Ionic strength effects on the photochemical degradation of acetosyringone in atmospheric deliquescent aerosol particles

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Abstract

A number of laboratory experimental investigations, field campaigns, and modeling results have emphasized the role of aqueous-phase photochemical reactions in the formation of secondary organic aerosols (SOA). However, investigations focused on aqueous-phase reactions under high ionic-strength conditions are scarce. Here we study the photochemical behavior of a lignin-derived compound, acetosyringone (AcS), upon addition of an inert salt ($NaClO_4$). The increase in the ionic strength modifies the acidic constant of AcS, enhancing its deprotonation. As a consequence, the UV-VIS absorption spectra of AcS undergo modifications due to red shifts at high ionic strength of the electronic transitions n $\rightarrow$ π* (from λ_{max} = 297 nm to λ_{max} = 355 nm) and π $\rightarrow$ π* (from λ_{max} = 214 nm to λ_{max} = 247 nm). At fixed pH = 4, representative of moderately acidic atmospheric aerosol deliquescent particles, the pseudo-first-order rate constants (k_{1st}) of AcS increased by ~6 times from a dilute aqueous phase to a solution with an effective ionic strength $I_{eff.}$ = 0.46 M. The rate constant then followed a saturation trend at elevated ionic strength up to $I_{eff.}$ = 3.1 M. A similar saturation effect of the observed rate constants with ionic strength was observed in presence of NaCl and Na_2SO_4. Differential absorption spectroscopy (DAS) methodology was applied to examine the changes in absorption spectra of AcS upon prolonged light irradiation. The very subtle pH-induced changes of the absorption spectra of irradiated AcS are due to the formation of acidic compounds emerged upon photochemical transformation of AcS.

INTRODUCTION

In the aerosol deliquescent particles the ionic strength ranges from 10^{-4} mol L^{-1} in the dilute aqueous phase (cloudwater, rain) to 10 mol L^{-1} in sea-salt aerosols, and up to 40 mol L^{-1} in urban aerosols (Herrmann, 2003, Fountoukis and Nenes, 2007, Herrmann et al., 2015). The physical matrix of concentrated electrolytes in high-ionic strength aerosol deliquescent particles in the atmosphere contains myriad of compounds that may be involved in aqueous-phase reactions (Zellner and Herrmann, 1995). The aqueous phase reactions that involve neutral-neutral or ion-neutral molecules are identified as primary kinetic salt effect type II (Herrmann and Zellner, 1998), and they can be rationalized within the Debye-McAulay framework (Debye and McAulay, 1925). In the regions most affected by acid rain, such as the north-eastern United States, Scandinavian countries and China, typical pH values of precipitation water are around 4 (Reid and Sayer, 2002), despite the fact that in China the concern about acid rain has emerged later than in Europe and North America (Zhao et al., 1988). The concentration of H^+ determines the acidity of aerosol deliquescent particles. Aerosol acidity may influence the pH-dependent aqueous phase processes that take place in the aerosol condensed phase, which in turn contribute to the formation and growth of SOA.

In the past, it has been widely assumed that the ionic strength effects on the rates of the reactions involving one neutral species can be neglected. While this may be true with respect to the Debye-Huckel theory in the range of low salt concentrations (I < 0.5), concentrated electrolyte solutions may significantly alter the rate constant for a reaction involving neutral species (Herrmann and Zellner, 1998; Jacobi et al., 1999; Umschlag et al., 2002; Herrmann, 2003; Weller et al., 2010; Mekic et al., 2018).

Therefore, aqueous-phase reactions should be studied at high ionic strength in order to improve the aerosol models (Herrmann, 2003). The importance of this kind of investigation emerges from the fact that such studies may yield correlations which, in the future, may allow for the estimation of reaction rates at high ionic strengths for different electrolyte composition and content (e.g., for marine *versus* urban deliquescent aerosol particles). However, to the best of our knowledge the information about ionic strength effects on aqueous-phase rate constants are scarce (Herrmann, 2003). In this study, for the first time the photoinduced degradation of acetosyringone (AcS) is evaluated in the aqueous phase in the presence of high ionic-strength conditions.

Only few kinetic studies in the past have focused on ionic strength effects on non-radical aqueous-phase reactions, despite the importance of these studies to improve our understanding of kinetic salt effects and ion pairing.

EXPERIMENTAL SECTION

Irradiation Procedures

A custom-built double-wall photoreactor made up of borosilicate glass, with a volume of 130 cm^3, was used to evaluate the photochemical degradation of AcS. The photoreactor is thermostated by thermostatic bath (LAUDA ECO RE 630 GECO, Germany). Samples were magnetically stirred during irradiation, and the temperature during all the experiments was held at 293 K.

