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Key Points:
- Kinetic isotopic measurements show that levoglucosan is chemically degraded when exposed to OH
- The KIE was determined for the oxidation of levoglucosan in liquid and aerosol phase
- Levoglucosan $\delta^{13}C$ in ambient samples can be used to quantify the reaction extent of aerosol from homogeneous sources

Supporting Information:
- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4

Correspondence to:
I. Gensch,
i.gensch@fz-juelich.de

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Chemical stability of levoglucosan: An isotopic perspective

X. F. Sang[1], I. Gensch[1], B. Kammer[1], A. Khan[1], E. Kleist[2], W. Laumer[1], P. Schlag[1], S. H. Schmitt[1], J. Wildt[2], R. Zhao[3], E. L. Mungall[3], J. P. D. Abbatt[3], and A. Kiendler-Scharr[1]

[1]IEK-8, Forschungszentrum Jülich, Jülich, Germany, [2]IBG-2, Forschungszentrum Jülich, Jülich, Germany, [3]Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Abstract The chemical stability of levoglucosan was studied by exploring its isotopic fractionation during the oxidation by hydroxyl radicals. Aqueous solutions as well as mixed $(NH_4)_2SO_4$-levoglucosan particles were exposed to OH. In both cases, samples experiencing different extents of processing were isotopically analyzed by Thermal Desorption-Gas Chromatography-Isotope Ratio Mass Spectrometry (TD-GC-IRMS). From the dependence of levoglucosan $\delta^{13}C$ and concentration on the reaction extent, the kinetic isotope effect (KIE) of the OH oxidation reactions was determined to be 1.00187 ± 0.00027 and 1.00229 ± 0.00018, respectively. Both show good agreement within the uncertainty range. For the heterogeneous oxidation of particulate levoglucosan by gas-phase OH, a reaction rate constant of $(2.67 \pm 0.03) \cdot 10^{-12}$ cm^3 molecule^{-1}s^{-1} was derived. The laboratory kinetic data, together with isotopic source and ambient observations, give information on the extent of aerosol chemical processing in the atmosphere.

1. Introduction

Biomass burning is an important source of primary organic aerosol (POA) and secondary organic aerosol (SOA) on a global scale [*Crutzen and Andreae*, 1990; *Hallquist et al.*, 2009], thus impacting human health, air quality, and climate. Uncertainties associated with the organic aerosol effects depend on the accuracy to which its global source is known. Here nonvolatile and nonreactive atmospheric chemical tracers are necessary for reliable source apportionment using chemical mass balance receptor models [*Schauer et al.*, 2008].

Levoglucosan (1,6-anhydro-β-D-Glucopyranose) has been for a long time employed as the specific molecular marker for long-range transport of biomass burning aerosol, based on its high emission factors and assumed chemical stability [*Simoneit et al.*, 2000, 1998]. Yet, recent ambient studies suggested significant atmospheric chemical degradation of levoglucosan [*Mochida et al.*, 2010]. Laboratory investigations of levoglucosan reactivity to hydroxyl radicals (OH) in aqueous or gas phase supported this finding. The emphasis of these experimental studies was placed upon mechanistic understanding of the wet oxidation chemistry [*Holmes and Petrucci*, 2007], determining the reaction kinetics in aqueous solutions [*Hoffmann et al.*, 2010], or both [*Zhao et al.*, 2014]. However, it was shown that levoglucosan degradation occurs on a timescale similar to that of tropospheric transport and deposition [*Hennigan et al.*, 2010]. High uptake coefficients of OH by levoglucosan particles determined in flow tube studies [e.g., *Kessler et al.*, 2010; *Slade and Knopf*, 2013] were interpreted to indicate a secondary loss pathway of levoglucosan in aerosol particles, additionally to the heterogeneous surface reaction. Predictions using equilibrium absorptive gas-particle partitioning of semi-volatile organics show that up to 10% levoglucosan can exist in the gas phase under typical atmospheric conditions, thus leading to a more rapid concentration decay in the particle phase [*May et al.*, 2012].

Complementary to concentration measurements, stable carbon isotope analyses can provide additional evidence for chemical processing. This rests upon the fact that reactions cause changes in the relative abundance of heavy to light isotopes in the precursor due to the kinetic isotope effect (KIE) [*Wolfsberg et al.*, 2010]. During other atmospherically relevant processes, such as dilution and mixing processes, the initial isotopic information is conserved. Several laboratory studies investigated the KIE for gas-phase oxidation of nonmethane hydrocarbons (NMHC) by OH [*Anderson et al.*, 2003; *Rudolph et al.*, 2000]. Information on KIE can be further used to determine the photochemical age of the studied compounds [*Rudolph and Czuba*, 2000] and thus for source apportionment. $\delta^{13}C$ measurements in gas and particle phase and their use in atmospheric chemistry

have been lately reviewed [*Gensch et al.*, 2014]. A method to measure the stable carbon isotope ratio of levoglucosan in source aerosol samples was recently developed and validated by *Sang et al.* [2012].

