



Short communication

Exploring the ionic strength effects on the photochemical degradation of pyruvic acid in atmospheric deliquescent aerosol particles

Majda Mekic^a, Marcello Brigante^b, Davide Vione^c, Sasho Gligorovski^{a,*}^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510 640, China^b Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000, Clermont-Ferrand, France^c Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 5, 10125, Torino, Italy

A B S T R A C T

There is increasing evidence that aqueous-phase atmospheric chemistry is an important source of secondary organic aerosols (SOA), but the related processes are currently not adequately represented in atmospheric chemistry models. Here we show that the absorption spectrum of pyruvic acid (PA) exhibits both an increase of the absorption intensity and a red shift of 13 nm while going from a dilute aqueous phase to a solution containing the inert salt sodium perchlorate (5M NaClO₄). If this phenomenon turns out to be more general, many compounds that do not absorb actinic light in clouds and fog could become light absorbers at elevated salt concentrations in aerosol deliquescent particles. Compared to the direct photolysis of PA in dilute aqueous solution, the photolysis rate is increased by three times at high ionic strength (5M NaClO₄). Such a considerable enhancement can be rationalized in the framework of the Debye-McAulay approach for reactions of ionic + neutral (or neutral + neutral) species, considering that the PA direct photolysis likely involves interaction between the photogenerated triplet state and water. This is, to our knowledge, the first report of a significant effect of the ionic strength on the rate of an atmospheric photochemical reaction. The phenomenon has important implications for the fate of PA and, potentially, of other organic compounds in atmospheric aerosol deliquescent particles.

1. Introduction

Atmospheric aqueous-phase photochemical processes occur in cloud droplets, fog and rain, which are characterized by low ionic strengths. On the other hand, the ionic strength is dramatically higher in aerosol deliquescent particles. Therefore, while photochemical processes in clouds and haze may be considered as photoreactions occurring in dilute electrolytes, this is not the case for high ionic-strength deliquescent particles. The ionic strength in dilute cloud, fog, and rain droplets is about 10⁻⁴ M (Herrmann, 2003). However, the ionic strength in atmospheric aerosol deliquescent particles can reach about 6 M in marine areas, 8–18 M in urban environments, and 2–17 M in continental regions (Herrmann et al., 2015). Fountoukis and Nenes using the ISOR-ROPIA-II model predicted high levels of ionic strength ranging between 13 and 43 M during the severe Beijing Haze, with PM_{2.5} levels higher than 300 μg m⁻³ (Fountoukis and Nenes, 2007). In some extreme cases the ionic strength of aerosol deliquescent particles can even reach 100 M (Cheng et al., 2015, 2016). Dicarboxylic acids are an important class of organic compounds and they usually comprise a fraction of up to ~10% of the organic carbon fraction of atmospheric aerosols (Ho

et al., 2010). Due to their hygroscopic properties, dicarboxylic acids may potentially act as cloud condensation nuclei and have an impact on the radiative forcing at the Earth's surface (Kerminen et al., 2000). Ervens et al. showed that aqueous-phase processes might produce similar amounts of organic mass as compared to other SOA formation processes only under favorable conditions, i.e. when clouds and/or high relative humidity are present (Ervens et al., 2011). The aqueous-phase photochemistry of PA has been evaluated in past studies, and its role demonstrated in atmospheric processes such as photosensitized transformation (Leermakers and Vesley, 1963; Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014; Rapf et al., 2017a, 2017b; Eugene and Guzman, 2017; Gómez Alvarez et al., 2012; Grgic et al., 2010). Out of 92 studied carbonyl compounds, only acetoacetic acid and PA exhibited aqueous photolysis rates that exceeded the rates of OH radical reaction (Herrmann et al., 2015). In high-ionic strength urban and continental aerosols, the excited PA triplet state can play an important role in the degradation of other carboxylic acids. In his 2003 review, Herrmann called for new practical solutions to evaluate the atmospheric reactions at elevated ionic strength (Herrmann, 2003). Since then, however, to the best of our knowledge this topic was barely

* Corresponding author.

E-mail address: gligorovski@gig.ac.cn (S. Gligorovski).

considered. In this study, for the first time the photoinduced degradation of PA is evaluated in the aqueous phase in presence of high ionic-strength conditions.

2. Experimental section

2.1. Irradiation procedures

A custom-built photoreactor made up of borosilicate glass, with a volume of 130 cm³, was used for the experiments. The photoreactor has a double-wall design and it is connected to a thermostatic bath (LAUDA ECO RE 630 GECCO, Germany). Samples were magnetically stirred during irradiation, and the temperature during all the experiments was held at 293 K.

