Does interfacial photochemistry play a role in the photolysis of pyruvic acid in water?

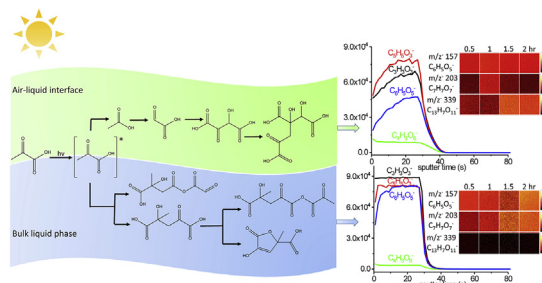Yao Fu[a,b], Yanyan Zhang[c,1], Fei Zhang[a,b,1], Jianmin Chen[a,d,**], Zihua Zhu[c,***], Xiao-Ying Yu[b,*]

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GRAPHICAL ABSTRACT

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ABSTRACT

Pyruvic acid (PA) exists in fogs, aerosols and clouds. The photochemistry-driven reaction pathways of PA in the aqueous phase are more elusive than the gas phase. The PA photochemical process may occur in the bulk liquid phase and at the air-liquid interface in ambient conditions. We conducted two sample preparation methods to simulate two possible scenarios: the air-liquid interface and the bulk liquid phase under photolysis. Time-of-flight secondary ion mass spectrometer (ToF-SIMS) was used to analyze samples because of its high sensitivity and mass accuracy in surface analysis. Both negative and positive ion mode mass spectra provide complementary information of the products under different reaction conditions. Spectral principal component analysis (PCA) is used to determine similarities and differences among various samples. The air-liquid interface facilitates more radical reactions and form higher molecular weight compounds (HMWCs) more quickly than the bulk liquid phase, which mainly has non-radical reactions such as anhydride reactions and decarboxylation reactions. Our results show that interfacial chemistry plays an important role in atmospheric scenarios. Moreover, different types of secondary organic aerosols (SOAs) are formed, suggesting the strong influence of interfacial photochemistry has on the earth atmosphere.

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1. Introduction

The air-liquid interface is inherently an asymmetric environment (Pruyne et al., 2014), where large changes over angstrom-scale distances in properties such as molecular composition, orientation, and density take place, leading to differences in the structure and chemistry between the interface and the bulk phase (Eisenthal, 1993; Petersen and Saykally, 2006). For example, the pH at the interface can be either more acidic or alkaline than that in the bulk phase (Buch et al., 2007; Petersen et al., 2004). Due to highly varied concentrations in the aqueous organic film at the air-liquid interface under solar radiation, photochemistry is known to occur at the aerosol surface (Donaldson and Vaida, 2006).

Interfacial processes have become a noticeable topic in atmospheric chemistry (George et al., 2015) due to its perceived importance in secondary organic aerosol (SOA) formation. Recent findings have shown that the interface, where specific chemical and sunlight-initiated photochemical reactions take place, can produce high-molecular-weight compounds (HMWCs) and aggregates (Baergen and Donaldson, 2013; Brüggemann et al., 2017; Ciuraru et al., 2015; Dupart et al., 2012; Enami et al., 2015; Fu et al., 2015; Griffith et al., 2014; Reed Harris et al., 2014; Renard et al., 2014; Rossignol et al., 2016). These products will affect SOA formation and organic mass, chemical composition, and optical properties of SOAs, resulting in a significant impact on climate, air quality, and human health (Vaida, 2016).

As a key oxidation product of isoprene in the atmosphere (Carlton et al., 2006; Ervens et al., 2011), pyruvic acid (PA) is observed in both gas and aqueous phases (Altieri et al., 2006; Andreae et al., 1987; Talbot et al., 1990; Veres et al., 2010; Warneck, 2005). PA is the simplest α-keto acid in the atmosphere, and it can absorb light in the near-UV region from the solar photon flux (Horowitz et al., 2001). The reactions of PA occur in the gas phase and in the aqueous phase, with photolysis or dark aging in a range of reactant concentrations and relative humidity (Altieri et al., 2006; Chang et al., 2014; Guzman et al., 2006; Larsen and Vaida, 2012; Lopalco et al., 2016; Mellouki and Mu, 2003; Plath et al., 2009; Rapf et al., 2017; Reed Harris et al., 2014, 2016; Vesley and Leermakers, 1964).

