half-maximum peak height) $>450\,000$ was determined at m/z 319, with <0.3 ppm absolute mass error.^{28,33}

The custom software was used to calculate all mathematically possible formulas for all ions with a signal-to-noise ratio above 10, using a mass tolerance of ± 1 ppm. The maximum number of atoms for the formula calculator was set to: 30 ^{12}C , 60 ^1H , 20 ^{16}O , 3 ^{14}N , 1 ^{32}S , 1 ^{13}C , 1 ^{18}O and 1 ^{34}S .^{34,35}

The aromaticity equivalent (X_c) has been suggested to use in order to improve the identification and characterization of aromatic and multi-core aromatic compounds.³⁶⁻³⁸ Therefore, X_c of the organic compounds, which contain C, H, O, and N in their chemical structures, was calculated as follows:

$$X_c = \frac{2C + H - O - 2N - 2S}{4C - 2H - O} + 1 \quad (\text{Eq-1})$$

where m and n represent the fraction of oxygen and sulfur atoms, involved in the π -bonds of a molecular structure.³⁶ In our calculations, the values of m and n were set to 0.5, since the negative mode of ESI is most sensitive to compounds that contain carboxylic functional groups.³⁷ Threshold values of X_c between 2.5 and 2.7 ($2.5 \leq X_c < 2.7$) and equal or greater than 2.7 ($X_c \geq 2.7$) were set as minimum criteria for the presence of aromatics or multi-core aromatic compounds in the identified ions.

3. Results and Discussion

3.1. Kinetic data treatment

The uptake coefficient (γ) of O_3 on aqueous o-VL, or on a mixture of o-VL with SO_4^{2-} , or on o-VL mixed with NO_3^- , was estimated as follows:

$$\gamma = \frac{2rk_{1st}H_{O_3}RT}{\bar{v}} \quad (\text{Eq-2})$$

where $\bar{v} = 36000$ (cm s^{-1}) at the temperature $T = 296$ K is the mean molecular velocity of O_3 , $r = 0.45$ cm is the internal radius of the flow tube, k_{1st} (s^{-1}) is the first-order rate constant for the reaction between O_3 and o-VL ($k_{1st} = k_{2nd} [\text{o-VL}]$), H_{O_3} is the Henry's law coefficient of O_3 in the dilute aqueous phase ($H_{O_3} = 1.13 \times 10^{-2} \text{ M atm}^{-1}$)³⁹, and $R = 8.314 \text{ J mol K}^{-1}$.

Eq. (2) holds when the diffusion process is not the rate-determining step.^{40,41} When the reaction in the bulk aqueous phase becomes fast enough compared to the diffusion of gaseous O_3 into the liquid phase, then the reaction will not take place across the entire liquid film but only in the upper surface layer. In such a case, the heterogeneous reaction of ozone with the liquid film is controlled by the aqueous-phase diffusion process.^{24,42} As a consequence, radial gas ozone concentration profiles build up from the liquid film surface to the inner glass tube walls, and the uptake coefficient of O_3 ought to be corrected to account for aqueous-phase diffusion.^{24,28,40,42,43}

When the uptake is controlled by diffusion, the uptake coefficient is given as follows:

$$\gamma = \frac{4H_{O_3}RT\sqrt{k_{1st}D_{aq}}}{\bar{v}} \quad \text{Eq-3}$$

Considering that $k_{1st} = k_{2nd} [\text{o-VL}]$, Eq-3 becomes:

$$\gamma = \frac{4H_{O_3}RT\sqrt{k_{2nd}[\text{o-VL}]D_{aq}}}{\bar{v}} \quad \text{Eq-4}$$

where D_{aq} is the diffusion coefficient of O_3 in the dilute aqueous phase ($D_{aq} = 1.176 \times 10^{-5} \text{ (cm}^2 \text{ s}^{-1})$).³⁹

According to Eq-4, Figure 1 shows the dependence of the measured uptake coefficients of O_3 with the square root of the concentration of o-VL in the aqueous phase.

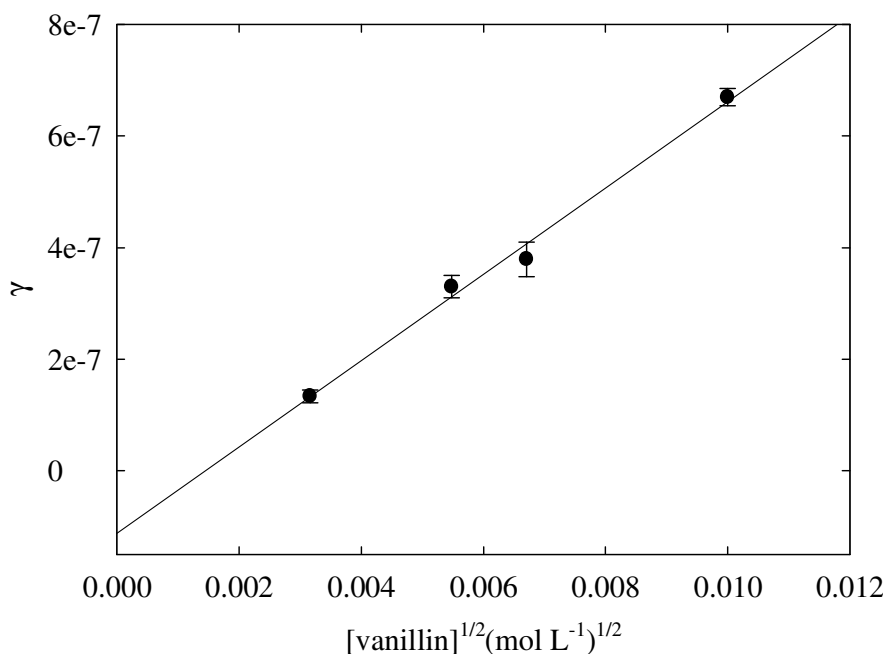


Figure 1: The uptake coefficients of O_3 (200 ppb) as a function of the square root of o-VL concentration in the aqueous phase. The solid line shows the fit according to Eq-3.