Fresh solutions of 5 mM PA (Sigma-Aldrich, 98.5%) in ultrapure water (18.2 MΩ cm, Millipore) were used in typical experiments. All the experiments were performed in duplicate. The solutions were irradiated for up to 8 h, and 20-mL aliquots were withdrawn from the reactor at fixed time intervals. When required by the experimental design, the ionic strength of the irradiated solution was adjusted by adding the required amount of sodium perchlorate (NaClO₄) up to a maximum concentration of 5 M. This inert salt was chosen because it shows no disturbing absorption of radiation, and because it exhibits no known unwanted chemical side-reactions (Weller et al., 2010).

2.2. Photochemical conditions

A high pressure Xenon lamp (500 W) was used as the light source, in combination with: (1) a water filter to remove infrared radiation, and (2) a cutoff filter at wavelength 300 nm ≤ λ ≤ 700 nm, to provide UV-Vis radiation that is relevant to the atmospheric boundary layer. The lamp emission spectrum was measured with a calibrated spectroradiometer (Ocean Optics, USA) equipped with a linear-array CCD detector (Fig. S1). The photoreactor was exposed to continuous light emission with a total irradiance of 6.9 × 10¹⁷ photons cm⁻² s⁻¹ nm⁻¹ in the wavelength region between 310 nm and 400 nm. For comparison, the total irradiance of sunlight in the same wavelength region (310–400 nm) is 6.7 × 10¹⁵ photons cm⁻² s⁻¹ nm⁻¹. UV-VIS spectra of initial (0 h) and irradiated samples (2 h, 4 h, 6 h, and 8 h 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.

3. Results and discussion

3.1. Effect of ionic strength

The influence of the solvent on the shift of λ_{max} (wavelength of maximum absorption in the near-UV region) in the UV absorption spectrum allows us to distinguish the kind of electronic transition. When a bathochromic shift is observed while reducing the dielectric constant of the solvent, the transition is n → π* (Reinhardt, 2003). Fig. 1 shows the absorbance of 5 mM PA in Milli-Q water and at different ionic strengths (adjusted by NaClO₄).

It seems that the ions of the inert salt NaClO₄ act as an auxochrome when attached to PA, altering both the absorption wavelength (bathochromic shift) and the absorption intensity (hyperchromic effect). When passing from a dilute aqueous solution (I = 0M) to I_{eff} = 3.1 M (5M NaClO₄, which is partially associated), the n → π* absorption band (λ_{max} = 318 nm) shifts towards longer wavelengths (Δλ ~ 13 nm, λ' _{max} = 331 nm). The bathochromic shift when going from water to less polar media is mainly caused by solute-solvent attractive dispersion interactions (London forces) (Reinhardt, 2003). Indeed, the dielectric constant of water decreases markedly upon addition of ions that affect its polarity (see the Supplementary Information). It is also well known that carbonyl compounds containing a n → π* absorption band exhibit

positive solvatochromism as the solvent polarity decreases (Reinhardt, 2003).

Rapf et al. (2017a,b) explored the effect of pH on the PA dissociation constant. These authors showed an increase of the absorption intensity when increasing the solution pH. Also a slight blue shift of the absorption maximum was observed, from λ_{max} = 320 nm to λ_{max} = 316 nm (Δλ_{max} = 4 nm). Lowering the pH to 1.54 induced a decrease of the absorbance and a slight red shift (Rapf et al., 2017b). In our study we examined the influence of ionic strength on the photolysis of PA, under non-adjusted pH conditions. The pH and the dissolved O₂ concentration in the solutions containing only PA (I = 0M) were, respectively, 2.33 and 8.17 mg L⁻¹ before irradiation, and 2.81 and 6.3 mg L⁻¹ after 8 h of irradiation. In the presence of both PA and 5 M NaClO₄, the pH and the concentration of dissolved oxygen were, respectively, 1.88 and 9.13 mg L⁻¹ before irradiation, and 2.57 and 5.38 mg L⁻¹ after 8 h of irradiation. Because, in our case, the slight decrease in pH before irradiation produced by 5 M NaClO₄ caused a red shift that was much larger than that reported in the literature, both the bathochromic shift of the absorbance and the hyperchromic effect we observed should be attributed to the ionic strength increase.

Although small, the hyperchromic effect and the bathochromic shift induced by the increasing ionic strength may have interesting implications if they can be generalized: many compounds that do not absorb actinic light in dilute solutions could become light-absorbing compounds at elevated salt concentrations in aerosol deliquescent particles. Because PA is ubiquitous in the aerosol deliquescent particles, the related photochemical processes might have a substantial impact on PA photoreactions, and on SOA formation as a consequence.