A fresh solution containing 1×10^{-4} mol L^{-1} of ACS (Sigma-Aldrich, 98.5%) was prepared in ultra-pure water (18.2 MΩ cm, SARTORIUS, Germany). The ionic strength of the solution was adjusted by adding the required amount of sodium perchlorate ($NaClO_4$) up to a maximum concentration of 5 M. $NaClO_4$ was used in these experiments because it is photochemically inert.[18] Additional control experiments were performed by adjusting the ionic strength of the solution with Na_2SO_4 and NaCl. When needed, pH was adjusted by adding drop-wise a concentrated (1 mol L^{-1}) HCl solution.

Photochemical Conditions

A high pressure Xenon lamp (500 W) was used as the light source to simulate the sunlight irradiation. A water filter was applied to remove the infrared radiation, and a cutoff filter letting radiation pass in the wavelength range of 300 nm ≤ λ ≤ 700 nm was used to provide UV-vis radiation that is relevant to the lower layer of the atmosphere, close to the earth surface. The emission spectrum was measured with a calibrated spectroradiometer (Ocean Optics, USA) equipped with a linear-array CCD detector (Figure 1S). The photoreactor was exposed to continuous light emission with a total photon flux density of 6.9×10^{17} photons cm^{-2} s^{-1} nm^{-1} in the wavelength region between 310 nm and 400 nm. For comparison, the photon flux density of sunlight in the same wavelength region (310-400 nm) is 6.7×10^{15} photons cm^{-2} s^{-1} nm^{-1}, i.e., around two orders of magnitude lower than our irradiation setup. UV-vis spectra of initial (0 h) and irradiated samples (2h, 4h, 6h, and 8h irradiation time) were recorded immediately after sample aliquot withdrawal, with a UV-VIS double-beam spectrophotometer (Shanghai Drawell Scientific, China) in quartz cuvettes with 1 cm optical path length. The AcS concentration was derived based on the maximum of its absorption spectrum at ~296 nm (the AcS absorption

maximum at pH ~ 4), after checking for the absence of spectral deformations in the absorption peak that might suggest the occurrence of important interference by radiation-absorbing transformation intermediates.

RESULTS AND DISCUSSION

Effect of ionic strength on the AcS absorbance

The pKa (7.8 ± 0.2) value of AcS is dependent on the ionic strength and the solvent used (Ragnar et al., 2000). The phenolic group is the most important lignin functional group, and the reactivity of lignin and lignin derivatives such as AcS is to great extent dependent on the acidity of the phenolic group. Figure 1 shows the absorbance of 1×10^{-4} mol L^{-1} AcS in the diluted aqueous phase and at different ionic strengths, adjusted by $NaClO_4$.

It can be observed a bathochromic (red) shift of the n→π* absorption band of AcS, from λ_{max} = 297 nm in the dilute aqueous phase to λ_{max} = 355 nm at in the presence of 5 mol L^{-1} $NaClO_4$. Also the π → π* band underwent a red shift, from λ_{max} = 214 nm to λ_{max} = 247 nm. A similar bathochromic shift has been reported for the absorption spectrum of pyruvic acid as a function of ionic strength (Mekic et al., 2018). The measured pH value of the AcS solution increased from 6.7 at zero ionic strength to 8 in the presence of 5 mol L^{-1} $NaClO_4$, but this is most likely a measurement bias induced by the large Na^+ excess (sodium error of the electrode). Typically, the weak London dispersion forces between a molecule and the surrounding H_2O/ClO_4^- species are responsible for the bathochromic shift (Reinhardt, 2003).
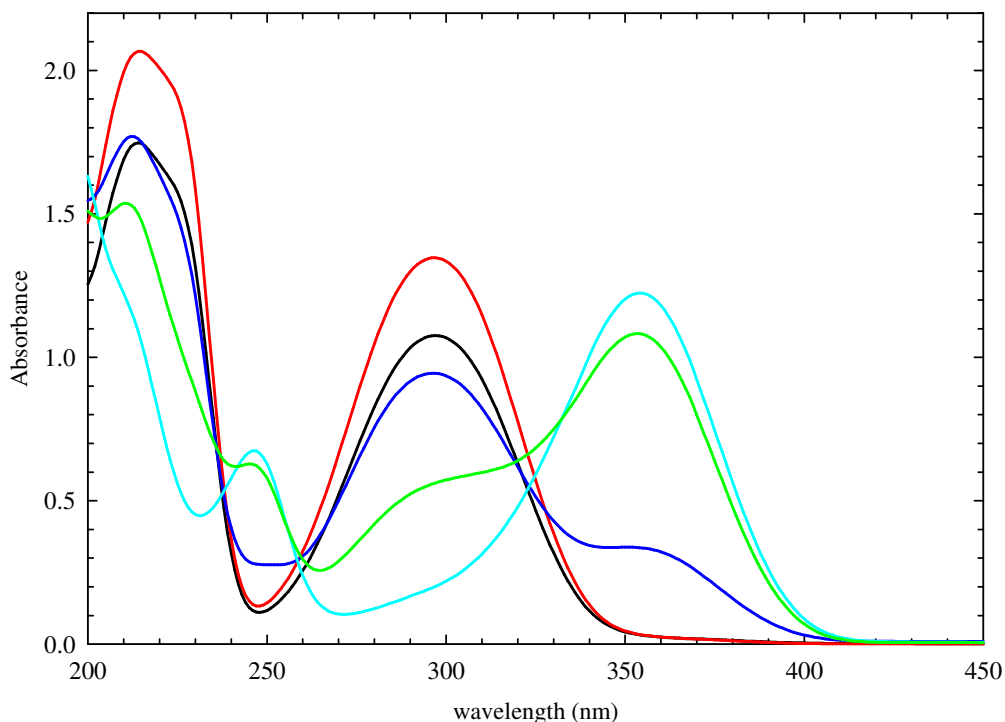
Figure 1: The absorption spectra of AcS (1×10^{-4} mol L^{-1} concentration) at zero ionic strength (black line), and in the presence of different concentrations of $NaClO_4$: 0.5 M (red line), 1 M (blue line), 2 M (green line) and 5 M (cyan line).

