



# Formation of high-molecular-weight compounds via the heterogeneous reactions of gaseous C<sub>8</sub>–C<sub>10</sub> n-aldehydes in the presence of atmospheric aerosol components



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## HIGHLIGHTS

- High-molecular-weight compounds were formed in the presence of atmospheric aerosols.
- Self-reactions of n-aldehydes are possibly mediated by atmospheric organic components.
- Reactions of n-aldehydes with atmospheric organic species are another possible pathway.

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## ABSTRACT

A laboratory study on the heterogeneous reactions of straight-chain aldehydes was performed by exposing n-octanal, nonanal, and decanal vapors to ambient aerosol particles. The aerosol and blank filters were extracted using methanol. The extracts were nebulized and the resulting compositions were examined using a high-resolution time-of-flight aerosol mass spectrometer. The mass spectral analysis showed that the exposures of the aldehydes to aerosol samples increased the peak intensities in the high mass range. The peaks in the organic mass spectra of the aerosol samples after exposure to different aldehydes were characterized by a homologous series of peak shifts due to the addition of multiple CH<sub>2</sub> units. This result is explained by the formation of high-molecular-weight (HMW) compounds that contain single or multiple aldehyde moieties. The HMW fragment peaks for the blank filters exposed to n-aldehydes were relatively weak, indicating an important contribution from the ambient aerosol components to the formation of the HMW compounds. Among the factors affecting the overall inter-action of aldehydes with atmospheric aerosol components, gas phase diffusion possibly limited the reactions under the studied conditions; therefore, their occurrence to a similar degree in the atmosphere is not ruled out, at least for the reactions involving n-nonanal and decanal. The major formation pathways for the observed HMW products may be the self-reactions of n-aldehydes mediated by atmospheric aerosol components and the reactions of n-aldehydes with organic aerosol components. The observed formation of HMW compounds encourages further investigations into their effects on the aerosol properties as well as the organic aerosol mass in the atmosphere.

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## 1. Introduction

Aldehydes constitute a portion of the oxygenated organic compounds in the atmosphere. They are present as gaseous volatile organic compounds (VOCs) and as particulate components

(Matsunaga et al., 2003, 2004; Kawamura et al., 2013). Aldehydes are emitted directly by biogenic and anthropogenic sources, and are also formed secondarily in atmospheric chemical reactions (Kesselmeier and Staudt, 1999; Lary and Shallcross, 2000; Hallquist et al., 2009). The formation pathways of aldehydes include gas-phase reactions initiated by the abstraction of hydrogen from the alkyl chains in organic molecules by hydroxyl radicals and the addition of hydroxyl radicals to double bonds. The ozonolysis of

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unsaturated organics also leads to the formation of aldehydes (Kawamura and Gagosian, 1987; Thornberry and Abbatt, 2004; Vesna et al., 2009). To understand the formation and transformation processes of gaseous/particulate organics in the atmosphere, detailed mechanisms of the further reactions of aldehydes (i.e., their fates) need to be clarified. Although several degradation pathways, including photolysis and oxidation to carboxylic acids, have been reported (Atkinson and Arey, 2003; Chacon-Madrid et al., 2010), efforts to investigate the chemical transformation processes of aldehydes and the associated roles of those processes in the atmosphere are still in progress.

An emerging topic in the role and fate of aldehydes is the interaction between gaseous aldehydes and aerosol particles. The reactions have been investigated in view of the secondary organic aerosol (SOA) mass in the atmosphere and the potential importance of other particle properties (e.g., optical and hygroscopic properties). Aqueous phase photochemical reactions of aldehydes may serve as a source of SOA in the atmosphere (Lim et al., 2010; Ervens et al., 2011), and the reactions in the absence of light are also a potential source of SOA (Jang et al., 2002, 2003). Aldehydes were proposed to undergo chemical reactions such as hydration, hemiacetal/acetal formation, polymerization, and aldol condensation to form SOA (Jang et al., 2002).

Thus far, short-chain aldehydes such as glyoxal and methylglyoxal have received much attention due to their ability to form SOA. In contrast, studies on the heterogeneous reactions of long-chain n-aldehydes are scarce and the significance of those reactions remains under debate. The formation of SOA from aldehydes, including octanal and decanal, has been reported (Jang et al., 2002). Garland et al. (2006) observed the substantial uptake of organic material during the exposure of acidic ammonium sulfate/sulfuric acid particles to hexanal vapor and identified aldol condensation and hemiacetal products. However, no growth of SOA was observed for most of the carbonyls studied by Kroll et al. (2005). Barsanti and Pankow (2004) reported that the hydration, polymerization, hemiacetal/acetal formation and aldol condensation of n-butanal, n-hexanal, and n-octanal were not thermodynamically favored when considering the gas/particle equilibrium. The reactive uptake was found to be important only under conditions of low relative humidity (RH) and high vapor concentration (Lee et al., 2008; Li et al., 2008).