3.2. Kinetic data treatment

The data of PA absorbance at λ_{max}, which varied from ~318 nm at 0 M NaClO₄ to ~331 nm at I_{eff} = 3.1 M, were plotted as a function of the irradiation time (see Fig. 2).

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 (e.g., transformation intermediates) also absorbing at λ_{max}. The experimental data were accordingly fitted with the following equation:

$$A_{\lambda_{\max}}(t) = \alpha e^{-k \cdot t} + \beta \quad (1)$$

where A_{λ_{max}}(t) is the absorbance at λ_{max} at the time t, α and β are fit parameters, and k is the first-order decay constant of PA. The overall first-order photoinduced decay constant of PA increased by ~3 times, from (4.1 ± 1.2) × 10⁻⁵ s⁻¹ at I_{eff} = 0M to (1.1 ± 0.1) × 10⁻⁴ s⁻¹ at I_{eff} = 3.1 M. These rate constants take into account both the geminal diol form and the protonated keto form of PA. (Rapf et al., 2017a)

The values of k obtained from the fit of the experimental data were transformed into their natural logarithms, and the resulting log k values were plotted as a function of I_{eff} following Eq-S6 from the supplementary information. The resulting linear trend is reported in Fig. 3. The line slope is b = (b_A + b_N · b_±) = 0.14 ± 0.03 M⁻¹ (σ-level uncertainty), and it represents the kinetic salting coefficient.

The linear plot in Fig. 3 is consistent with Eq-S6 that predicts a straight line. This phenomenon may be ascribed to an increase in the PA activity coefficient, in agreement with the theoretical prediction of the primary kinetic salt effect (Type II) as described by Debye and McAulay (Eq-S6). (Debye and McAulay, 1925).

Herrmann (2003) described the observed effect of increasing rate constant with increasing ionic strength by assuming a stabilization of the activated complex by the ions of the added electrolyte (NaClO₄). This effect leads to a lower energy barrier, resulting in a faster reaction rate. However, in all the previously-studied reactions between radicals (NO₃, OH, Cl, and Cl₂⁻) and organics it is reported a saturation effect of

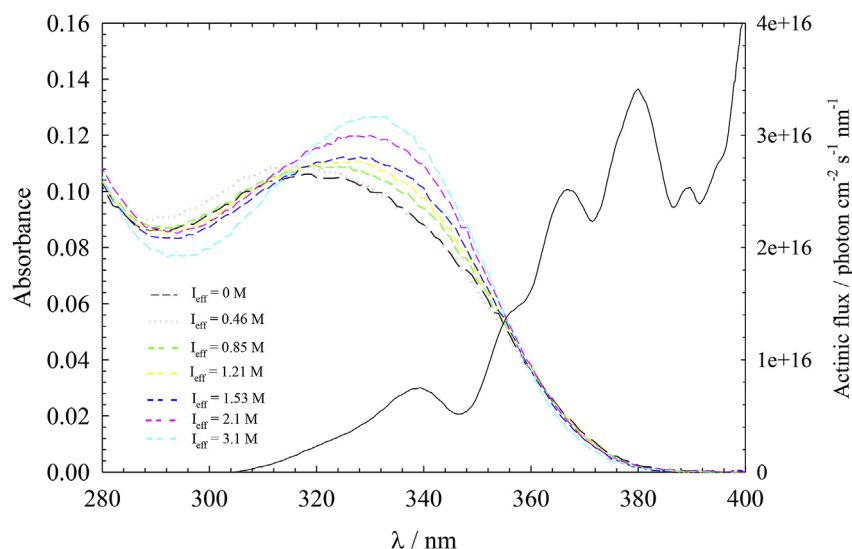


Fig. 1. The absorption spectra of 5 mM PA in the presence of different ionic strengths, and the photon flux emitted by the Xe lamp (black solid line). The left axis corresponds to the absorption spectra of PA and the right axis corresponds to the emission spectrum of the Xe lamp.

the measured rate constants at elevated ionic strength (Herrmann, 2003; Weller et al., 2010; Umschlag et al., 2002). Interestingly, the cited authors also used NaClO₄ to adjust the ionic strength of the solution which enables to do the comparison. Similarly, the rate constants for the reaction system SO₄⁻ + H₂O exhibited a saturation curve starting from I = 1 M up to 2 M of NaClO₄ (Bao and Barker, 1996). The reason for this discrepancy with our results is not known at the current state of knowledge. Therefore, lots of efforts are needed in order to properly understand the ionic strength effects in atmospheric deliquescent aerosol particles. On the other hand, the consideration of only the rate constants measured in the dilute aqueous phase may lead to huge errors into atmospheric photochemical models (Herrmann, 2003).