A variation in the ionic strength may modify the pKa of acid-base equilibria, which may in turn affect the protonation/deprotonation degree of an acidic solute and, as a consequence, its absorption spectrum. It is possible to assess the ionic-strength effects on the pKa values by means of the Davies approach (Davies, 1962); in the case of neutral AcS undergoing deprotonation to H^+ and the AcS phenolate anion, the pKa value would be modified as follows:

$$pK_a = pK_a - \frac{2A\sqrt{I}}{1+\sqrt{I}} + bI \qquad \text{(Eq-1)}$$

where pK_a = 7.8 is the value at zero ionic strength, and A = 0.51. The value of b = $b_{H^+} + b_{AcS^-} - b_{AcS}$ (where AcS^- is the conjugated base of AcS) defines the so-called salting-out of neutral and charged solutes because of, among others, the decreasing activity of the solvent. The values of b_{AcS^-} and b_{AcS} are unfortunately not available, thus only reasonable guesses for b can be made. The trend of pKa as a function of the ionic strength of the solution for different values of b is reported in Figure 2. The plot shows a decrease of pKa (i.e., an increase of the AcS acidity) as the ionic strength increases, but the initial decrease is offset at high ionic strength if the value of b is high enough.
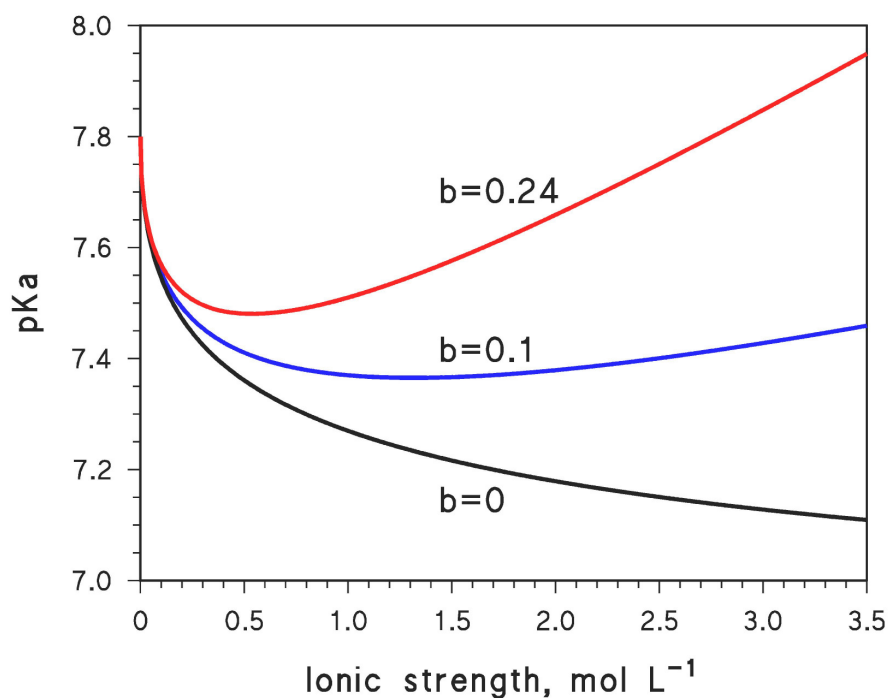
Figure 2. Trend of pKa as a function of ionic strength, following Eq-1 for different values of b.

