



Short communication

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

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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 ISORROPIA-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

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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 M Ω 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 $\leq \lambda \leq$ 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 6.9×10^{17} 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 6.7×10^{15} 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 $n \rightarrow \pi^*$ (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 ($I = 0\text{M}$) to $I_{\text{eff}} = 3.1\text{M}$ (5M NaClO₄, which is partially associated), the $n \rightarrow \pi^*$ absorption band ($\lambda_{\max} = 318\text{nm}$) shifts towards longer wavelengths ($\Delta\lambda \sim 13\text{nm}$, $\lambda'_{\max} = 331\text{nm}$). 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 $n \rightarrow \pi^*$ 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 $\lambda_{\max} = 320\text{nm}$ to $\lambda_{\max} = 316\text{nm}$ ($\Delta\lambda_{\max} = 4\text{nm}$). 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 ($I = 0\text{M}$) 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 $\sim 318\text{nm}$ at 0 M NaClO₄ to $\sim 331\text{nm}$ at $I_{\text{eff}} = 3.1\text{M}$, 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 $A_{\lambda_{\max}}(t)$ 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 $(4.1 \pm 1.2) \times 10^{-5}\text{s}^{-1}$ at $I_{\text{eff}} = 0\text{M}$ to $(1.1 \pm 0.1) \times 10^{-4}\text{s}^{-1}$ at $I_{\text{eff}} = 3.1\text{M}$. 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 $b = (b_A + b_N \cdot b_{\pm}) = 0.14 \pm 0.03\text{M}^{-1}$ (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

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