Although there is no data of ionic strength effects on the rate constant of the OH + PA reaction, from the data reported by Herrmann (2003) one obtains a typically weak influence of the ionic strength on the OH radical reactions with organic compounds. Considering that the photolysis of PA proceeds faster than the reaction of OH with PA

(Herrmann et al., 2015), the results shown in Fig. 3 suggest that the photoinduced removal of PA in highly concentrated electrolyte solutions can be much faster than the reaction with OH radicals (Ervens et al., 2003).

3.3. Mechanistic insights into PA photodegradation at high ionic strength

The rate of PA photolysis can be expressed by the following equation (Braslavsky, 2007):

$$R_{PA} = \int_{\lambda} p^{\circ}(\lambda) \Phi_{PA}(\lambda) [1 - 10^{-A_{PA}(\lambda)}] d\lambda \quad (2)$$

where $p^{\circ}(\lambda)$ is the incident spectral photon flux density of the lamp, $\Phi_{PA}(\lambda)$ the direct photolysis quantum yield of PA, and $A_{PA}(\lambda)$ its absorbance inside the photoreactor. The photon flux absorbed by PA can be expressed as follows: (Braslavsky, 2007)

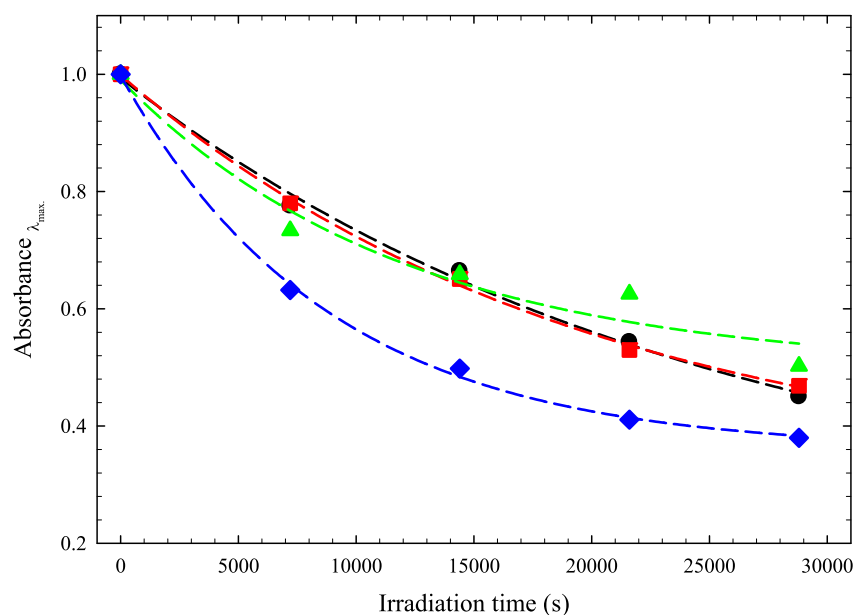


Fig. 2. Trend of the λ_{\max} absorbance of the solution ($A_{\lambda_{\max}}$), as a function of the irradiation time of 5 mM PA in the presence of different concentration values of NaClO₄. ● $I_{\text{eff}} = 0$ M; ■ $I_{\text{eff}} = 1.53$ M; ▲ $I_{\text{eff}} = 2.37$ M; ◆ $I_{\text{eff}} = 3.1$ M. See Supporting Information for the relationship between I_{eff} and the NaClO₄ concentration.