An increase of AcS acidity with increasing ionic strength would favor deprotonation, causing a decrease in the absorption maximum of protonated AcS (297 nm) and an increase in the absorption maximum of AcS$^-$ (355 nm). The ionic strength trend of the AcS absorption spectra reported in Figure 1 suggests that the pKa value should decrease monotonically with the ionic strength. This means that b should be lower than 0.1. Also note that the ionic strength value does not coincide with the NaClO$_4$ concentration, because the salt is partially associated (vide infra).

AcS Irradiation: Results and Kinetic Data Treatment

The pH value is an important property of condensed aerosols. Indeed, pH is a sensitive parameter that can significantly affect the light-absorbing properties and the degree of photochemical degradation of organic compounds (Nieto-Gligorovski et al., 2010; Nguyen et al., 2012; Smith et al., 2014; Zhao et al., 2015; Hinrichs et al., 2016, Cai et al., 2018). AcS has a pKa value that is not far from neutrality, and small pH modifications in ~neutral solution might affect the acid-base equilibrium of AcS. For this reason, and to assess the effect of ionic strength alone on the photoinduced AcS degradation, we fixed the solution pH to 4 in both the dilute aqueous phase and in the presence of different ionic strengths. The chosen pH for the irradiation experiments corresponds to moderately low pH values of the atmospheric aerosol deliquescent particles (Guo et al., 2015).

The inert salt sodium perchlorate (NaClO$_4 \cdot$ H$_2$O) was used to adjust the ionic strength of the solution. NaClO$_4$ is not completely dissociated in the aqueous solution, and a correction of the ionic strength was thus applied by considering the association equilibrium constant of NaClO$_4$: K(NaClO$_4$/Na$^+$,ClO$_4^-$) = 0.2 M^{-1} at T = 298 K (von Bünau G and Wolff, 1987). The ion association constant depends on the ionic strength because the latter affects the activity

coefficients, while in turn the ionic strength depends on ion association (van Boekel, 2009). To the best of the authors' knowledge, the dependence of K on the ionic strength is not known. Therefore, we assumed that K = 0.2 M^{-1} for Na$^+$ClO$_4^-$ at all ionic strength values.

The effective ionic strength (I$_{eff}$) can be calculated by applying the following equation (von Bünau G and Wolff, 1987):

$$I_{eff} = \sqrt{\frac{[NaClO_4]}{K} + \frac{0.25}{K^2}} - \frac{1}{2K} \tag{Eq-2}$$

The maximum absorbance of AcS (λ_{max} ~296 nm) was plotted as a function of the irradiation time (see Figure 3). The absorbance decay with time followed a mono-exponential trend with a residual, where the residual absorbance was most likely accounted for by other species that, although not modifying the overall shape of the absorption spectrum, also absorb at λ_{max}. The experimental data were fitted with the following three-parameter function:

$$A_{\lambda_{max}}(t) = \alpha \cdot e^{-k_{1st} t} + \beta \tag{Eq-3}$$

where $A_{\lambda_{max}}(t)$ is the absorbance at λ_{max} at the time t, α and β are fitting parameters, and k_{1st} is the pseudo first-order rate constant of ACS decay.

The value of k_{1st} increased by ~6 times, from $(9.6\pm1.5)\times10^{-6}$ s^{-1} at I$_{eff.}$ = 0 M to $(5.5\pm0.7)\times10^{-5}$ s^{-1} at I$_{eff.}$ = 0.5 M. At higher ionic strength the value of k_{1st} decreased slightly (see Figure 4). The increase of the rate constants by increasing the ionic strength up to I $\approx$ 0.5 M can be reasonably described by the Debye-Huckel-Bronsted-Davies equation (Liu et al., 2003):