The influence of the particulate phase composition on the accretion reactions of n-aldehydes is not clear. Most of the previous laboratory studies on the formation of SOA from aldehydes used simple inorganic components as seed particles. However, such particles are not commonly present in the atmosphere. Chan and Chan (2011) found that the reactive uptake of nonanal by acid particles was enhanced in the presence of hydrophobic particle-phase organics (i.e., oleic acid), which was supposedly due to the enhanced solubility of nonanal and thus its increased availability for particle-phase reactions. Considering the large fraction of organic aerosols in the real atmosphere, the products from heterogeneous reactions of long-chain monofunctional aldehydes could be different from those observed in previous laboratory studies. Given that the reactions in/on complex ambient aerosol particles cannot be fully elucidated theoretically with our current knowledge, experimental studies on the interactions of long-chain aldehydes with ambient aerosol components are essential to evaluate their contributions to SOA formation.

In this study, we investigated the possible contributions of atmospheric aerosol components to the heterogeneous reaction of long-chain n-aldehydes, which are n-octanal, n-nonanal, and n-decanal. These aldehydes have been detected in the atmosphere (Kesselmeier and Staudt, 1999; Matsunaga et al., 2003, 2004), and their reactive uptakes by inorganic seed particles have been

investigated (Jang et al., 2003; Li et al., 2008; Lee et al., 2008). Here, we report the heterogeneous reactions of n-aldehydes in the presence of atmospheric aerosol components, based on a laboratory study using ambient aerosol samples as the medium for these reactions. The products and the ambient aerosol components were extracted using methanol, and the extracts were atomized and analyzed using aerosol mass spectrometry. The formation of high-molecular-weight (HMW) compounds is investigated based on the mass spectral patterns of aerosol samples exposed to n-aldehyde vapors. The chemical structural characteristics and the temporal evolution of the HMW compounds are analyzed. Furthermore, the formation pathways of the HMW compounds and the potential significance of these reactions in the atmosphere are discussed.

## 2. Experimental methods

### 2.1. Aerosol sampling and aldehyde-exposure experiments

Urban atmospheric aerosols were sampled on a balcony (approximately 10 m above ground level) of a building at Nagoya University, Japan (35.15° N and 136.97° E) in June 2010. The sub-micron aerosol particles were collected on quartz fiber filters (20 × 25 cm<sup>2</sup>) for 72 h using a high-volume air sampler (model 120B, Kimoto Electric Co. Ltd., Osaka, Japan) with a cascade impactor (50% cut-off diameter of 0.95 μm, TE-230, Tisch Environmental Inc., OH, USA). The blank samples were collected by switching on the pump of the air sampler for only 15 s. Among the collected filter samples, two aerosol samples and two blank filters were used in the following aldehyde exposure experiments. Another two aerosol samples were used to assess the potential artifacts of HMW compounds in the measurement procedures.

n-Octanal, nonanal and decanal vapors were generated using a Permeator (PD-1B, GASTEC Co., Kanagawa, Japan) equipped with diffusion tubes. Pure dry nitrogen (99.99995%) was used as the carrier gas. Table 1 summarizes the mixing ratios of the n-aldehydes and the other experimental conditions. The experimentally determined mixing ratios of the n-aldehydes were derived from the weights of the diffusion tubes with the n-aldehydes before and after the exposure experiments. They are close to the mixing ratios calculated theoretically from the geometry of the diffusion tubes and the estimated diffusion coefficients. We use the experimentally determined mixing ratios for the following analysis. For each exposure experiment, one slice was punched from one filter sample, and another was punched from the other filter sample (9.1 cm<sup>2</sup> each). The filter slices were placed into a 10.6 L stainless steel reaction vessel, to which a mixture of n-aldehyde vapor and nitrogen was introduced continuously at a flow rate of 0.285 L min<sup>-1</sup>. In some experiments, blank filters and aerosol samples were exposed to aldehydes in the reaction vessel at the same time. As no water vapor was added, the exposures were considered to be performed under dry conditions. All the exposure experiments were performed under room temperature conditions, whereas the temperature inside the reaction vessel may have been influenced by the temperature of the permeator with diffusion tubes (set to 50 °C). No light was illuminated to the ambient aerosol samples in the reaction vessel, although the possible transmission of a small amount of light via the tubes attached to the reaction vessel was not eliminated.

### 2.2. Sample extraction and measurement

After the exposures to aldehyde vapors, the aerosol components on the filter samples were extracted ultrasonically using 6 g methanol for 30 min (2 g × 10 min × 3 times). The extracts were filtered through 0.22 μm pore size Millex-GV filters (Millipore Co.,

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