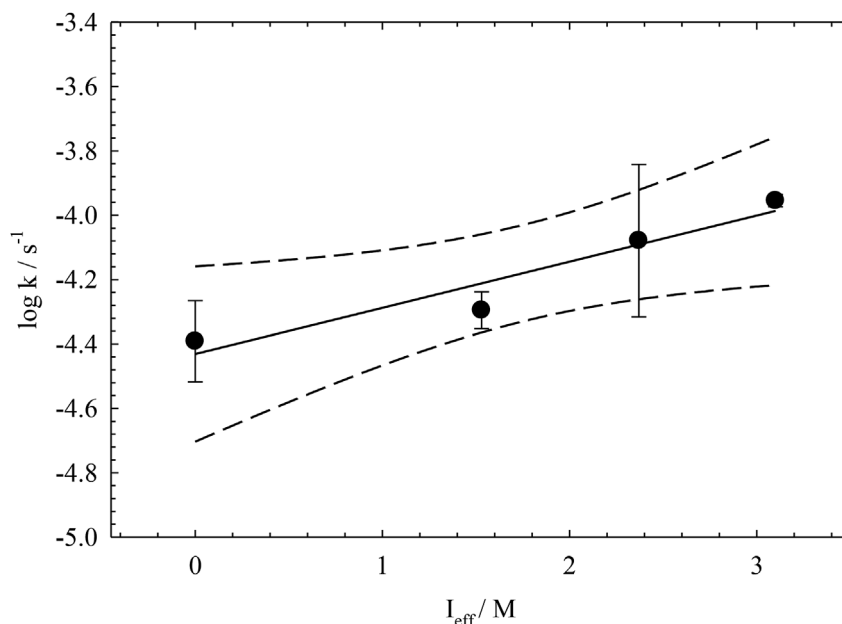
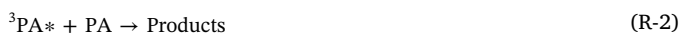


Fig. 3. Trend of $\log k$ vs. I_{eff} , according to Eq-S6 (see Supporting Information). The error bounds represent the σ -level uncertainty of the exponential data fit used to obtain k . The solid line shows the linear fit of $\log k$ vs. I_{eff} , and the dashed curves are the 95% confidence limits of the fit.

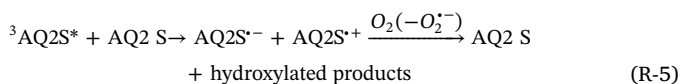
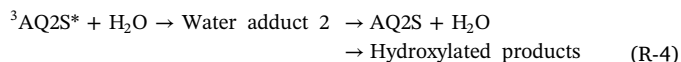
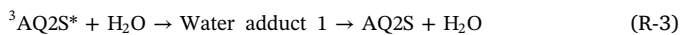
$$P_{\text{PA}} = \int_{\lambda} p^{\circ}(\lambda) [1 - 10^{-A_{\text{PA}}(\lambda)}] d\lambda \quad (3)$$

Interestingly, despite the 13-nm red shift of the PA absorption maximum in high- I solutions, the corresponding values of P_{PA} at $I_{\text{eff}} = 0\text{M}$ and $I_{\text{eff}} = 3.1\text{M}$ would differ by less than 1%. Therefore, the spectral modifications cannot account for the changes observed here in the photochemical degradation kinetics of PA as a function of the ionic strength, and the ionic-strength effect on the PA direct photolysis should rather deal with the photodegradation quantum yield.

A previous study into the PA photolysis mechanism has advanced the following general reaction scheme (ISC = inter-system crossing) (Reed Harris et al., 2014):



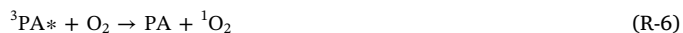
However, several studies have dealt with the triplet-state reactivity with molecular oxygen and with other species such as water. In particular, the triplet state of anthraquinone-2-sulfonate (AQ2S) (Bedini et al., 2012) has been shown not to react with O_2 , and to rather undergo reaction with water (Bedini et al., 2012):



The reaction between ${}^3\text{AQ2S}^*$ and H_2O prevails at low $[\text{AQ2S}]$ and it does not produce variations in the direct photolysis quantum yield as a function of $[\text{AQ2S}]$. In contrast, the reaction of ${}^3\text{AQ2S}^* + \text{AQ2S}$ gets faster as $[\text{AQ2S}]$ increases, it becomes important above 0.1 mM AQ2S and prevails over the other processes above 1 mM AQ2S. A reaction such as (R-2) or (R-5) between the triplet-state and the ground-state substrate causes both the photodegradation rate constant and the photolysis quantum yield to increase considerably as the substrate concentration increases (Bedini et al., 2012). In the case of PA, the photolysis rate constant has been found to decrease as $[\text{PA}]$ increases

(Reed Harris et al., 2014), which rules out (R-2) as the prevailing direct photolysis pathway.