$$\log k = \log k(I \to 0) + 2Z_A Z_B A \frac{\sqrt{I}}{1+\sqrt{I}} + b\, I \tag{Eq-4}$$
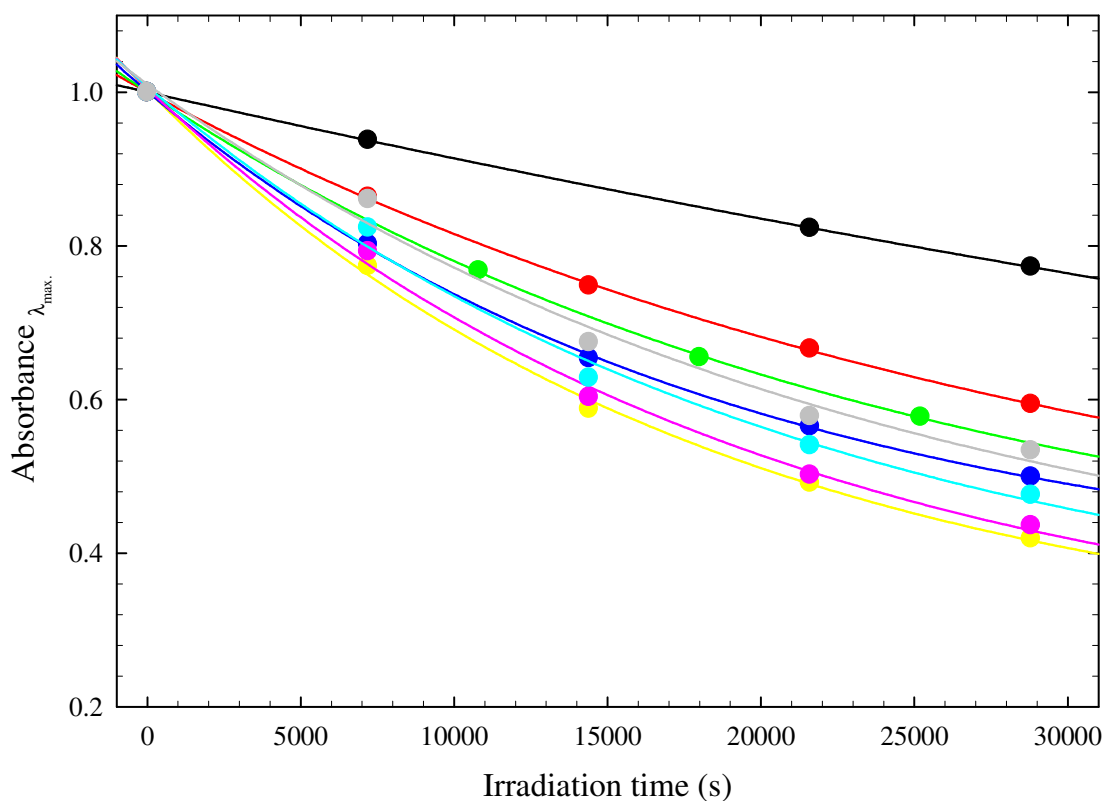
Figure 3. Trend of the λ_{max} absorbance of the solution ($A_{\lambda_{max}}$), as a function of the irradiation time of AcS (initial concentration of 1×10^{-4} mol L^{-1}), in the presence of different concentration values of NaClO$_4$. ●) I$_{eff}$ = 0 M; ●) I$_{eff}$ = 0.001 M; ●) I$_{eff}$ = 0.098 M; ●) I$_{eff}$ = 0.46 M; ●) I$_{eff}$ = 0.85 M; ●) I$_{eff}$ = 1.53 M; ●) I$_{eff}$ = 2.11 M; ●) I$_{eff}$ = 3.11 M.

When the reaction involves a neutral molecule, the second term in Eq-4 is zero and the rate constant depends on the empirical linear term (b I). Eq-5 can be applied to fit the natural logarithm of the pseudo first-order rate constants of AcS as a function of the effective ionic strength values (Bao and Barker, 1996, Herrmann, 2003, Mekic et al., 2018).

$$\log k = \log [k(I_{eff.} \rightarrow 0)] + b\ I_{eff.} \tag{Eq-5}$$

where $k(I_{eff.} \rightarrow 0)$ is the rate constant at infinite dilution, and b is the empirical kinetic salting coefficient derived from the slope of the linear regression in the plot of log k *versus* $I_{eff.}$. The value of b determines the acceleration of the observed reaction in the presence of added salt (Debye and Mc Aulay, 1925; Davies, 1962).
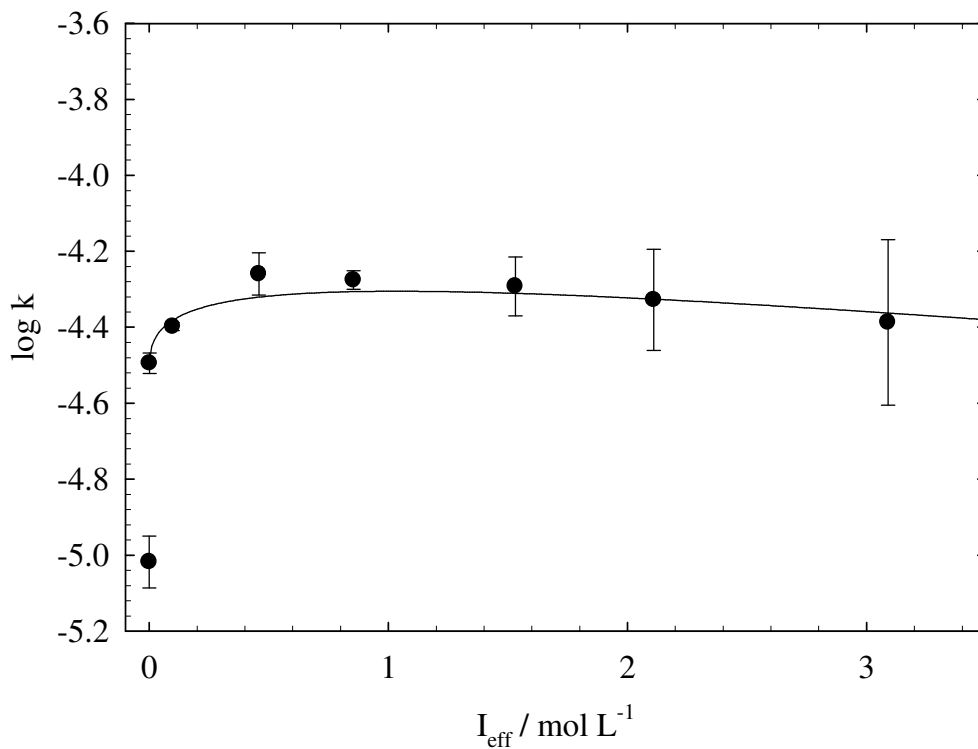
Figure 4. Trend of log k vs. $I_{eff.}$. The error bounds represent the σ-level uncertainty of the exponential data fit used to obtain k.