Here we present laboratory evidence based on isotopic observations that levoglucosan is oxidized by OH radicals. Additionally, the KIE of levoglucosan atmospheric degradation is derived from the isotopic fractionation of the reactant during the oxidation reaction in aqueous solutions as well as in a heterogeneous system, by exposing atmospherically relevant particles to gas-phase OH. This is an exemplary look at the chemical degradation of a typical tracer, implementing isotopes as internal clock. Such laboratory experiments under conditions simulating atmospheric aerosol can be extended to other compounds of interest.

2. Methods

The heterogeneous oxidation experiments were carried out in the reaction chamber of the Jülich Plant Atmosphere Chamber (JPAC), operated as a continuously stirred tank reactor. Details of the setup are described in *Mentel et al.* [2009]. The overall supply flow, split in three air streams, was 20.6 L min^{-1}, resulting in a reactant residence time of 55 min in the chamber. One inlet was reserved for injecting mixed levoglucosan-ammonium sulphate aerosol particles. Ozone and water vapor were added to the second inlet, while the third stream contained eucalyptol and ethanol from diffusion sources, to quantify the OH concentration used in each experiment. A Teflon fan provided homogeneous mixing in the course of reaction. Temperature (19.5 ± 0.5°C) and relative humidity (70 ± 1%, to insure that the particles remain liquid) were kept constant during all experiments. Instrumentation measuring at the chamber outlet included an Aerosol Mass Spectrometer (AMS, Aerodyne Research, USA) for online quantitative monitoring of aerosol particle composition, a Scanning Mobility Particle Sizer (SMPS3080, TSI, USA) for particle size distribution characterization, a GC-MS system (GC 6890 + MSD 5973, Agilent, USA) and a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-ToF8000, Ionicon, Austria) for gas-phase measurements, as well as an ozone monitor (Model 49 Ozone Analyzer, Thermo Environmental Instruments, USA). Aerosol filter samples were collected for offline isotopic analyses. Initially, levoglucosan/ammonium sulphate aerosol particles were injected with a constant flow of 4.4 L min^{-1} into the reactor, together with 8.2 L min^{-1} O_3 enriched air. Aerosol was generated from a 0.15 mM stock solution of levoglucosan and $(NH_4)_2SO_4$ (Chromatographie Service Gmbh, Germany and Merck KGaA, Darmstadt, Germany, respectively). An aerosol generator (Model 3076, TSI, USA) was therefore employed, producing particles with mass-weighted median diameters between 130 and 160 nm. After reaching a constant O_3 concentration in the chamber, the internal UV lamp (Philips, TUV 40W, $\lambda_{max} = 254$ nm) was turned on. Thus, OH radicals were generated by ozone photolysis and subsequent reaction of O(1D) with water. By changing the rate of ozone photolysis and thus the OH production rate, different OH concentrations could be adjusted to vary the extent of the levoglucosan oxidation reaction (see Table 1). For the lower end of the used range (Experiments 1–7 in Table 1), OH concentration was inferred from the decay of eucalyptol measured by GC-MS [*Kiendler-Scharr et al.*, 2009]. The ethanol decay measured by a calibrated PTR-ToF [*Jordan et al.*, 2009] was utilized to determine the OH concentration in Experiments 8–10. The AMS [*Canagaratna et al.*, 2007] provided real-time quantitative information on mass loadings for chemical components, including total organic, nitrate, ammonium, sulfate, and chloride. The peaks at m/z 60 ($C_2H_4O_2^+$) and 73 ($C_3H_5O_2^+$) are used as mass fragment markers for levoglucosan [*Alfarra et al.*, 2007]. In this work, the decay of levoglucosan concentration during the experiments was derived from the ratio between m/z 60 and ammonium ($[C_2H_4O_2^+]/[NH_4^+]$), thus accounting for aerosol wall losses, potential atomizer output fluctuations, and changes in AMS collection efficiency. A SMPS (TSI3081 + TSI3786) was used to measure the size distributions of aerosols between 14 and 500 nm. After establishing steady state in the chamber (i.e., three times residence time), the aerosol particle sampling started on precleaned quartz fiber filters (at 500°C for 10 h). Aerosol particles were collected for 3–5 h, resulting in approximately 85–175 μg levoglucosan on each filter. The samples were placed into petri dishes and stored at −20°C until isotopic analysis.