Combining Eq-4 with the slope value from the linear regression of the plot depicted in Figure 1, one can estimate the second-order rate constant (k_{2nd}) for the reaction between O_3 and o-VL in the bulk aqueous phase. The estimated $k_{2nd} = 5.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the aqueous-phase reaction of O_3 with o-VL is of the same order of magnitude as the observed second-order rate constants of O_3 with lignin-derived compounds in the bulk aqueous phase ($k_{2nd} = 2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).⁴⁴ However, it can be seen that the intercept of the fit of the observed uptake coefficients with Eq-4

is negative. The negative intercept has no physical meaning, implying that the linear relationship is accurate only for the highest concentrations of o-vanillin, while the equation does not describe the features of the uptake coefficients at low concentrations.^{45,46} This means that the bulk aqueous-phase reaction of O₃ with o-VL takes place together with an additional reaction involving O₃ at the liquid surface. This transition between a surface-controlled regime at low concentrations of reactants and a bulk aqueous-phase regime at high reactant concentrations has been observed previously, and it can be described by the following equation:^{42,43,47,48}

$$\gamma = \frac{4H_{O_3}RT\sqrt{k_{2nd}[o-VL]D_{aq}}}{\sigma} + \gamma_{surf} \quad \text{Eq-5}$$

where γ_{surf} represents the surface reaction between O₃ and aqueous o-VL.

The negative intercept of the fit of the observed uptake coefficients as a function of $\sqrt{[o-VL]}$ also demonstrates that the uptakes of ozone are not controlled by liquid-phase diffusion.⁴²

When Na₂SO₄ and NaNO₃ are added to the aqueous solution, the Henry's law coefficient of ozone ought to be adjusted by the Setchenow equation that takes into account the ionic strength effect.^{24,28,49} For details about the estimation of the Henry's law coefficients of O₃ at different salt concentrations, the readers are referred to our previous studies.^{24,28} The estimated Henry's law coefficients of O₃ at different Na₂SO₄ and NaNO₃ concentrations are reported in Table S4.

3.2. Effect of ionic strength on the uptakes of O₃

The ionic strength can alter the kinetics and products distribution of reactions that occur within the aerosol deliquescent particles, by which it can affect the aerosol composition and optical properties.^{22,24,28,32,50-53} The presence of inorganic ions modifies the pKa of o-VL, which in turn impacts its protonation/deprotonation degree and, as a consequence, its absorption spectrum.^{32,33}

Figure S1 shows the absorbance of 1×10^{-5} mol L⁻¹ o-VL at different ionic strengths, adjusted by

Na₂SO₄. It can be observed a bathochromic shift of the n→π* absorption band of o-VL, from λ_{max} = 340 nm in the dilute aqueous phase to λ_{max} = 385 nm at I = 0.9 mol L⁻¹. A similar red shift has been reported for the absorption spectra of acetosyringone (ACS) and vanillin (VL) as a function of the ionic strength.^{32,33} The measured pH values ranged between 8.79 and 10.11 for ionic strength values between 0.11 and 2.1 mol L⁻¹, (Table S2), and the ionic-strength dependence of the uptake coefficients of O₃ at non-adjusted pH values is shown in Figure S2. The effect of ionic strength was investigated for an o-VL concentration of 1 × 10⁻⁵ M. It can be seen that the uptake coefficients of ozone (500 ppb) first increased sharply, from (4.9±0.3)×10⁻⁷ at I = 0 to (1.9±0.2)×10⁻⁶ at I = 0.3 mol L⁻¹, and then decreased down to γ = (1.7 ± 0.2)×10⁻⁶ at I = 3 mol L⁻¹ (Figure S2).

Because the phenolic group of o-VL becomes ionized at higher ionic strength and pH values, the molecule tends to expand due to the electrostatic repulsion generated by the charge increment.⁵⁴ At the same time, -O⁻ is a stronger activating group than -OH⁴⁹, which leads to enhanced reactivity of o-VL towards ozone.

To evaluate solely the ionic strength effect on the uptake coefficients of O₃, we fixed the pH to 5.6 in both the dilute aqueous phase and in the solutions containing different ionic strengths (Na₂SO₄). The chosen conditions correspond to moderate pH values in the aerosol deliquescent particles.^{55,56} Figure 2 shows the plot of log γ vs. I (Na₂SO₄) at pH 5.6, which suggests an initial increase of the uptake coefficients of O₃ on aqueous o-VL, from γ = (1.9 ± 0.1)×10⁻⁷ at I = 0, to γ = (3.5 ± 0.1)×10⁻⁷ at I = 0.3 mol L⁻¹ (Figure 2). At higher ionic strength, up to 2.1 mol L⁻¹, the uptakes decreased again down to (2.0±0.1)×10⁻⁷. This behavior is in agreement with previous studies, focused on the ionic-strength effects on the reaction kinetics in the atmospheric aqueous phase.^{30,53,57,58}

