



Experimental study of particulate products for aging of 1,3,5-trimethylbenzene secondary organic aerosol

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ABSTRACT

Secondary organic aerosol (SOA) from the photooxidation of aromatic compounds is a very complex mixture containing products with a different chemical nature that are dependent on aging processes. In this study, we focus on the chemical characterization of major products that are formed from the OH-initiated oxidation of 1,3,5-trimethylbenzene and subsequent aging through OH-initiated reactions in the presence of NO_x. The chemical composition of aged particles were measured in real-time by an aerosol laser time of flight mass spectrometer (ALTOFMS) coupled with Fuzzy C-Means (FCM) clustering algorithm. Experimental results demonstrated that methyl glyoxylic acid, 2-methyl-4-oxo-2-pentenoic acid, 3,5-dimethylbenzoic acid, 2-methyl-2,3-dihydroxyl-4-oxo-pentanoic acid, dimethyl-nitrophenol, 3,4-dimethyl-2-hydroxy-3-oxo-pentandioic acid, 2,4-dimethyl-2,3-dihydroxy-6-oxo-4-heptenoic acid, 2,4-dimethyl-4-hydroxy-2,3-epoxy-heptylic acid, 2,4-dimethyl-2,3,4-trihydroxy-5,6-dioxo-heptylic acid, and oligomer components were the predominant products in the aging particles. The possible reaction mechanisms leading to these aged products were also discussed and proposed.

Keywords: 1,3,5-trimethylbenzene, secondary organic aerosol, Fuzzy C-Means clustering (FCM) algorithm, laser desorption/ionization, aging mechanisms



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1. Introduction

Secondary organic aerosol (SOA) on average accounting for about 80% of organic aerosol (Zhang et al., 2007), is believed to affect human health (Zhao et al., 2013; Pui et al., 2014), climate (Altartatz et al., 2014; Zhou and Savijarvi, 2014), and visibility (Baltensperger, 2010; Tiwari et al., 2014). Aromatic hydrocarbons are typical SOA precursors emitted into the atmosphere from anthropogenic emission sources (Ziemann and Atkinson, 2012; Zheng et al., 2014). 1,3,5-trimethylbenzene (135-TMB) is a simple surrogate of aromatic hydrocarbons that are emitted to the atmosphere by automobile tailpipe exhaust and evaporative emissions (Gudiyella and Brezinsky, 2012; Lan and Minh, 2013). The SOA yield, chemical composition and the reaction mechanism relevant to SOA formation from atmospheric oxidation of 135-TMB have been the subject of many research studies (Yu et al., 1997; Smith et al., 1999; Fisseha et al., 2004; Rickard et al., 2010; Huang et al., 2014). As shown by the previous studies that the SOA formation from the gas-phase oxidation of 135-TMB tends to take place in the first few hours after emission, SOA can continue to age chemically over its atmospheric lifetime (Rudich et al., 2007; Andreae, 2009). Not only the chemical composition changes as SOA ages, but also the physical and chemical properties of aerosol particles such as the volatility, hygroscopicity, toxicity, and the optical properties will change (Tritscher et al., 2011; Sareen et al., 2013). The aging process of SOA is currently a focus of research interest in the field of atmospheric chemistry.

Limited information is available on the oxidation processes that form the molecular basis of aromatic SOA aging processes. Loza et al. (2012) carried out long-photoirradiation (about 36 h) laboratory chamber experiments to investigate the photooxidation of m-xylene, and reported the average rate of increase of the O/C ratio to be 0.0019 h⁻¹ during SOA aging. Recently, Sato et al. (2012) measured the chemical structure of aged SOA from the photo-oxidation of 135-TMB in the presence of NO_x using liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS). Sato et al. (2012) observed ring-opened products such as dialdehydes, carboxylic acid, ketoaldehydes, ketocarboxylic acids and oxocarboxylic acids. However, for the LC/TOF-MS measurements sampling with Teflon membrane filter followed by extraction with methanol is necessary. It is labor intensive and prone to artifacts. In the sample handling process sample evaporation may occur which would result in the loss of some chemical components.

