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Degradation kinetics of levoglucosan initiated by hydroxyl radical under different environmental conditions

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HIGHLIGHTS

- Mixing state significantly slows down the reactivity of levoglucosan toward OH.
- Low RH and high temperature are favorable to degradation of levoglucosan.
- Degradation of levoglucosan should be prominent in the atmosphere.

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ABSTRACT

To understand the atmospheric stability of levoglucosan, which is a major molecular tracer used for source apportionment of biomass burning aerosols, degradation kinetics of levoglucosan by hydroxyl radical (OH) have been investigated using a flow reactor under different conditions. The second-order rate constant (k_2) for the degradation of pure levoglucosan by OH is $(9.17 \pm 1.16) \times 10^{-12}$ cm^3 molecules^{-1} s^{-1} at 25 °C and 40% relative humidity (RH), while it depends on environmental conditions such as temperature, RH, and mixing state. At 25 °C, k_2 of pure levoglucosan linearly decreases with increasing RH ($k_2 = (1.50 \pm 0.04) \times 10^{-11} - (1.31 \pm 0.11) \times 10^{-11} RH$), while it increases with increasing temperature and follows the Arrhenius equation $k_2 = (6.2 \pm 5.6) \times 10^{-9} \exp[(-1922.5 \pm 268.2)/T]$ when the RH is 40%. At 25 °C and 40% RH, compared to pure levoglucosan, levoglucosan coated on $(NH_4)_2SO_4$ or NaCl (levoglucosan@$(NH_4)_2SO_4$ and levoglucosan@NaCl) shows larger k_2 to OH with $(9.53 \pm 0.39) \times 10^{-12}$ and $(10.3 \pm 0.45) \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}, respectively, whereas levoglucosan coated on soot (levoglucosan@soot) shows the smaller k_2 of $(4.04 \pm 0.29) \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}. Either $(NH_4)_2SO_4$ or NaCl internally mixed with levoglucosan ($(NH_4)_2SO_4$@levoglucosan and NaCl@levoglucosan) prominently inhibits the degradation of levoglucosan. Based on the rate constants, atmospheric lifetimes of levoglucosan were estimated to be 1.2–3.9 days under different conditions. All the results indicate that the degradation of levoglucosan by OH is prominent during air mass aging, and it should have an important influence on the uncertainty of source apportionment if the contribution of degradation to levoglucosan concentration is not considered in source apportionment models.

1. Introduction

Submicron particles can affect the radiation budget of earth, and also cause adverse health effects on human beings under high concentrations (Vermote et al., 2009; Yttri et al., 2009). In order to develop effective control strategies, it is critical to understand which sources contribute to their total mass (Chow and Watson, 2002; Saarnio et al., 2010). Source apportionment techniques, such as chemical mass balance (CMB) (Stone et al., 2008, 2010) and positive matrix factorization (PMF) (Healy et al., 2010; Lanz et al., 2007), have been developed and widely used for source apportionment. In both CMB and PMF models, concentrations of tracers for different sources are necessary as input parameters. In early studies, metal elements were widely used as tracers in source apportionment. However, organic tracers have become more and more commonly used recently due to the fact that they are more specific than metal elements in pollutant sources (Lin et al., 2010).

Biomass burning is one of the main source for atmospheric aerosols on the global scale, which has strong influence on the atmospheric aerosol composition. Levoglucosan (1,6-Anhydro-β-D-glucopyranose) is a specific component of particles emitted through biomass burning, and has recently been widely used as a

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molecular tracer in source apportionment (Engling et al., 2006; Mochida et al., 2010; Simoneit and Elias, 2001). A basic assumption in source apportionment models is that the tracers are stable in the atmosphere. Levoglucosan was thought to be stable enough in the past (Schauer et al., 1996), but a few recent studies have indicated that levoglucosan shows high reactivity to oxidizing radicals. For instance, using a smog chamber, Hennigan et al. (2010) found that levoglucosan can degrade quickly by OH radicals, with an atmospheric lifetime of 0.7–2.2 days. Using a flow reactor, Kessler et al. (2010) studied the heterogeneous oxidation of pure levoglucosan, with the second-order rate constant to be $(3.09 \pm 0.18) \times 10^{-13}$ cm^3 $molecules^{-1}$ s^{-1}. Slade and Knopf (2013) investigated the uptake coefficients of OH by levoglucosan and some other biomass burning organic aerosol surrogate compounds, and identified the volatilized products and volatilization mechanisms. Shiraiwa et al. (2012) studied the reactions between levoglucosan and NO_3 radicals and showed levoglucosan can be stable for just one week during NO_3 aging. On regional scale, Mochida et al. (2010) observed a significant decay of levoglucosan in summer after long range transport. Using the SPACCIM model, Hoffmann et al. (2010) also concluded that the lifetime of levoglucosan is 12.7–33.1 h in summer and 72.8–83.2 h in winter due to the oxidation of levoglucosan by OH radicals in aqueous phases. The shorter lifetime of levoglucosan compared to the residence time of aerosols means atmospheric degradation should have an important influence on its measured concentration, and subsequently on the source strengths estimated by apportionment models.