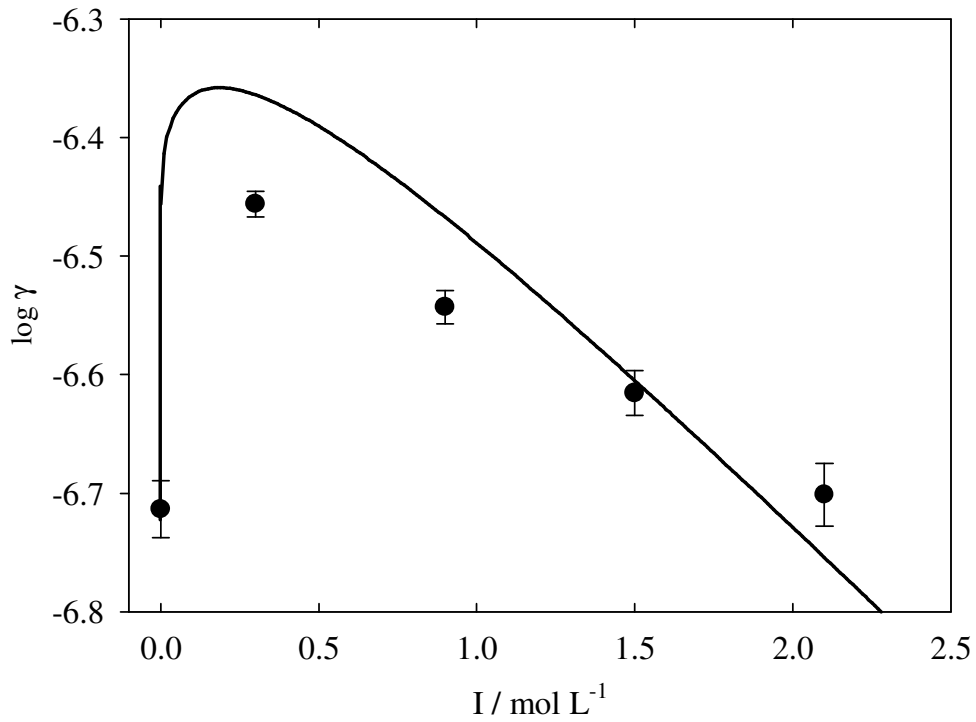


Figure 2: Uptake coefficients of gaseous ozone (200 ppb) on aqueous o-VL (1×10^{-5} mol L⁻¹) as a function of the molar ionic strength I (Na_2SO_4) at pH 5.6. The error bars represent 2σ .

The increase of the rate constants with increasing ionic strength, up to $I \approx 0.5$ M, can be described by the Debye-Huckel-Brønsted-Davies equation upon application of the hypothesis of Guggenheim.⁵⁹⁻⁶¹

$$\log k = \log k(I \rightarrow 0) + A \frac{\sqrt{I}}{1 + \sqrt{I}} + F_{ij} c_{ij} \quad (\text{Eq-6})$$

where I is the ionic strength, A is an empirical parameter ($A = 0.51$ for water at $T = 298$ K), F_{ij} is an adjustable kinetic parameter, and c_{ij} is the concentration of Na_2SO_4 .

Considering that the uptake coefficient is proportional to the square root of the measured pseudo first order rate constants, Eq-6 can be approximated as follows:

$$\log \gamma = \frac{1}{2}(\log \gamma(I \rightarrow 0) + A \frac{\sqrt{I}}{1 + \sqrt{I}} + F_{ij} c_{ij}) + \frac{1}{2} \log D_{aq} - \log \frac{\nu}{4H_{O_3} RT} \quad (\text{Eq-7})$$

Note that γ in Eq-7 is the uptake coefficient of ozone and should not be misinterpreted with activity coefficients of the reactant¹⁹. At low ionic strengths, a catalytic effect of the SO_4^{2-} ions leads to a sharp linear increase of the uptake coefficients, in agreement with previous studies^{53, 62}.

The higher-order empirical term $F_{ij} c_{ij}$ in Eq-7 could describe the decrease of the observed uptake coefficients at higher ionic strength values, without any further physical insight.⁶²

The kinetic parameter F_{ij} emerging from the fit with Eq-7 is $-(0.28 \pm 0.01)$. The obtained fit of the data predicts that the uptake coefficients would further decrease at higher ionic strength values.

The dependence of the uptake coefficients of O_3 with the ionic strength adjusted by NaNO_3 is shown in Figure 3.

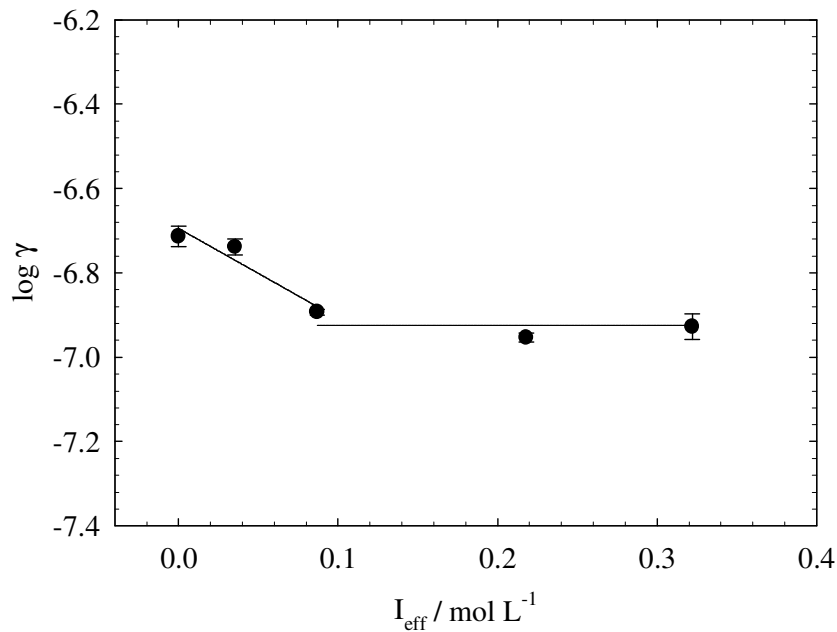


Figure 3: Uptake coefficients of gaseous ozone (200 ppb) on aqueous o-VL (1×10^{-5} mol L⁻¹) as a function of the effective ionic strength I_{eff} (NaNO₃) at pH 5.6. The error bars represent 2σ .