Experiments of levoglucosan photo oxidation in aqueous phase were carried out in the Department of Chemistry at the University of Toronto. The experimental details are given elsewhere [*Zhao et al.*, 2014], including sample preparation, different reaction component measurements, and data analysis by using the Aerosol Time-of-Flight Chemical Ionization Mass Spectrometry (Aerosol-ToF-CIMS). Here only the steps necessary for the withdrawal of levoglucosan samples, experiencing different extent of oxidation and being assigned for the isotopic measurements are briefly described. A 1 mM H_2O_2 solution (Sigma Aldrich, >30%, Trace SELECT) was added to a 30 μM levoglucosan solution (Sigma Aldrich, 99%). The reaction solution was placed in a cylindrical photo reactor (Radionex, RMR-200) equipped with lateral UV-B lamps (λ_{max} = 310 nm), equidistantly

Table 1. Summary of Conditions Used for the Heterogeneous Oxidation of Levoglucosan in Particles Exposed to Gaseous OH

	OH Concentration (molecule cm^{-3})	Tracer[a] Measured By	Ozone Inlet (ppb)	Ozone Outlet (ppb)	Number of Isotope Measurements
B1[b] (4)	-	-	-	-	21
B2[c] (1)	-	-	-	-	3
B3[d] (2)	-	-	153	-	9
1	2.70E+07	GC-MS	34	9	5
2	2.82E+07	GC-MS	34	9	3
3	4.20E+07	GC-MS	49	14	4
4	6.47E+07	GC-MS	90	27	6
5	7.24E+07	GC-MS	93	-	9
6	7.96E+06	GC-MS	15	4	3
7	1.02E+08	GC-MS	120	34	3
8	2.97E+08	PTR-ToF	233	70	4
9	1.98E+08	PTR-ToF	184	90	5
10	1.35E+08	PTR-ToF	138	45	3

[a]The tracers used to determine the OH concentration were eucalyptol and ethanol.
[b]Blank experiments with UV light, no ozone.
[c]Blank experiments without UV light, no ozone.
[d]Blank experiments without UV light, with ozone. The numbers in parentheses show how many times the different blank experiments were repeated.

placed around the sample flask. The UV-induced oxidation reaction started after switching on the lamps, when OH radicals formed from H_2O_2 photolysis. The levoglucosan solution was constantly stirred during photo oxidation. 4.5 mL aliquots of solution were withdrawn from the reaction bottle at various irradiation times, i.e., 5, 10, 15, 20, 25, 30, 40, 50, 60, 75, 90, 105, and 120 min, corresponding to different extent of the levoglucosan degradation. Catalase was immediately added to each sample in order to breakdown the remaining H_2O_2. Additionally to the irradiated samples, blank solutions of levoglucosan + water, levoglucosan + water + H_2O_2 and levoglucosan + water + H_2O_2 + catalase, were prepared without irradiation. The 16 samples were shipped to Forschungszentrum Jülich, being kept at 4°C until isotopic analysis.

Stable Carbon Isotope Analyses. To measure the stable carbon isotope ratios of levoglucosan in the samples collected during the oxidation experiments in the aerosol and aqueous phase, a Thermal Desorption-Gas Chromatography-Isotope Ratio Mass Spectrometry (TD-GC-IRMS) was used. This simplified procedure, employing one-column instead of heart-cut two-dimensional GC, was adapted from the method developed by *Sang et al.* [2012] to measure levoglucosan in source and ambient filter samples. While samples collected from biomass burning contain complex matrices of very low to semi-volatile organic compounds and cover a broad range of polarity, the mixtures originating from the levoglucosan OH oxidation experiments were composed of few components, with similar polarity. Their chromatographic separation was accomplished by using one-dimensional GC (Figure S2 in the supporting information). A pretreatment of the aerosol-and aqueous-phase samples was necessary to prevent the introduction of $(NH_4)_2SO_4$ and water, respectively, in the GC system. Details on the selective liquid extraction of levoglucosan from the filter samples, as well as of the freeze drying of the levoglucosan aqueous solutions are described in the supporting information section S2. A small piece of prebaked quartz filter (approximately 0.2–0.3 cm^2) was placed in a glass tube. 3 µL levoglucosan extract was injected on the filter piece. The sample was volatilized inside the Thermal Desorption Unit (TDU) at 240°C and subsequently trapped in the cooled injection system (CIS) at −100°C. By abruptly heating up the CIS to 240°C, the compound mixture was transferred to a midpolar GC column (Rtx225, 30 m length, 0.25 mm ID, 0.25 µm film thickness, Restek, USA) for chromatographic separation. Helium was used as carrier gas, at a flow of 2.5 mL min^{-1}. The GC (Agilent6890, Agilent Technologies Inc., USA) temperature program started at 80°C, ramped to 200°C by a rate of 5°C min^{-1}. The baseline-separated organic compounds