Therefore, the following general reaction scheme can be proposed for the PA triplet state:

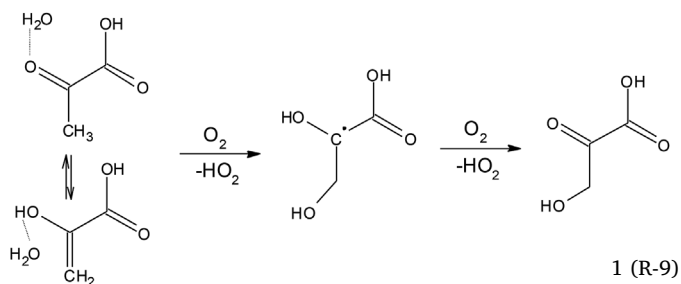


Reactions (R6-R8) can be differentiated by comparing the PA degradation kinetics in the presence and in the absence of oxygen (i.e., aerated solution vs. N_2 atmosphere). The kinetics of PA degradation did not vary significantly in the two cases (data not shown). Note that reactions (R-6) and (R-7) require O_2 for ${}^1\text{O}_2$ to be formed, thus the associated degradation process should be inhibited in the absence of oxygen. Reaction (R-8) between ${}^3\text{PA}^*$ and H_2O can be independent of O_2 only if it is the main scavenging process for ${}^3\text{PA}^*$. In other words, if a significant role of ${}^1\text{O}_2$ in the degradation of PA is excluded, there are two scenarios left: (i) O_2 plays an important role in the scavenging of ${}^3\text{PA}^*$, but the ${}^1\text{O}_2$ thus formed is poorly reactive towards PA and contributes very little to its degradation (in this case, ${}^1\text{O}_2$ would be inactivated by other routes including most notably the collision with the water molecules) (Wilkinson and Brummer, 1981); (ii) O_2 plays very little role in the scavenging of ${}^3\text{PA}^*$, which reacts almost exclusively with H_2O (this is for instance the case of ${}^3\text{AQ2S}^*$ (25)). Oxygen would scavenge most of ${}^3\text{PA}^*$ within scenario (i), but the net PA degradation would be accounted for by reaction (R-8) between ${}^3\text{PA}^*$ and H_2O . In this case the degradation of PA should be favored under N_2 atmosphere, which would ensure an enhanced occurrence of ${}^3\text{PA}^*$ for reaction (R-8) to take place. This scenario is not in agreement with the experimental data. In the scenario (ii), the ${}^3\text{PA}^*$ levels would be unaffected by O_2 because the occurrence of the triplet state would be controlled by the reaction with H_2O . In this case one does not expect an important effect of O_2 on the degradation kinetics of PA, in agreement with the experimental findings.

At the experimental pH values (pH 2–3) PA is partially dissociated to the carboxylate anion, thus the reaction between ${}^3\text{PA}^*$ and H_2O would involve either a negative species and a neutral one, or two neutral species. Both cases are consistent with the observed increase of

the photolysis rate constant with increasing ionic strength, according to the Debye-McAulay approach (primary kinetic salt effect, type II) (Debye and Mc Aulay, 1925) (Fig. 3).

PA direct photolysis yields several oxidized/hydroxylated compounds (Reed Harris et al., 2014), which is consistent with a reaction between $^3\text{PA}^*$ and water in the context of the AQ2S/PA analogy. Actually, the reaction between $^3\text{AQ2S}^*$ and water yields hydroxylated compounds (Wilkinson and Brummer, 1981), which in the past has led to the erroneous interpretation that irradiated AQ2S may produce ^1OH . This is not the case (Bedini et al., 2012), because the water adducts in oxygenated solution can lead to the same products as the ^1OH reactions. The following process could for instance account for the formation of hydroxylated PA derivatives:



3.4. Atmospheric implications

Dicarboxylic acids account for approximately 1–3% of the total organic carbon in the urban aerosols (Ho et al., 2010) and up to 14% of the total organic carbon in the marine aerosols (Hoque et al., 2015). Although the contribution of these acids is small to the total aerosol mass, the photochemistry of α -ketocarboxylic acids, such as pyruvic acid and glyoxylic acid has been recognized to contribute significantly to the formation and processing of SOA (Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014; Rapf et al., 2017a, 2017b; Eugene and Guzman, 2017; Eugene et al., 2016). The bathochromic shift and hyperchromic effect of pyruvic acid in the presence of salt indicate that light-absorbing, water-soluble organic carbon in presence of high ionic strength can largely affect the total aerosol solar light absorption which in turn impacts the Earth's radiative forcing. The influence of an inert salt to the absorption properties of pyruvic acid suggests that the absorptive properties of SOA need to be constrained as a function of ionic strength within atmospheric models.

This effect can potentially impact other light-absorbing organic compounds. Another important class of organic compounds that absorb light in the solar actinic window are the polycyclic aromatic hydrocarbons (PAHs), which account for \sim 7% of the total organic aerosol mass but contribute up to nearly 40% of the total absorbance (Lu et al., 2015).