However, the plot of log k *versus* I_{eff} depicted in Figure 4 is inconsistent with Eq-5, which predicts a linear dependence. Higher order empirical terms in Eq-5 could describe the saturation behavior in Figure 4 without any further physical insight (Bao and Barker, 1996).

Therefore, it seems worthwhile to compare the obtained results with those expected from the theory of ionic solutions. For this purpose, we used Eq-6 that is obtained by modifying Eq-4 and applying the hypothesis of Guggenheim (Guggenheim and Wiseman, 1950, Perlmutter-Hayman et al., 1963).

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

where I is the ionic strength, A is an empirical parameter that depends on the solvent and the temperature ($A = 0.51$ for water at $T = 298$ K), F_{ij} is an adjustable kinetic parameter which depends on the solvent, the temperature and the nature of the ions i and j, and c_{ij} is the concentration of the supporting electrolyte. Figure 4 shows the fit of the experimentally obtained kinetic data with Eq-6. It can be seen that at higher ionic strengths the term F_{ij} becomes predominant. The F_{ij} value is found to be -0.06. A number of studies reported such a saturation behavior of the measured rate constants at high ionic strength (Lagrange et al., 1993, Bao and Barker, 1996, Umschlag et al., 2002, Herrmann, 2003, Weller et al., 2010). In a previous study, the plateau trend followed by the rate constants at high ionic strength (NaCl) values for the reaction between SO_2 and H_2O_2 was explained by two opposing factors: 1) a slight decrease of the rate constants when the term F_{ij} becomes predominant, and 2) a catalytic effect of the Cl^- ions leading to a linear increase of the rate constants as a function of the Cl^- concentration (Lagrange et al. 1993). The rate constants of the bimolecular reactions between atmospherically relevant radicals (NO_3, OH, Cl, and Cl_2^-) and organic compounds exhibited a saturation effect at elevated ionic strength (Umschlag et al., 2002, Herrmann, 2003, Weller et al., 2010). Similarly, the rate constants for the reaction system $SO_4^- + H_2O$ exhibited a saturation curve starting from I

= 1 M up to 2 M of NaClO$_4$ (Bao and Barker, 1996). Interestingly, the above-cited authors also used NaClO$_4$ to adjust the ionic strength of the solutions, which enables to do the comparison.

Spectral modifications of irradiated AcS

The irradiation processes may induce small pH variations of the solutions, which in turn may cause changes in the absorption spectra of the solutes that are present from the start or formed as intermediates. Other spectral changes may arise from the occurrence of peculiar transformation intermediates, irrespective of the pH variations. A method that has demonstrated its usefulness to highlight the spectral changes induced by the effect of pH variation is the differential absorbance spectroscopy (DAS) (Dryer, et al., 2008, Janot et al., 2010, Cai et al., 2018). Typically, the pH-related spectral changes are ascribed to the deprotonation of chromophores that possess acidic functional groups (Dryer, et al., 2008, Janot et al., 2010, Phillips and Smith, 2014, Phillips et al., 2017, Cai et al., 2018). The differential absorbance spectra can be calculated as follows:

$$\Delta\alpha(\lambda)_{pH} = \frac{1}{l[AcS]}\left[A(\lambda)_{pH} - A(\lambda)_{pH_R}\right] \qquad \text{(Eq-7)}$$

where $\Delta\alpha(\lambda)$ (cm^{-1} mol^{-1} L) is the change of pseudo-absorbance cross section of aqueous AcS induced by pH variation, l (cm) is the optical path length through the solution, and $A(\lambda)_{pH}$ and $A(\lambda)_{pH_R}$ are the absorbance values at the measured pH and the reference pH, respectively.