We recently measured SOA formed from the photooxidation of 135-TMB using aerosol laser time-of-flight mass spectrometer (ALTOFMS) and reported that ALTOFMS is a useful tool to reveal the formation and transformation processes of SOA particles (Huang et al., 2014). Unlike the conventional aerosol instruments, ALTOFMS can derive thousands of mass spectra during data acquisition in each experiment, which requires an efficient statistical method to classify these mass spectra according to their chemical composition. One of the most useful way is Fuzzy C-Means (FCM) algorithm (Bezdek, 1981), which is an efficient

method of intelligently finding clusters in data sets with large numbers of variables and also is one of the most popular clustering methods based on minimization of a criterion function. It has been successfully applied to solve a wide variety of problems, such as pattern recognition, image analysis, bioinformatics and data mining (Tsai and Lin, 2011). Very recently, FCM algorithm has been developed by our group to classify the mass spectra of large numbers of particles obtained by ALTOFMS (Huang et al., 2013a). Our previous study has demonstrated the ability of FCM to pick out four type of particles as expected from mixed particles generated from the standards benzaldehyde, phenol, benzoic acid, and nitrobenzene solutions, and allowed a clear identification of ten distinct chemical classes of 135-TMB SOA, showing that the real-time ALTOFMS detection approach coupled with the FCM data processing algorithm can make cluster analysis of SOA successfully (Huang et al., 2013a). In this study, we focus on the chemical characterization of major products that are formed upon formation of 135-TMB SOA and subsequent aging through OH-initiated reactions in the presence of NO_x . The use of ALTOFMS offers the advantage in that it allows the detection of the size and chemical composition of aged SOA in real-time, whereas the use of FCM algorithm is suitable for extracting out potential clusters. The spectral patterns of aged SOA particles determined by FCM are interpreted in detail and tentative structures for the oxidation products are proposed. Also, the possible reaction mechanisms leading to these aging products were also proposed.

2. Experimental Method

2.1. Smog chamber experiment of 135-TMB SOA aging

135-TMB (>99%) was obtained from Sigma-Aldrich Chemistry Corporation, Germany. Sulfuric acid (>99%), sodium nitrate (>99%) and methanol (>99%) were purchased from the Tianjin (The third Reagent Manufactory), and nitrogen oxide (99.9%) from Nanjing Special Gas Factory. Methyl nitrite was synthesized by the dropping sulfuric acid into a methanol solution of sodium nitrate and was used after vacuum distillation to remove any methanol and NO_x impurities.

The details of the experimental procedure were explained elsewhere (Huang et al., 2013a; Huang et al., 2014). The aging experiments were conducted in an 850 L sealed collapsible polyethylene smog chamber. Prior to each experiment, the chamber was continuously flushed with dried, purified laboratory compressed air for >120 minutes until the total particle number was less than $10 \text{ particles cm}^{-3}$. After chamber purification, 135-TMB was sampled by a micro liter injector and delivered to the chamber by sending air through a small heated glass tube. NO and methyl nitrite were expanded into the evacuated manifold to the desired pressure through Teflon lines, and introduced into the smog chamber, mixed with the pre-existing purified air. The chamber was filled with the purified air to 850 L full volume. The concentration of 135-TMB, CH_3ONO and NO is 2.0 ppm, 20.0 ppm, 2.0 ppm, respectively. Four black lamps (the output power of each black lamp is 20 W with radiation wavelength in range of 300–400 nm, and peak intensity at 365 nm, the rate constant of NO_2 photolysis is $0.21 \pm 0.01 \text{ min}^{-1}$) were turned on and the photooxidation reaction was initiated. Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths longer than 300 nm (Atkinson et al., 1981). The time series of the OH concentration was estimated assuming that aromatic hydrocarbon decreased by the reaction with OH radicals, where the rate constants used for calculations were taken from Aschmann et al. (2006). In the experiment, the OH concentration reached a maximum immediately after the start of irradiation and then decreased with time, but the OH concentration maintained $>5 \times 10^5 \text{ molecules cm}^{-3}$ during irradiation. This indicates that particles and vapors in the reaction chamber were continuously oxidized during irradiation.