Future studies should focus on the effects of the ionic strength on the photolysis of other soluble light-absorbing compounds, e.g., glyoxylic acid, acetone, and phenolic substances (e.g. vanillin acid, o-vanillin, acetosyringone). Such studies would reveal more information about the optical properties of these compounds within the aerosol deliquescent particles. Potentially, many other soluble compounds that do not absorb near-UV light in the dilute aqueous phase could become light-absorbers at high salt concentrations in aerosol deliquescent particles. This phenomenon can largely affect the radiative properties of SOA.

It is also important to note that the high concentrations of salts in the aerosol deliquescent particles can significantly influence the solubility of the organic compounds. The increase of solubility is a “salting in” and the decrease of solubility is a “salting out” effect. The latter effect would cause the separation of organic compounds from the dissolved ions (Waxman et al., 2015), with the consequence that organics would reside in the organic phase of the aerosols. Then, the

bathochromic shift and the hyperchromic effect observed here would change as a function of the polarity of the organic phase. Future studies should also consider these phenomena, in order to better understand the impact of SOA on climate-change issues.

4. Conclusion

In this study, we demonstrate that the absorption spectrum of pyruvic acid (PA) exhibits both a bathochromic shift of the absorbance ($\Delta\lambda \sim 13$ nm) and the hyperchromic effect while going from a dilute aqueous phase to a solution containing elevated ionic strength ($I_{\text{eff}} = 3.1\text{M}$). This study expands the current understanding of the photochemical processes in the aerosol deliquescent particles, by investigating the ionic strength dependence of PA photodegradation. The photochemical processes involving PA in the aqueous phase are an important topic in atmospheric chemistry, because they contribute to the formation of secondary organic aerosols in the atmosphere. This work shows that photochemical processes in aerosol deliquescent particles result in different kinetics compared to the analogous diluted aqueous-phase chemistry, with the potential to significantly affect aerosol composition and optical properties (Zhao et al., 2015).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2018.05.016>.

References

- Bao, Z.-C., Barker, J.R., 1996. Temperature and ionic strength effects on some reactions involving sulfate radical $[\text{SO}_4^{\cdot-}(\text{aq})]$. *J. Phys. Chem.* 100, 9780–9787.
- Bedini, A., De Laurentiis, E., Sur, B., Maurino, V., Minero, C., Brigante, M., Mailhot, G., Vione, D., 2012. Phototransformation of anthraquinone-2-sulphonate in aqueous solution. *Photochem. Photobiol. Sci.* 11, 1445–1453.
- Braslavsky, S.E., 2007. Glossary of terms used in photochemistry. 3rd edition. *Pure Appl. Chem.* 79, 293–465.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Cheng, Y., Su, H., Koop, T., Mikhailov, E., Pöschl, U., 2015. Size dependence of phase transitions in aerosol nanoparticles. *Nat. Commun.* 6, 5923. <http://dx.doi.org/10.1038/ncomms6923>.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., Su, H., 2016. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Sci. Adv.* 2, 1–11.
- Debye, P., Mc Aulay, J., 1925. Das elektrische Feld der Ionen und die Neutralsalzwirkung. *Physik. Zeitschr* 26, 22–29.
- Ervens, B., Gligorovski, S., Herrmann, H., 2003. Temperature dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions. *Phys. Chem. Chem. Phys.* 5, 1811–1824.
- 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.
- Eugene, A.J., Guzman, M.I., 2017. Reactivity of ketyl and acetyl radicals from direct solar actinic photolysis of aqueous pyruvic acid. *J. Phys. Chem. A* 121, 2924–2935.
- Eugene, A.J., Xia, S.-S., Guzman, M.I., 2016. Aqueous photochemistry of glyoxylic acid. *J. Phys. Chem. A* 120, 3817–3826.
- Fountoukis, C., Nenes, A., 2007. ISORROPIA ii: a computationally efficient aerosol thermodynamic equilibrium model for K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , H_2O aerosols. *Atmos. Chem. Phys.* 7, 4639–4659.
- Gómez Alvarez, E., Wortham, H., Strekowski, R., Zetzsch, C., Gligorovski, S., 2012. Atmospheric photo-sensitized heterogeneous and multiphase reactions: from outdoors to indoors. *Environ. Sci. Technol.* 46, 1955–1963.
- Grčić, I., Nieto-Gligorovski, L.L., Net, S., Temime-Roussel, B., Gligorovski, S., Wortham, H., 2010. Light induced multiphase chemistry of gas-phase ozone on aqueous pyruvic and oxalic acids. *Phys. Chem. Chem. Phys.* 12, 698–707.
- Griffith, E.C., Carpenter, B.K., Shoemaker, R.K., Vaida, V., 2013. Photochemistry of aqueous pyruvic acid. *Proc. Natl. Acad. Sci. U. S. A* 110 (29), 11714–11719.
- Guzman, M.I., Colussi, A.J., Hoffmann, M.R., 2006. Photoinduced oligomerization of aqueous pyruvic acid. *J. Phys. Chem. A* 110 (10), 3619–3626.
- Herrmann, H., 2003. Kinetics of aqueous phase reactions relevant for atmospheric chemistry. *Chem. Rev.* 103, 4691–4716.
- Herrmann, H., Schaefer, T., Tilgner, A., Styler, A.S., 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.
- Ho, K.F., Lee, S.C., Hang Ho, S.S., Kawamura, K., Tachibana, E., Cheng, Y., Zhu, T., 2010. Dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006). *J. Geophys. Res.* 115, D19312. <http://dx.doi.org/10.1029/2009JD013112>.