The DAS methodology evaluates the changes in UV-VIS absorption spectra associated with evolving reaction conditions, and in this case it can be applied to examine the changes in absorption spectra as the initial pH of the solution is altered upon prolonged light irradiation. This approach can detect very subtle changes in absorption spectra during AcS degradation. Figure 4 shows the DAS (with 0h-spectrum as reference) of two representative samples, i.e, a

dilute aqueous phase that corresponds to cloud water (panel A), and the solution added with 1 M NaClO$_4$ (I$_{eff.}$ = 0.85 M) that represents aerosol deliquescent particles (panel B).

Light-induced transformation of phenolic substances leads to a pH decrease (Ragnar et al., 2000), which in the atmosphere would translate into a light-induced acidification of the aerosol particles due to liberation of protons. Indeed, in our case the initial pH value of the solution in the absence of salt was 3.94, which after 8 h of irradiation decreased to 3.61 and suggests the formation of acidic compounds produced by photochemical transformation of AcS (see inset in Figure 4A). The latter is in agreement with some recent studies (Sun et al., 2010, Yu et al., 2014), showing that carboxylic acids and hydroxylated compounds can be formed during the photochemical transformation of phenols. Figure 4A shows that DAS has a broad absorption band centered at λ = 306 nm, which clearly decreases upon prolonged light irradiation of aqueous AcS. At the same time, the DAS values in the wavelength range of 340 nm < λ < 550 nm display an enhancement of ca. 3 times, from 2 h to 8 h of irradiation, which suggests the formation of light-absorbing compounds (see inset in Figure 4A). The increase of light absorption at longer wavelengths is consistent with the formation of oligomers having large conjugated π-electron systems (Smith et al., 2016). If oligomers are produced in the process, the reaction represents a promising pathway towards SOA formation (Huang et al., 2018).

In the presence of 1M NaClO$_4$, the pH value of the solution decreased slightly from 4.03 before irradiation to 3.93 after 8 h of irradiation. A similar behavior in the DAS spectra was observed in the presence of 1 M NaClO$_4$ (Figure 4B). However, in the latter case (see inset to Figure 4B, and compared with inset to Figure 4A) one has a narrower band in the wavelength region between 340 nm and 550 nm, and a lesser enhancement of this band is observed between 2 and 8 h of light irradiation.
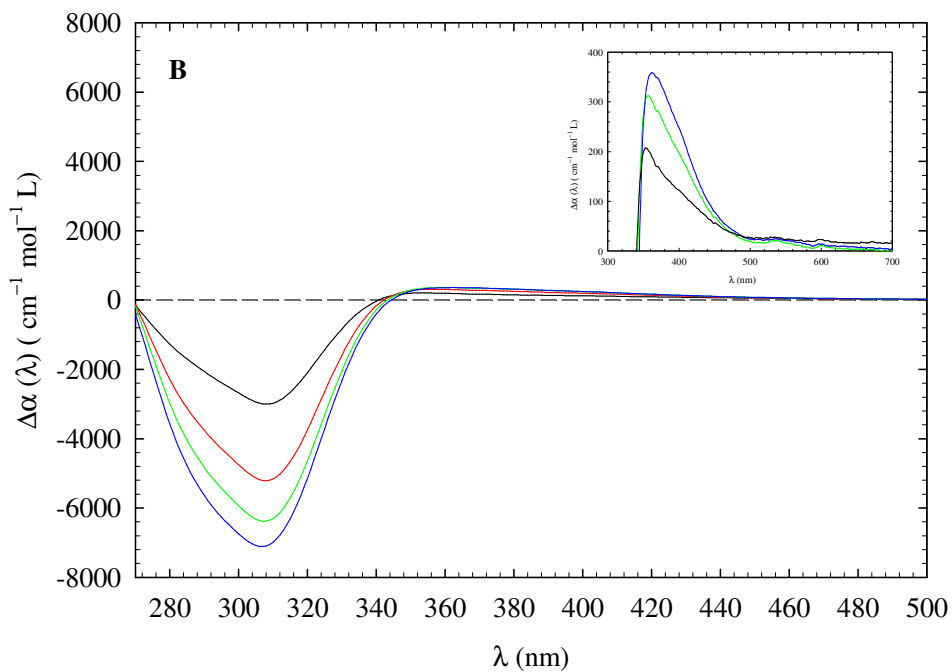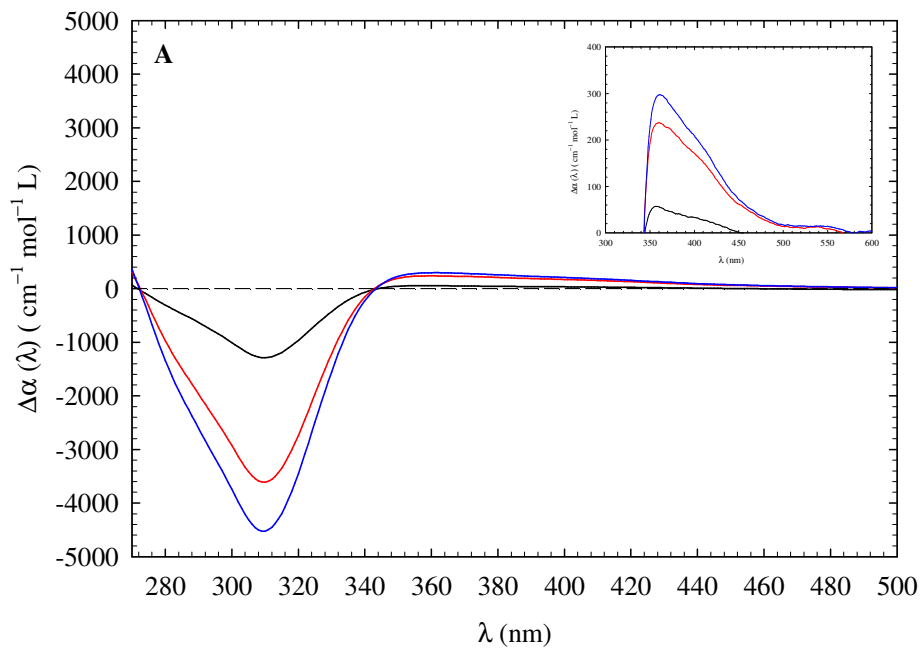
Figure 5: Differential absorbance spectra of AcS obtained upon 2h (black line), 4 h (green line), 6 h (red line) and 8 h (blue line) irradiation, A) in the absence of salt and B) in the presence of 1 M NaClO$_4$. The inset in panel A shows the formation of light absorbing compounds due to acidity change from pH = 3.94 before irradiation to 3.61 after 8 h of irradiation. The inset in panel B shows the formation of light absorbing compounds due to acidity change from pH = 4.03 before irradiation to 3.93 after 8 h of irradiation

