

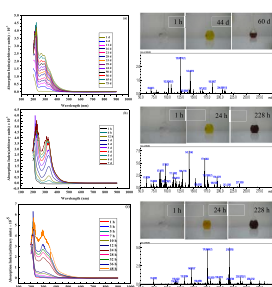
Formation of aqueous-phase secondary organic aerosols from glycolaldehyde and ammonium sulfate/amines: A kinetic and mechanistic study



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GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric particles are largely represented by secondary organic aerosols (SOAs) produced by either aqueous- or gas-phase reactions. Recently, the contribution of the former to SOA formation has been shown to substantially increase and even reach that of the latter, which necessitates in-depth mechanistic investigations. For a deeper understanding of aqueous-phase SOA generation, we herein studied the production of these aerosols in the dark from glycolaldehyde (GALD) and ammonium sulfate (AS)/amines (methylamine (MAM) and glycine (Gly)). UV-vis spectroscopy showed that reaction mixtures featured two main absorption bands (at 209–230 and 280–330 nm) that were attributed to the π - π^* transitions of Schiff bases and the n - π^* transitions of oligomers produced in the above reactions, respectively. Further studies revealed that irrespective of reactant concentration and pH, all the investigated reactions were well fitted by first-order kinetics and were accelerated by increasing AS/MAM concentrations and solution pH under acidic conditions. The reaction rate constants (determined from changes of absorption at 300 nm) followed the order of Gly ($k^1 = 2.39 \times 10^{-6} \text{ s}^{-1}$) > MAM ($k^1 = 1.19 \times 10^{-6} \text{ s}^{-1}$) > AS ($k^1 = 8.33 \times 10^{-7} \text{ s}^{-1}$) at identical low AS/amine concentrations and were in the order of MAM ($k^1 = 2.5 \times 10^{-6} \text{ s}^{-1}$) > AS ($k^1 = 1.39 \times 10^{-6} \text{ s}^{-1}$) at high AS/MAM concentrations. The main reaction pathways corresponded to the aldol self-condensation of GALD and the nucleophilic attack of AS/amines on GALD followed by dehydration, which afforded imines as the major products. The stronger light absorption of (GALD + Gly) mixtures than that of (glyoxal/methylglyoxal + Gly) mixtures was ascribed to the increased amount of imine- and carbonyl group-containing products produced in the former case.

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1. Introduction

Secondary organic aerosols (SOAs) are a major component of atmospheric fine particulate matter, accounting for up to 40–50% of the total aerosols formed by the oxidation of volatile organic compounds (VOCs) (Zhang et al., 2011) and significantly influencing air quality, visibility, human health, climate, and the oxidative capacity of the atmosphere (Lim et al., 2010; Volkamer et al., 2009). Originally, Pankow (1994) and Odum et al. (1996) reported that SOAs are formed by the gas-particle conversion of low volatile products of atmospheric VOC oxidation. However, the above perception has changed, and it has recently been demonstrated that SOA formation involves heterogeneous and particle-phase chemical reactions (Kampf et al., 2012). Lately, SOA formation through aqueous-phase reactions in clouds, fogs, and aerosols has been shown to be as significant as traditional gas-phase reactions (Carlton et al., 2007). Carbonyl-containing (semi-)volatile organic compounds such as glyoxal, methylglyoxal, and glycolaldehyde (GAlD) can participate in aqueous-phase reactions to form SOAs after being absorbed by aqueous aerosol particles or cloud droplets (Altieri et al., 2008; Carlton et al., 2009; Sareen et al., 2010; Volkamer et al., 2006) and undergo browning or aldol condensation reactions (Galloway et al., 2009; Nozière et al., 2007; Powelson et al., 2014; Schwier et al., 2010) with nitrogen-containing compounds such as ammonium salts (Sareen et al., 2010; Shapiro et al., 2009), amino acids (De Haan et al., 2009a; Sedehi et al., 2013), and alkylamines (De Haan et al., 2009b) to form organic carbons with C–C/C–N/C=N functionalities capable of absorbing UV radiation. Unsurprisingly, these reactions are known to be a potential source of brown carbon (BrC) (Woo et al., 2013).

BrC is a brown- or yellow-appearing fraction of light-absorbing organic carbon that strongly absorbs light in the near-UV region (Gelencsér, 2006), and is mainly produced by incomplete combustion of fossil/biomass fuels, heterogeneous reactions of (semi)volatile organic species with nitrogen-containing compounds (NH_3 , NH_4^+ , etc.), and aqueous-phase reactions of carbonyl compounds (Liu et al., 2015; Srinivas and Sarin, 2014; Woo et al., 2013). BrC significantly contributes to aerosol radiative forcing, e.g., Feng et al. (2013) estimated that atmospheric BrC contributes nearly 19% to the total absorption by anthropogenic aerosols with a radiative forcing of 0.25 W m^{-2} . Strongly light-absorbing compounds formed in the aqueous phase can significantly affect radiative forcing (Shapiro et al., 2009; Yu et al., 2011b), e.g., Sareen et al. (2010) estimated that the absorption coefficient at 282 nm (A_{282}) of products formed in reactions of methylglyoxal with ammonium sulfate (AS) or ammonium nitrate was as high as $\sim 10^{-5}$. Additionally, Shapiro et al. (2009) claimed that the extinction coefficient at 550 nm (ϵ_{550}) of solutions containing 2.21 M glyoxal and 3.11 M AS was $\geq 0.71 \text{ cm}^{-1}$, with the corresponding absorption index (A_{550}) being $\geq 3.1 \times 10^{-6}$. The absorption of UV radiation by BrC produced in aqueous-phase reactions has the potential to reduce tropospheric O_3 levels (Sareen et al., 2010) and thus significantly influence atmospheric oxidative capacity.