- 1029/2009JD013304.
- Hoque, M., Kawamura, K., Seki, O., Hoshi, N., 2015. Spatial distributions of dicarboxylic acids, ω -oxoacids, pyruvic acid and α -dicarbonyls in the remote marine aerosols over the North Pacific. *Mar. Chem.* 172, 1–11.
- Kerminen, V.-M., Ojanen, C., Pakkanen, T., Hillamo, R., Aurela, M., Kinenet, J.M., 2000. Low molecular weight dicarboxylic acids in an urban and rural atmosphere. *J. Aerosol Sci.* 31 (3), 349–362.
- Leermakers, P.A., Vesley, G.F., 1963. Photolysis of pyruvic acid in solution. *J. Org. Chem.* 28 (4), 1160–1161.
- Lu, Z., Streets, D.G., Winijkul, E., Yan, F., Chen, Y., Bond, T.C., Feng, Y., Dubey, M.K., Liu, S., Pinto, J.P., Carmichael, G.R., 2015. Light absorption properties and radiative effects of primary organic aerosol emissions. *Environ. Sci. Technol.* 49, 4868–4877.
- Rapf, R.J., Perkins, R.J., Carpenter, B.K., Vaida, V., 2017a. Mechanistic description of photochemical oligomer formation from aqueous pyruvic acid. *J. Phys. Chem. A* 121, 4272–4282.
- Rapf, R.J., Dooley, M.R., Kappes, K., Perkins, R.J., Vaida, V., 2017b. pH dependence of the aqueous photochemistry of alpha-keto acids. *J. Phys. Chem. A* 121 (44), 8368–8379.
- Reed Harris, A.E., Ervens, B., Shoemaker, R.K., Kroll, J.A., Rapf, R.J., Griffith, E.C., Monod, A., Vaida, V., 2014. Photochemical kinetics of pyruvic acid in aqueous solution. *J. Phys. Chem. A* 118 (37), 8505–8516.
- Reinhardt, C., 2003. *Solvents and Solvent Effects in Organic Chemistry*, third ed. Wiley-VCH, Weinheim.
- Umschlag, T., Zellner, R., Herrmann, H., 2002. Laser-based studies of NO₃ radical reactions with selected aromatic compounds in aqueous solution. *Phys. Chem. Chem. Phys.* 4, 2975–2982.
- Waxman, E.M., Elm, J., Kurten, T., Mikkelsen, K.V., Ziemann, P.J., Volkamer, R., 2015. Glyoxal and methylglyoxal setschenow salting constants in sulfate, nitrate, and chloride solutions: measurements and Gibbs energies. *Environ. Sci. Technol.* 49 (19), 11500–11508.
- Weller, C., Hoffmann, D., Schaefer, T., Herrmann, H., 2010. Temperature and ionic strength dependence of NO₃-radical reactions with substituted phenols in aqueous solution. *Z. Phys. Chem.* 224, 1261–1287.
- Wilkinson, F., Brummer, J., 1981. Rate constants for the decay and reactions of the lowest electronically excited singlet-state of molecular oxygen in solution. *J. Phys. Chem. Ref. Data* 10, 809–1000.
- Zhao, R., Lee, A.K.Y., Huang, L., Li, X., Yang, F., Abbatt, J.P.D., 2015. Photochemical processing of aqueous atmospheric brown carbon. *Atmos. Chem. Phys.* 15, 6087–6100.