It has to be noted, that NaNO₃ is not completely dissociated in the aqueous phase. To account for this, the ionic strength values were corrected by considering the association equilibrium constant of NaNO₃: $K(\text{NaNO}_3/\text{Na}^+, \text{NO}_3^-) = 1.73 \text{ M}^{-1}$ at $T = 298 \text{ K}$.¹⁹ The effective ionic strength (I_{eff}), for a 1:1 electrolyte such as NaNO₃, can be estimated as follows:⁶³

$$I_{\text{eff}} = \sqrt{\frac{[\text{NaNO}_3]}{K} + \frac{0.25}{K^2}} - \frac{1}{2K} \quad (\text{Eq-8})$$

When NaNO₃ was used as the electrolyte in aqueous solutions containing o-VL, the uptake coefficient of O₃ slightly decreased from $\gamma = (1.9 \pm 0.1) \times 10^{-7}$ in the absence of NaNO₃ to $\gamma = (1.3 \pm 0.1) \times 10^{-7}$ at $I_{\text{eff}} = 0.09 \text{ mol L}^{-1}$. A further increase of the ionic strength to $I_{\text{eff}} = 0.33 \text{ mol L}^{-1}$ did not affect the uptake coefficients any longer (Figure 3). The linear dependence depicted in Figure 3 can be described with Eq-9¹³.

$$\log k_{1\text{st}} = \log [k_{1\text{st}}(I_{\text{eff}} \rightarrow 0)] + b I_{\text{eff}} \quad (\text{Eq-9})$$

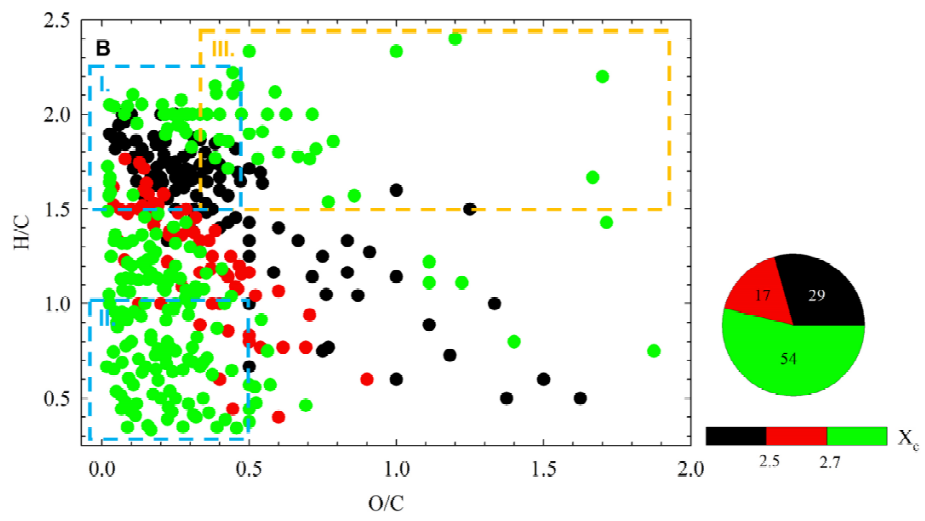
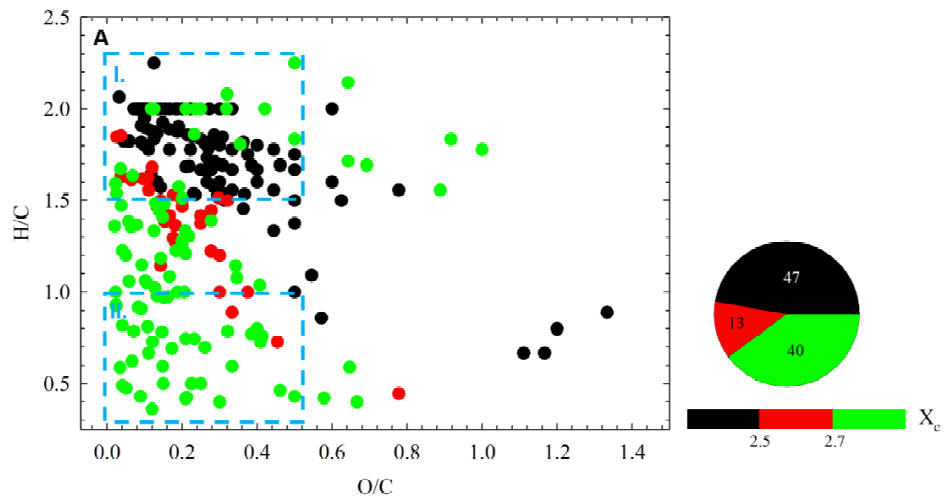
The value of b is an empirical kinetic salting coefficient that determines the acceleration or the deceleration of the observed reaction at different ionic strengths^{19,20}. The slope of the linear regression in Figure 3 gives $b = -(2.1 \pm 0.6) \text{ L mol}^{-1}$ (σ -level uncertainty), which describes the deceleration of the reaction between ozone and o-VL. The decrease of the rate constants with ionic strength leading to a plateau was previously observed both in our lab³³ and by other researchers¹⁹.

The effect of light on the relationship between the uptake coefficients of ozone and the ionic strength was evaluated as well (Figure S3 and Figure S4), and the results show that the O_3 uptakes are not affected by light although o-VL absorbs radiation in the actinic region, and its absorption spectrum overlaps with the emission spectrum of the used lamps (Figure S1). The concentration of o-VL used in this study was quite low ($1 \times 10^{-5} \text{ mol L}^{-1}$), which explains the low absorbance values reported in Figure S1. Low o-VL absorbance, in combination with relatively low spectral irradiance values, could account for the observed similar uptake coefficients in the dark and in the presence of light. Coherently, the liquid-phase products observed upon light-induced heterogeneous reactions of O_3 with aqueous o-VL did not differ from the reaction products obtained under dark conditions. For this reason, only the liquid-phase products that were observed in the dark, upon heterogeneous reaction of O_3 with o-VL in the dilute aqueous phase and in the presence of NO_3^- and SO_4^{2-} are discussed in the section below.