The photolysis rate of PA is faster than other reactions, and photochemistry is the main atmospheric sink of PA (Lopalco et al., 2016; Mellouki and Mu, 2003; Reed Harris et al., 2014; Schöne and Herrmann, 2014). For instance, PA can release CO_2 and acetaldehyde due to photolysis according to earlier works (Chang et al., 2014; Mellouki and Mu, 2003; Takahashi et al., 2008). The photochemical pathways of PA are still under debate. Especially in the aqueous phase, the photochemistry is considered different due to the water environment (Vaida, 2011). For example, the electronic structure of PA will change and generate organic radicals (e.g., $CH_3\dot{C}(OH)$ CO_2H, $\dot{C}H_2C(O)CO_2H$) in water (Rapf et al., 2017). These radicals will then recombine to form oligomers, contributing to the production of SOAs (Boris et al., 2014; Eugene and Guzman, 2017; Griffith et al., 2013; Guzman et al., 2006; Leermakers and Vesley, 1963; Lim et al., 2010; Reed Harris et al., 2014). Although SOA is perceived as a main contributor of interfacial reactions in atmospheric aerosols and cloud water, the challenge to clearly obtain organic speciation often existed in trace amount remains one of the grand challenges in atmospheric chemistry (Carlton et al., 2006, 2009; Ervens et al., 2011). Therefore, it is of significant importance to analyze the surface composition because it can differ from that in the bulk (Jungwirth and Tobias, 2006; Krieger et al., 2012; Shiraiwa et al., 2010).

Among surface analytical techniques, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful tool and has been widely used in many research areas such as contamination, adhesion, corrosion, cell chemistry, and biocompatibility (Fearn, 2015; Hagenhoff, 2000). SIMS is a highly sensitive surface analysis technique, and it can provide detailed elemental and molecular mapping of solid surfaces, thin films, gas-solid interfaces, and three dimensional chemical

mapping of solid samples (Benninghoven, 1994; Lanni et al., 2014; Robinson et al., 2012; Yu et al., 2010). Previous studies have shown that SIMS was a useful technique for exploring aerosol surface characterization. Not only inorganic composition but also organic compounds including hydrocarbons, alcohols, aldehydes, ethers, carboxylic acids, amines, amides, nitriles and a number of polycyclic aromatic hydrocarbons (PAHs) and nitroPAHs can be studied using SIMS (Chan et al., 2018; Huang et al., 2017; Peterson and Tyler, 2002, 2003; Tervahattu, 2002; Zhang et al., 2016; Zhu et al., 2001).

In this work, PA photochemistry occurred at the air-liquid interface and bulk liquid phase were studied using ToF-SIMS. Different dry sample preparation steps were used to simulate two possible atmospheric reaction scenarios: 1) the bulk liquid phase and 2) the air-liquid interface. The photochemical process occurred at the air-liquid interface could lead to aqueous SOA (aqSOA) formation (Bernard et al., 2016; Brüggemann et al., 2017). It is postulated that distinct photochemical processes happened at the air-liquid interface and in the bulk phase, which lead to the formation of dissimilar products. HMWCs, a main constituent of SOAs, are discovered to form at the air-liquid interface due to more photochemical oxidation compared to the bulk liquid photolysis as summarized in Fig. 1.

2. Experimental information and methods

2.1. Chemicals

Pyruvic acid (98%, Sigma-Aldrich, St. Louis, MO, USA) was diluted with DI water (18.2 MΩ) dispensed from a Barnstead water purification system (model: Nanopure diamond) to prepare a 0.1 M solution. The initial pH of the 0.1 M PA solution was ~1.7 measured by a portable pH meter (accumet, Fisher Scientific, CA, USA).

2.2. Photolysis and sample substrates

A Hg-Ar UV lamp (ORIEL, lamp model 6035, USA) with a power supply (ORIEL model 6060, USA) was used as the UV source for photochemical aging, and the wavelength was 334.15 nm. Si wafers (10 × 10 mm diced, Ted Pella Inc., CA, USA) were cleaned by acetone, isopropanol, and high-purity DI water for 3 min sequentially. After thorough cleaning, UV-O₃ plasma (Model No.342, Jelight Company Inc., USA) was applied to remove residual organic contaminations on the Si wafer surface for 2 min. Afterwards, the wafers were used as substrates for dry sample preparation (Jensen et al., 2013; Kanyal et al., 2015; Mahoney et al., 2006; Song et al., 2011; Sui et al., 2018). The distance between the Si wafer surface and the UV lamp was set at 10 cm (Sui et al., 2018). All sample preparation was conducted in a fume hood (Hamilton Laboratory Solutions LLC., WI, USA). The samples were analyzed immediately after photolysis treatment to reduce possible interferences.

2.3. Sample preparation

The details of samples studied in this work are summarized in Fig. S1 and Table S1. In order to simulate the bulk and the air-liquid interface scenarios, two methods were performed to prepare dry samples in Fig. 2. The first method (Fig. 2a) was described in the following steps: (1) the Si wafer was put in a clean petri dish; (2) then 20 μL of sample solution was taken and deposited it on the cleaned Si wafer; and (3) the droplet was dried under the UV light for a specific time (0.5 h, 1 h, 1.5 h, and 2 h). This method simulated the photochemistry at the air-liquid interface. The operation sequence of the second preparation approach (Fig. 2b) was different from those in the first one: (1) the sample solution of 10 mL was stored in a glass vessel under the UV light for a specific time (0.5 h, 1 h, 1.5 h, and 2 h); (2) 20 μL of solution was taken out of the vessel immediately after the photochemical aging was ended; (3) the solution was deposited on a treated Si wafer in a clean