Hence, it can be suggested that the enhanced photodegradation of AcS in the presence of high ionic strength as compared to the dilute aqueous phase is compensated for by the lower production of acidic, light-absorbing compounds in the concentrated salt solutions.

Effect of other salts (NaCl, Na$_2$SO$_4$)

Test experiments for the dependence of the kinetic data on the ionic strength, adjusted by addition of atmospherically more relevant salts such as Na$_2$SO$_4$ and NaCl were also performed (see the supplementary information). The kinetic parameters F_{ij} emerging from the fit with Eq-6 are 0.11 and 0.15 for NaCl and Na$_2$SO$_4$, respectively.

CONCLUSIONS

This study expands the current understanding of the photochemical processes occurring in the aerosol deliquescent particles, by investigating the ionic strength effect on AcS photodegradation. The water droplets in the clouds grow around aerosol deliquescent particles, and there are several consecutive phases of condensation-evaporation cycles during the droplet's life in clouds. During this period, the ionic strength of the droplets is variable and may reach high values.

AcS was here studied as a known, typical SOA precursor, and we show that an increase in the ionic strength of the solution affects the AcS light-absorption properties. The most likely explanation is to be found in a decrease of the compound's pKa, which enhances deprotonation in ~neutral conditions and produces a bathochromic shift of the absorbance. This means that the absorption properties of SOA need to be constrained as a function of ionic strength (as well as

pH) within atmospheric photochemical models. Indeed, the bathochromic shift in the AcS spectrum indicates that the optical properties of light-absorbing, water-soluble organic carbon are altered by high ionic strength, which can thus largely affect the total sunlight absorption by aerosols and impact the Earth's radiative forcing as a consequence.

The AcS photodegradation kinetics was enhanced as well under high ionic strength conditions. The observed effect can potentially be operational with other methoxyphenols having H-atom-donating properties. Therefore, this work shows that the photochemical degradation of AcS and, potentially, of other methoxyphenols in aerosol deliquescent particles would proceed with much faster kinetics compared to the analogous diluted aqueous-phase chemistry, which could thus significantly affect the composition and optical properties of the aerosol.

It is important to note that the first-order reaction rate constant of methoxyphenols such as AcS is a function of the nature and the concentration of the supporting electrolyte. However, although less steep in the initial phase, the AcS rate constant trend with ionic strength in the presence of $NaCl$ and Na_2SO_4 as compared to $NaClO_4$ produced a similar order-of-magnitude acceleration of the reaction kinetics.

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