3.3. Assessing the reaction products by FT-ICR MS

3.3.1. CHO class of compounds

In this study, 256 CHO compounds were detected in ESI during the heterogeneous oxidation reaction between gaseous ozone and an aqueous o-VL film. The van Krevelen (VK) diagram, showing typical H/C versus O/C ratios, is generally used for displaying averaged compositional properties of complex organic mixtures.⁶⁴ This approach can provide a rough estimation of the different chemical characteristics of a large number of products, identified by UHR mass spectrometry.⁶⁵ The VK plot of the identified CHO compounds is illustrated in Figure 4: on the basis of H/C and O/C ratios, the identified organic products are separated into two different regions (I and II, respectively). The detected products in region I have high H/C ratio (≥ 1.5) and O/C ratio lower than 0.5, thereby suggesting that they are oxygenated aliphatic CHO compounds.^{37,66} In contrast, compounds in region II have molecular formulas with both low H/C (≤ 1.0) and low O/C (≤ 0.5) ratios, which suggests a degree of unsaturation. For this reason, they should be monoaromatic compounds, or compounds with more than one aromatic ring. Aromatic properties of the aqueous-phase CHO compounds were further examined by the use of the aromaticity equivalent (X_c) (Eq-1), a mathematical parameter for the identification and characterization of aromatics with a benzene core structure ($2.50 \leq X_c < 2.71$) and of multi-core aromatic compounds ($X_c \geq 2.71$). The calculation and use of X_c has been explained in detail by Yassine et al. (2014), Kourtchev et al. (2016), and Wang et al. (2017).³⁶⁻³⁸ Based on this parameter, a large fraction of CHO compounds (47%) would have oxygenated aliphatic groups. However, still a significant fraction (40%) of products of the heterogeneous reaction of gas-phase ozone with aqueous o-VL are multi-core aromatics, as can be seen by the position of those compounds in the lower left corner of the VK diagram.



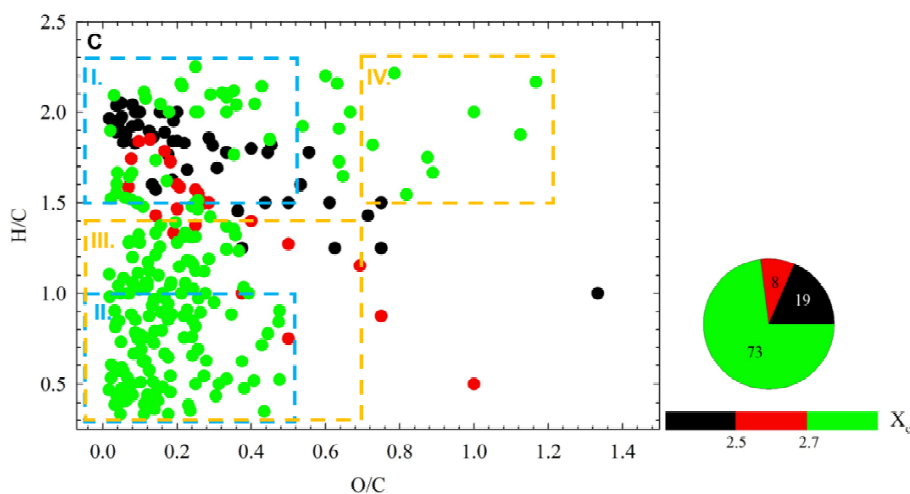


Figure 4: The van Krevelen graph for the CHO, CHON, and CHOS groups of compounds, formed upon dark heterogeneous reaction of O_3 with o-VL (A), with a mixture of o-VL and SO_4^{2-} (B), and a mixture of o-VL and NO_3^- (C). The color-coding indicates the calculated DBE values, based on Eq. S1 of the Supporting Information. The aromaticity equivalent (black with $X_c < 2.5$, red with $2.5 \leq X_c < 2.7$, and green with $X_c \geq 2.7$) follows the color bar, while the pie chart shows the percentage value of each color-coded group in the sample. See the text for the description of regions I to IV.

3.3.2. Formation of organosulfur compounds

In this study, 399 products were detected in ESI^- mode when substantial amounts of SO_4^{2-} ions ($I = 2.1$ M) were added to an aqueous solution of o-VL that was then exposed to gaseous ozone. Out of 399 identified ions, 221 were found to be CHO compounds, while 178 were assigned as CHOS compounds. Most of the CHOS products (114) possess a single sulfur atom in their molecular structure, while the others (64) have two sulfur atoms. Compared to the products of the heterogeneous reactions involving o-VL in the absence of any salt, the products of o-VL + SO_4^{2-} are clearly more numerous (see Figure 4B). More than half of the detected products of o-VL + SO_4^{2-} + O_3 (54%, see Figure 4B) should be multi-core aromatics, as suggested by their X_c .

values ($X_c \geq 2.7$). The formation of compounds with more than one aromatic ring is slightly favored (increase by 14%) when $I = 2.1 \text{ M}$ (SO_4^{2-} ions), compared to the aqueous solution containing o-VL in the absence of any electrolytes. Coherently, these compounds show $\text{H/C} < 1.0$ and $\text{O/C} < 0.5$ (see Figure 4B, region II). However, still a significant fraction (29%) of the identified CHOS products are characterized by a high degree of saturation ($\text{H/C} > 1.5$) and a low degree of oxidation ($\text{O/C} < 0.5$) (see Figure 4B, region D). The addition of sulfate (S(VI)) ions does not favor the formation of products with a benzene-like core ($2.5 \leq X_c < 2.7$, denoted with red color coding on the VK diagram), because the formation of these aromatics is comparable with and without SO_4^{2-} ions. A 33% fraction of all the assigned CHOS molecular formulas has more than four oxygen atoms ($\text{O} \geq 4 \text{ S}$), and is also characterized by quite high degree of saturation ($\text{H/C} > 1.5$). Among all the assigned CHOS molecular formulas, 75% meet the threshold condition for being associated with organosulfates ($-\text{OSO}_3\text{H}$), and they are highlighted with the light-orange box in Figure 4B.

Table S1 comprises 61 compounds (CHO and CHOS) detected upon heterogeneous reaction of O_3 with o-VL in the presence of SO_4^{2-} ions, which are consistent with compounds identified in ambient aerosol samples. However, the same chemical formulas does not necessarily imply agreement between structures as multiple structural isomers are possible for each formula.⁶⁷ Nevertheless, these results suggest that the effect of ionic strength on heterogeneous ozone processing can affect the products distribution in aerosol particles.