When exposed to OH, hydrogen abstraction should be the sole reaction pathway between OH and levoglucosan. Theoretical calculations showed the reactant complex (OH–OC) should be formed firstly before hydrogen abstraction occurs when organic compounds react with OH (Iuga et al., 2012). Levoglucosan is a polyhydroxy compound, thus it can easily interact with water through hydrogen bond. Therefore, it is reasonable to postulate that H_2O might affect the formation of levoglucosan–OH complex. Accordingly, the reactivity of levoglucosan to OH may be dependent on the reaction relative humidity (RH, which usually varies from 20% to 90% in the atmosphere). Furthermore, the tropospheric temperature varies notably with the changing seasons, and some studies have already found that temperature will affect the reactions between different organic compounds and OH radicals (Lee et al., 2003; Perry et al., 1977). Therefore, it is significant to investigate the effect of relative humidity and temperature on the reaction between levoglucosan and OH radicals to evaluate the atmospheric lifetime of levoglucosan. To our knowledge, previous laboratory studies have not systematically considered the effect of these environmental factors on levoglucosan degradation by OH radicals.

In the real atmosphere, organic compounds always mix with other particulate matters during transport, thus their reactivity to oxidants can be modified. For instance, the uptake coefficient of N_2O_5 on mixtures of humic acid and $(NH_4)_2SO_4$ decreases more than a factor of two compared with the case for single-component $(NH_4)_2SO_4$ (Badger et al., 2006). The heterogeneous reactivity of benzo[a]pyrene (BaP) toward O_3 was reduced substantially by a thin (4–8 nm), solid eicosane coating and entirely suppressed by thick (10–80 nm) solid eicosane coatings (Zhou et al., 2012). During biomass burning, a number of air pollutants will be generated, and soot may be the most significant one (Kozinski and Saade, 1998). Sodium chloride, as the principal component of sea salt, as well as secondary $(NH_4)_2SO_4$, are significant fractions of the total atmospheric particulate mass (Weis and Ewing, 1999). These particles are all likely to mix with levoglucosan in the real atmosphere. At the present time, however, it is as yet unknown how the mixing state with such particles will influence the stability of levoglucosan.

In this study, the degradation kinetics of levoglucosan exposed to OH radicals under different environmental conditions has been studied using a flow reactor. The aim of this work is to determine the degradation kinetic parameters and atmospheric lifetimes of levoglucosan under different relative humidity, different temperature, and in different mixing states with $(NH_4)_2SO_4$, NaCl and soot. The results obtained from this work will update the understanding of the fate of levoglucosan in the atmosphere.

2. Experimental

2.1. Reaction procedure and analytical methods

The set-up utilized in this study is shown in Fig. S1. All the experiments were performed using a flow system with a stainless steel reactor. The interior walls were coated with Teflon to provide a chemically inert surface. The volume of the reactor is 30 cm^3. A Teflon disc (geometric surface area 3.39 cm^2) was used as sample holder. For the kinetic studies, (0.50 ± 0.01) μg of solid levoglucosan film on the disc was evenly generated by gently drying levoglucosan/CH_3CN solution (Saarnio et al., 2010). In the case of reactions for the mixed samples, (100.0 ± 0.1) mg of each sample was evenly deposited on the disc. The reactor was purged with simulated air (80% high purity N_2 and 20% high purity O_2) and bubbled H_2O_2 flow. The RH of the system was controlled by varying the ratio of wet N_2 flow, which is achieved by bubbling H_2O with nitrogen, to dry N_2 flow. The total flow rate is kept at 500 mL min^{-1}. RH was determined by a humidity temperature meter (CENTER-314) at the exit of the reactor with an uncertainty less than 3% RH. Temperature of the system was controlled by a circulating water bath (CCA-20, Gongyi City YUHUA Instrument Co., Ltd) and can be accurately adjusted with an uncertainty of less than 0.5 °C. The water partial pressure in the system may change while the temperature changes, but a constant RH was kept at different temperatures by adjusting the ratio of wet N_2 flow to dry N_2 flow in this study.

The reacted samples were ultrasonically extracted using (20.0 ± 0.1) mL CH_3CN and then filtered using a glass fiber filter which had been previously cleaned by ultrasonication in CH_3CN. Subsequently, the eluate was evaporated to nearly dryness, transferred into a 1.5 mL graduated vial and then dried under a gentle nitrogen stream.

The high polarity of levoglucosan demands a derivatization step prior to GC analysis. In this study, *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) was used as silylation reagent for the derivatization of levoglucosan (Pietrogrande et al., 2010). 50 μL of BSTFA plus 1% TMCS and 50 μL of pyridine was added to the residue from previous steps, and the silylation reaction was performed at 333 K for 60 min. Then 1.0 μL of the silylation product was injected into the GC–MS system. Detailed GC–MS parameters and procedures are shown in the Supporting information.

2.2. OH generation and detection

OH radicals were generated in a quartz chamber by the UV photolysis of H_2O_2. Two ultraviolet light lamps (18 W, Beijing Lighting Research Institute) which provided UV-radiation with a central wavelength around 254 nm were used. The concentration of OH radical was controlled by varying the ratio of pure N_2 and H_2O_2 flow passing through the lamp.

Salicylic acid has strong reactivity with OH radical, and is commonly used to trap OH radicals (Chiueh et al., 1992). Detailed descriptions of the rationality for using salicylic acid as the reference compound to detect OH concentration in this study and the