The volume of the reactor limits the duration of experiments in a chamber operated in batch mode; when sampling with all instruments continuously, nearly half of the chamber volume is depleted in 6 h. To achieve longer OH exposure times with all instruments sampling, the concentrations of 135-TMB, nitric oxide and nitrogen dioxide, and the volume concentration and mobility size distributions of particles were measured by GC-FID (Agilent 7820A, USA), NO- NO_2 - NO_x analyzer (TEI model 42i) and scanning mobility particle sizer (SMPS; TSI 3080L DMA, TSI 3775 CPC) every 30 min, respectively. After 24 h photooxidation, the aged SOA particles were analyzed continuously using the ALTOFMS connected directly to the chamber using a Teflon line.

2.2. Data acquisition and treatment

The ALTOFMS setup has been described in detail previously (Huang et al., 2013a; Huang et al., 2014). Particles were introduced into the instrument through the aerodynamic lens and undergo a supersonic expansion. The particles were accelerated to a terminal velocity that is inversely proportional to their diameter (Liu et al., 1995). The particles then enter a sizing region where they pass through two continuous wave laser beams. After being sized, the particle travels to the ion source region of a time-of-flight mass spectrometer. Chemical species in the particle were desorbed/ionized, using the pulsed output from an ultraviolet laser. Upon absorption of the laser pulses, the particle was heated in a rapid fashion, vaporized and individual molecules from the particle were ionized. The resulting positive ions were mass analyzed in a linear time-of-flight mass spectrometer. Thus, for each particle analyzed, the size was obtained through the particle velocity and the corresponding particle composition was determined through the positive ion mass spectra. Each of the obtained mass spectrum contains 4 096 data points, corresponding to ion signal intensity. The particle mass spectra are calibrated using software which was developed by our laboratory and compiled in Visual C++. A list containing the area and exact mass-to-charge ratio of all peaks in each particle mass spectrum is generated. Peaks less than 10 arbitrary units above the baseline on a 256-unit scale or with areas of less than 30 arbitrary units are rejected. Each revised spectrum is then converted to a normalized 300-point vector, each point representing one mass unit. Then the positive ion mass spectra of a single particle are described as 300-dimensional data vectors using the ion masses as dimensions and the ion signal peak areas as values. The data vectors of all particles measured are written into a classification matrix. Each spectrum's data is stored as one row in this matrix. Then, the individual particles were clustered using the Fuzzy C-Means algorithm (FCM) (Bezdek, 1981) based on their individual mass spectrum as described in detail in our previous study (Huang et al., 2013a).

2.3. Fuzzy C-Means algorithm (FCM) clustering criteria

The FCM algorithm is coded and compiled in Visual C++ and then linked with the data acquisition software. It is an iterative method starting the calculation with random class centers to find a substructure in the data. The procedure works in such a way that finally similar objects (particle spectra) have a minimum distance between their corresponding data vectors. Basically, FCM calculates fuzzy partition matrix to group some of the data points into k clusters. And the membership coefficients u_{ik} of each particle i to each class center k are determined. The class centers and membership coefficients provide for a detailed characterization of all the measured particles. Each class center can be represented as "mean" mass spectra pattern. This provides for the characterization of the mean chemical composition of the particle class.

The important problem accompanying the application of the Fuzzy c-means algorithm is the choice for the optimum cluster number, which much research has focused on (Hinze et al., 1999). The first step in determination of this optimum cluster number is to estimate an upper limit of the number of clusters, C_{max} .

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