3.3.3. Formation of organonitrate compounds

The heterogeneous reaction between gaseous ozone and a liquid solution, containing a mixture of o-VL and NO_3^- ($I_{\text{eff}} = 0.32\text{M}$) yielded several different classes of organic compounds, as

detected in the ESI⁺ mode. Altogether, FT-ICR MS detected 285 ions, among which 133 ions (47%) contained a single nitrogen (N) atom in their molecular structure while the others (53%) were assigned a CHO-type formula. Both identified groups of compounds covered wide mass ranges, starting from m/z 112.0 till m/z 799.0.

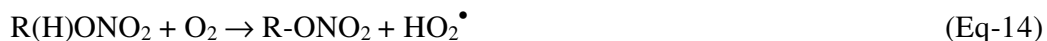
As shown in Figure 4C, the detected products are differentiated into four different regions (I-IV) that possess specific compositional characteristics. Compounds in boxes I and IV have high H/C ratio ($H/C > 1.5$), which suggests the occurrence of highly saturated molecular structures. At the same time, the identified products in the light-blue region I possess low O/C ratio, suggesting the presence of slightly oxygenated aliphatic-like groups, which is in agreement with the low value of X_c (see black color-coding bar in Figure 4C). The compounds located in the upper right region (IV) of the VK diagram are rich in oxygen atoms and exhibit high oxygen-to-nitrogen ratio ($O/N \geq 3$), implying the formation of nitrooxy ($-ONO_2$) or oxygenated nitrooxy groups (organonitrates). The unsaturated compounds are located in the lower left part of the VK plot (regions II and III). Here, the CHON compounds that meet the criteria of $O/C < 0.72$ and $H/C \leq 1.36$ ³¹ are highlighted by the light-orange box (see Figure 4C, region III) and are most probably nitroaromatics.^{31,68} Compared to a dilute aqueous phase consisting of o-VL alone, the addition of NO_3^- ions substantially favored the formation of multi-core aromatics (73%), as suggested by the X_c values (see Figure 4C, green color-coding part in the pie chart).

Table S2 comprises 22 compounds (CHO and CHON) detected upon heterogeneous reaction of O_3 with o-VL in presence of NO_3^- ions, which were also identified in ambient aerosol samples collected from different locations. Through the chemical composition of all detected compounds, which was assigned by the used software (Compass DataAnalysis, Bruker), some tentatively assigned nitroaromatics with accurately detected m/z , intensity, and DBE values are listed in

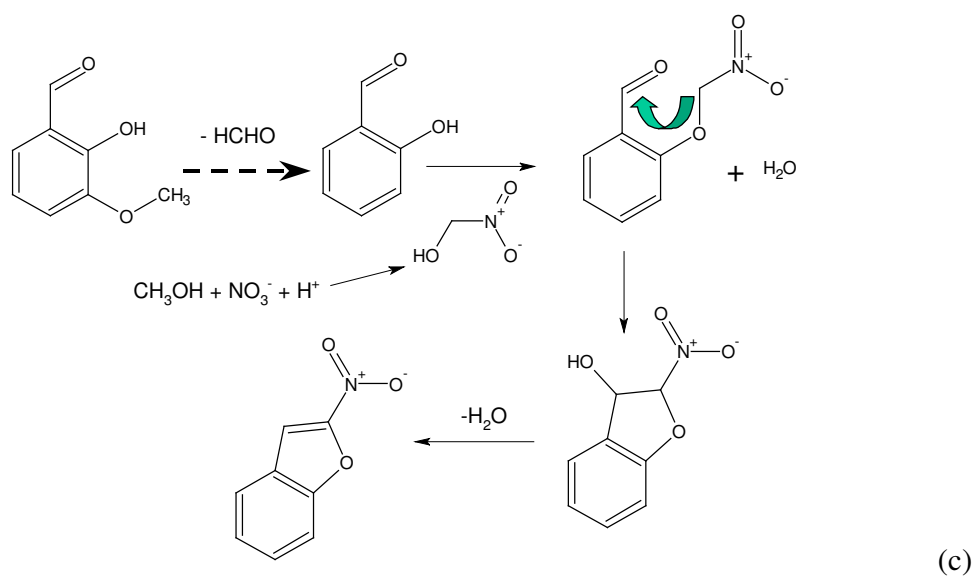
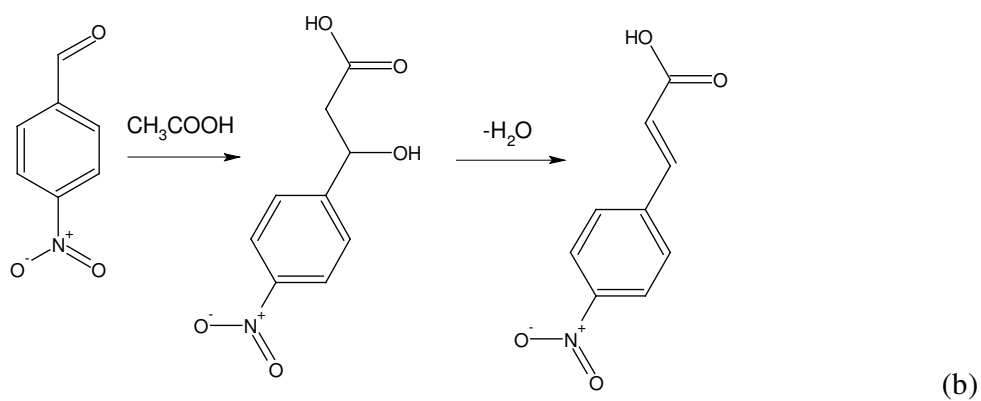
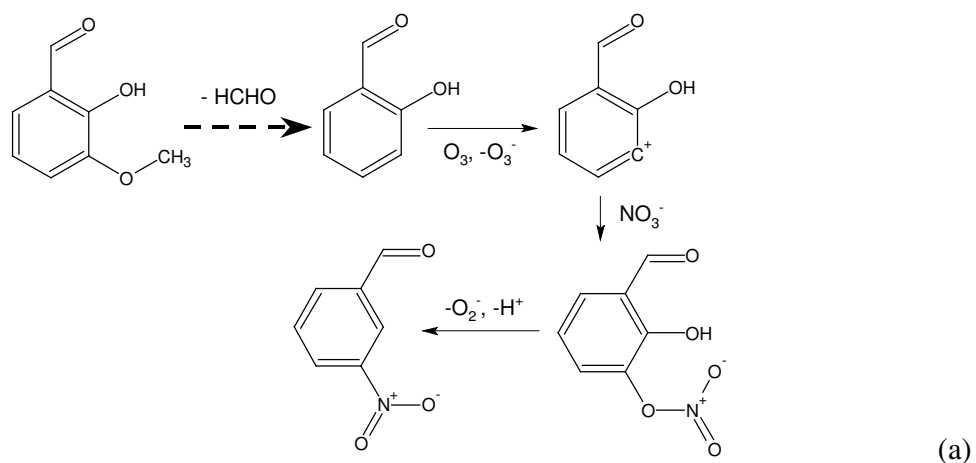
Table S3. Furthermore, the tentative structural properties of those nitroaromatics, which have not been detected in previous studies are depicted in SI.