GAlD (HOCH_2CHO), an atmospherically relevant bifunctional carbonyl compound (Kawamura et al., 2013), is produced by biomass burning (primary source) (Goode et al., 1999; Mason et al., 2001; Yokelson et al., 1997) and the oxidation of VOCs (secondary source) such as ethene, 1,3-butadiene, isoprene, 2-methyl-3-buten-2-ol, methyl vinyl ketone, acrolein, and 4-hydroxy-2-butenal (Ferronato et al., 1998; Grosjean et al., 1992; Grosjean and Grosjean, 1999; Noda et al., 2000). The concentration of GAlD in the gas phase lies in the range of mid-part-per-trillion to low-part-per-billion. Moreover, GAlD is also found in atmospheric cloud water (0.3–3.6 μM) (Brüggemann et al., 2005) and fog/aqueous aerosols (0–1 300 pmol m^{-3}) (Kua et al., 2013; Matsunaga et al., 2004). The gas-phase lifetime of GAlD is estimated as 1 day (Bacher et al., 2001), which is high enough for this compound to reach into clouds, fogs, or aerosols and accounts for the fact that $\sim 90\%$ of atmospheric GAlD is present in the hydrated state (Perri et al., 2009; Sørensen et al., 1972). Recently, the photochemical and dark reactions

of GAlD have been increasingly often investigated in lab-scale experiments (Bacher et al., 2001; Nguyen et al., 2013; Perri et al., 2009), as exemplified by a large number of studies on the gas- and aqueous-phase photochemical oxidation of GAlD (Bacher et al., 2001; Butkovskaya et al., 2006; Karunanandan et al., 2007; Magneron et al., 2005; Nguyen et al., 2013; Perri et al., 2009, 2010; Warneck, 2003) and the dark reactions of GAlD in the aqueous phase performed in recent years. Powelson et al. (2014) reported that GAlD and glycine (Gly) mixtures had the most intense absorbance among (carbonyl compound + amine/AS) combinations. However, few researchers investigated the reaction kinetics, the impacts of pH, and mechanisms of reactions between GAlD and AS/amines.

Herein, we investigated reactions between GAlD and AS/amines (methylamine (MAM) and Gly) in aqueous solutions at room temperature by UV–vis spectrophotometry and kinetic measurements, additionally probing the effects of pH in the range of 4–7. Additionally, we analyzed reaction products by liquid chromatography coupled with time-of-flight and ion trap mass spectrometry (LCMS-IT-TOF) and established possible reaction mechanisms.

2. Experimental

2.1. Sample preparation

Experiments were performed in sealed glass vials wrapped by Al foil to avoid light exposure. At room temperature ($298 \pm 2 \text{ K}$), glass vials containing 0.5–2.5 M aqueous solutions of AS (AR, $\geq 99.0\%$), MAM (Aladdin, 40 wt% in water), or Gly (AR, 99.5–100.5%) were charged with a 0.1 M GAlD (Sigma-Aldrich) solution in deionized water using a microsyringe. The obtained mixtures were vigorously stirred, and their pH was measured using a pH meter and adjusted to values of 4–7 with acetic acid (AR, $\geq 99.5\%$) and sodium phosphate ($\geq 98.0\%$) to simulate the values of clouds, fog, and aqueous aerosols in the atmosphere (Keene et al., 2004; Straub et al., 2012). Meantime, the blank experiments of separate GAlD, AS, MAM, and Gly solution were performed, respectively, which were measured by a UV–vis spectrophotometer.

2.2. UV–vis spectrophotometry

The UV–vis absorption spectra of reaction mixtures were recorded on a TU 1900 spectrophotometer (Purkinje General Instrument, Beijing) using a quartz cuvette with an optical path length of 1 mm.

2.3. Product analysis

An LCMS-IT-TOF instrument (Shimadzu, Japan) equipped with an electrospray ionization source was used to analyze reaction products in negative- and positive-ion modes under the following conditions: source voltage = 3.6 kV, nebulizer nitrogen gas flow rate = 1.5 L/min, detector voltage = 1.75 kV, mass acquisition range = 50–500, resolution = 10,000 full width at half-maximum. Data were collected by-passing the LC system. Since the reactions of GAlD with AS, MAM, and Gly exhibited different rates, mixtures of 0.1 M GAlD and 0.5 M AS/MAM/Gly were analyzed by LCMS-IT-TOF after 20, 7, and 3 days, respectively.

2.4. Reaction kinetics

A detailed description of reaction kinetics can be found in the study of Nozière et al. (2009). Briefly, kinetic data were obtained by applying the Beer-Lambert law, and sample absorbance ($A_b(\lambda)$) was converted into extinction coefficients (ϵ_λ) (Eq. (1)). Subsequently, absorption indices (A_λ) were calculated by Eq. (2) for direct comparison with the optical properties of atmospheric aerosols. Reactions obeying first-order kinetics were fitted using Eq. (3), and then the corresponding rate constants, k^1 (s^{-1}), were obtained from Eq. (4).

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