

# Aqueous-phase photochemical oxidation and direct photolysis of vanillin as a model compound of methoxy-phenols from biomass burning

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Aqueous-phase reactions of organic compounds are an important source of secondary organic aerosol (SOA) (Ervens 2011). Previous laboratory studies focused mostly on small aldehydes such as glyoxal (De Haan 2009; Tan 2009) as precursors, and recently on pinene oxidation products (Lee 2011).

Here we showed experimental results of aqueous-phase reactions of a semi-volatile and slightly water soluble methoxy-phenol from biomass burning, vanillin ( $C_8H_8O_3$ ). Reactions were performed in a vessel (Lee 2011) with UV (254 nm) irradiation under two conditions: (1) photochemical oxidation with  $H_2O_2$  as an OH radical source; and (2) direct photolysis without  $H_2O_2$  added. Solution of the resulted products, as well as the ammonium sulfate added (Lee 2011), was atomized continuously and dried before on-line analyses. An Aerodyne High-resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was used to measure the dried particle compositions, and a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) and a Cloud Condensation Nuclei counter (CCNc) were used to determine the particle growth factor and CCN activity respectively.

Prior to UV irradiation, most of vanillin evaporated to the gas phase during drying and gave negligible organic mass in particles (Figure 1, before time < 0 min). A large amount of SOA was formed and retained after reactions under both conditions, although products might be different under these two conditions according to HR-ToF-AMS characterization (Figure 1). Off-line analyses by liquid chromatography-mass spectrometry (LC-MS) and derivatization prior to gas chromatography-mass spectrometry (GC-MS) also confirmed that the product identities from these two conditions are different. Organic mass first increased rapidly and then decreased under condition (1), but kept increasing slowly under condition (2), as shown in Figure 1A and 1C, respectively. It was found that the degree of oxygenation of products from condition (1) first increased and then decreased, suggesting a competition between functionalization and fragmentation (Kroll 2009; Lee 2011), while it kept decreasing under condition (2). Hygroscopic behavior and CCN activity of ammonium sulfate decreased substantially with the organic products retained in the particles. The resolved growth factor of organics correlated with the increase of degree of oxygenation (O:C ratio) of organics formed.

Our results suggest that aqueous-phase reactions of methoxy-phenolic compounds from biomass burning

can retain this portion of carbon mass in the particle phase even after extensive drying/dilution processes. This portion of carbon mass, once retained, significantly alters the particle hygroscopicity and CCN activity, which is not being considered in current climatic and visibility models.

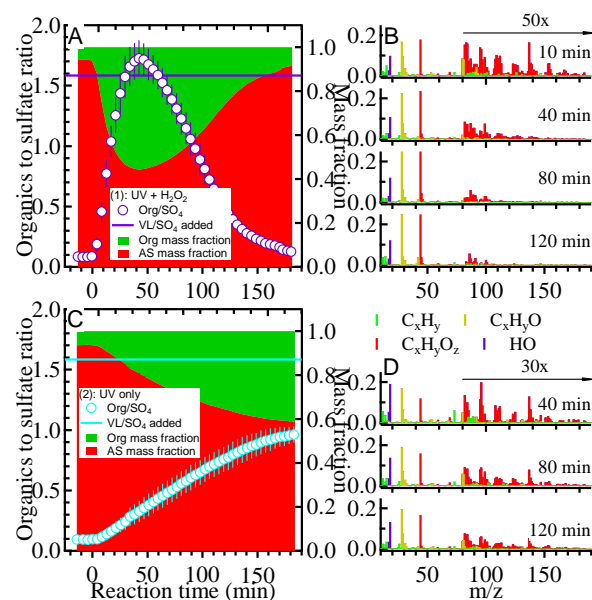


Figure 1. Changes of organic to sulfate ratio, organic mass fraction, and mass spectral feature during reactions under conditions (1) (A and B) and (2) (C and D).

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