3.3.4. Possible formation pathways of organosulfates and organonitrates

The formation of compounds containing the $-\text{OSO}_3\text{H}/-\text{OSO}_3^-$ and $-\text{ONO}_2$ groups might originate from one-electron oxidation of organic (aliphatic or aromatic) precursors by O_3 . A tentative reaction scheme may be the following:



It is also possible to propose tentative reaction pathways to account for the formation of some nitroaromatic compounds (Scheme 1), the structures of which are reported in the SI. Nitration by nitrate would likely involve pre-oxidation by, *e.g.*, ozone,^{xx} while aliphatic groups might get attached to the aromatic skeleton by means of aldolic condensation. Such a process, followed by dehydration, could account for the occurrence of intermediates showing C=C double bonds.^{yy} In Scheme 1, we tentatively invoke both detachment and addition of small fragments (HCHO, CH₃COOH, CH₃OH and its derivatives). Multiple additions of these smaller species might account for the formation of the intermediates having more complex structures (see SI for a whole list of the identified nitroaromatic compound structures).



Scheme 1. Tentative formation pathways that could account for the formation of some of the detected nitroaromatic compounds.

xx) von Sonntag, C.; von Gunten, U. *Chemistry of Ozone in Water and Wastewater Treatment. From Basic Principles to Applications*. IWA Publishing, London, UK, 2012, 320 pp.

yy) Smith, M. B. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 7th ed., Wiley, NY, 2013, 2080 pp.

3.3.5. Relationship between DBE and C number

Figure 5 illustrates the distribution of the calculated double bond equivalents (DBE; which takes into account number of π -bonds and rings in a molecule) along the molecular chains in all the identified products, as a function of the number n of C atoms. In general the DBE values range from 1 up to 50 for n values of up to 60, and the plots follow a linear increase of the molecular masses in the presence and absence of salts. If the associated values of X_c are also considered (color code in Figure 5), it can be observed how the ozonation of o-VL with and without electrolytes affected the formation of homologous series with the same functional groups and similar chemical properties.

The heterogeneous ozonolysis of o-VL in the absence of any inorganic ions yielded long and numerous homologous series with low DBE values ($DBE \leq 5$), which would consist of saturated, long-chain aliphatic compounds (see black color-coding peaks in Figure 5A). Several homologous series such as saturated aliphatic compounds could also be observed in the presence of SO_4^{2-} ions (black circles in Figure 5B). In contrast, the presence of NO_3^- ions reduced the formation of aliphatic compounds and produced fewer and shorter homologous series. Indeed, in analogy with previous findings, homologs were way shorter when possessing heteroatoms like S or N in their molecular structures, compared to the series composed of only CHO compounds (see black circles in Figure 5C).⁶⁹

The presence of unsaturated compounds is suggested by relatively high DBE values ($4 \leq DBE \leq 12$) which, combined with $2.5 < X_c < 2.7$, indicates the occurrence of benzene-like core structures (see red homologous series in Figure 5).

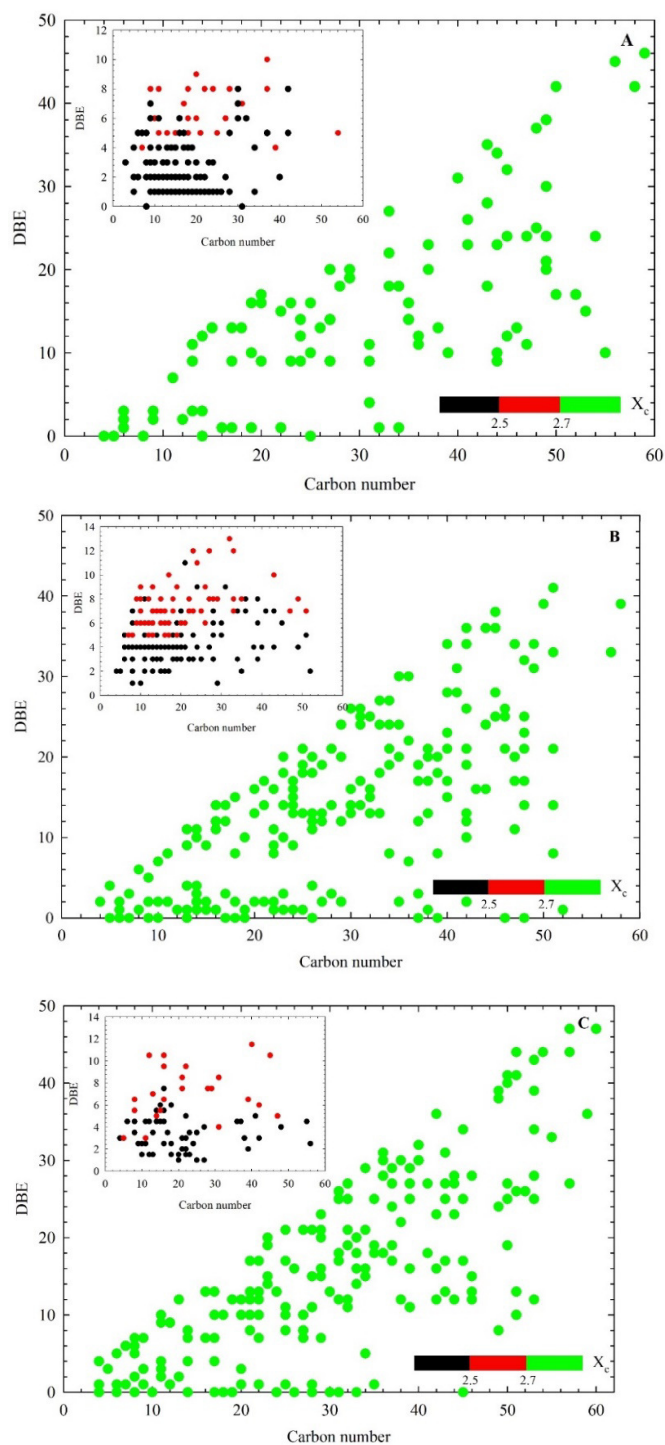


Figure 5: Iso-abundance plot of DBE vs. carbon numbers for the CHO species (green circles), detected upon dark heterogeneous reaction of O_3 with aqueous *o*-VL (A), with a mixture of *o*-VL and SO_4^{2-} (B), and with a mixture of *o*-VL and NO_3^- (C). The color-coding indicates the calculated DBE values from Eq. S1 of the Supporting Information.

There was no significant difference in the formation of monoaromatic compounds (see red circles in Figure 5) upon heterogeneous ozonolysis of o-VL with or without electrolytes.

Compounds with more than one aromatic ring occurred in significant fraction upon addition of SO_4^{2-} and NO_3^- (see green circles in Figure 5B and Figure 5C, respectively), when compared to the case of o-VL alone (Figure 5A). They feature much shorter homologous series compared to aliphatic and monoaromatic compounds, which is most likely due to their rigid molecular structure, containing mostly hydrogen and carbon atoms coupled in a series of polyaromatic-core structures.

Furthermore, the formation of homologous series is additionally explored in the form of KMD vs. KM plot (Figure S5). This plot, by using a regular spacing pattern of $-\text{CH}_2$, arranges all the classified ions to make them follow the same horizontal line, if they are part of the same homologous series. The variation of DBE in those series is depicted by color-coding.

These results highlight the importance of the ionic strength effect on the heterogeneous ozone reactions of methoxyphenols in the liquid core of aerosol deliquescent particles, compared to those occurring in the dilute aqueous phase of cloud droplets.

Based on the determined uptake coefficients, we estimated the atmospheric lifetime of o-VL as follows:

$$\tau = \frac{4N_{\text{tot}}}{\gamma \bar{v} [\text{ox}]_{\text{g}}}$$

where N_{tot} is the surface concentration of o-VL (molecules cm^{-2}), \bar{v} is the mean thermal velocity of ozone (cm s^{-1}), and $[\text{ox}]_{\text{g}}$ is the concentration of ozone (molecules cm^{-3}). Here, it was assumed $N_{\text{tot}} = 10^{14} \text{ cm}^{-2}$.^{24, 70-72} Taking into account the average ozone concentration (7.4×10^{14} molecules cm^{-3}), the atmospheric lifetimes of o-VL due to heterogeneous reaction with ozone at

pH = 5.6, in a dilute aqueous phase and in the presence of $0.1 \text{ mol L}^{-1} \text{ SO}_4^{2-}$, were calculated as 78 s and 22 s, respectively. There is a competitive process between the interface reaction of OH, O_3 and also other oxidants with methoxyphenols enriched in the liquid water of aerosols. The results by Rana and Guzman (2020)⁷³ showed that gas-phase ozone with mixing ratios ranging between 45 and 66 ppb can break the aromatic ring of vanillin and also induce the formation of OH radicals, which in turn can react with the methoxyphenols.

For comparison, the atmospheric lifetime of vanillin was estimated as 7.8 h due to reaction with OH [$\text{OH}(aq)] = 7.5 \times 10^{-15} \text{ radicals L}^{-1}$] on the surface of water and in aqueous particles, at pH 5.⁷³ The atmospheric lifetime of vanillin was estimated as 105 s due to interfacial oxidation with OH radical ($[\text{OH}]_{\text{interface}} = 2.0 (\pm 0.5) \times 10^{-12} \text{ radicals L}^{-1}$).⁷³

The Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry indicates the formation of oxygenated aliphatic CHO compounds and multi-core aromatics upon heterogeneous ozone processing of o-VL in dilute aqueous phase. The addition of SO_4^{2-} that is typical for the liquid core of aerosol deliquescent particles increase the formation of condensed aromatics, but also organosulfates (-OSO₃H) arose upon ozone reactions with o-VL. The addition of NO_3^- ions substantially favors the formation of multi-core aromatic compounds through heterogeneous ozone processing of o-VL. More importantly, the addition of NO_3^- ions favors the formation of organonitrates, which are potential components of the still poorly characterized light-absorbing organic matter (“brown carbon”) that has the potential to affect both climate and air quality.

Considering the high concentrations of inorganic salts occurring in aerosol deliquescent particles during haze events, these observations can have a significant impact on the SOA formation

processes through heterogeneous processing of ozone on methoxyphenols, and could thus affect the radiative properties of clouds and aerosol particles.

Associated content

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Supporting Information

Additional 5 figures and 3 tables. The supporting information is available free of charge via the Internet on the ACS Publications website at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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