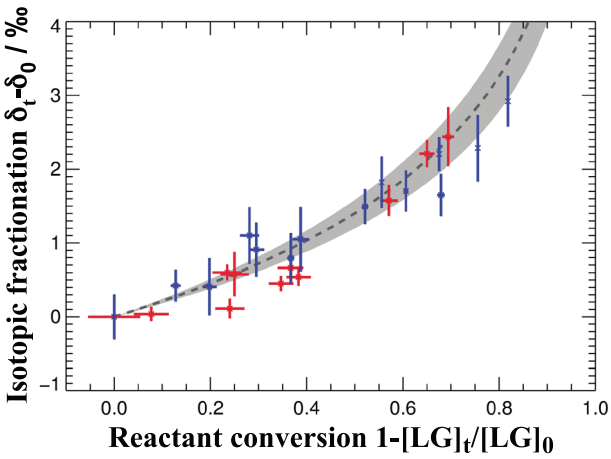

Figure 1. Levoglucosan isotopic fractionation during the oxidation, in aqueous solutions (blue crosses), and by exposing atmospherically relevant particles to gas-phase OH (red crosses). The dashed line and the grey shaded area show the calculated levoglucosan isotopic fractionation during the reaction with error ranges, respectively, using an epsilon value of 2.08 ± 0.32‰ (the mean of the KIE observed in the two experiments).

were sent to the combustion oven (CuO, 1030°C), for complete oxidation to CO_2 and water. The latter was removed by a semipermeable nafion membrane. CO_2 was transferred via a continuous flow, open split device (ConfloIV) to the IRMS for the stable carbon isotope ratio measurements.

3. Results and Discussion

The levoglucosan concentration during the oxidation reaction in aqueous and particle phase was derived from Aerosol-ToF-CIMS and AMS measurements, showing a decreasing trend with increasing OH exposure. Correspondingly, levoglucosan isotopic composition was determined in the samples probed at different extents of processing. The measurements of levoglucosan stable carbon isotope ratio and concentration in samples experiencing different OH exposure were employed to calculate the KIE of the liquid and heterogeneous oxidation reactions (for details, see supporting information).

Mechanistic studies of OH levoglucosan oxidation suggest several pathways of reaction [e.g., *Bai et al.*, 2013; *Holmes and Petrucci*, 2007; *Zhao et al.*, 2014]. Yet there is a general agreement that the initial H abstraction likely occurs from a carbon atom neighboring one of the hydroxyl functional groups, to form at the end a carbonyl group. From the isotopic point of view, the implication of the OH radical attack on the hydrogen-carbon bond is the change in the relative abundance of [^{13}C]/[^{12}C] in levoglucosan due to the carbon kinetic isotope effect. Figure 1 depicts the observed isotopic fractionation of levoglucosan as function of the reaction progress. For both oxidation experiments, levoglucosan became enriched in the heavier isotope ^{13}C in the course of the reaction, showing an isotopic fractionation of up to 3‰ at a levoglucosan conversion of 80%. This is an evidence that levoglucosan is chemically degradable in the presence of OH, in qualitative agreement with previous concentration measurement studies. Levoglucosan oxidation reaction by OH exhibits a normal kinetic isotope effect, i.e., KIE>1, where the lighter isotope reacts at a slightly faster rate, causing the ^{13}C enrichment in the reactant during the reaction. From the dependence of levoglucosan δ^{13}C and concentration on the reaction extent, the KIE of levoglucosan oxidation by OH in aqueous solution and aerosol particles was determined. For the aqueous oxidation experiment, the observed data were plotted as $\ln([LG]_t/[LG]_0)$ versus $\ln((1000+\delta^{13}C_t)/(1000+\delta^{13}C_0))$ (supporting information equation (S4)), where $[LG]_t/[LG]_0$ represents the levoglucosan concentration at different irradiation times, normalized to the initial value. $\delta^{13}C_t$ represents the isotopic composition in the corresponding solution samples, while $\delta^{13}C_0$value was measured in the "blank" containing levoglucosan + water + H_2O_2 + catalase and being not irradiated. Similarly, the concentration and isotopic data collected during the heterogeneous oxidation experiments in the continuously stirred flow reactor were plotted as $([LG]_t^x/[LG]_0-1)$ versus $\ln((1000+\delta^{13}C_t^x)/(1000+\delta^{13}C_0))$ (supporting information equation (S7)).

The KIE of the aqueous- and particle-phase oxidation reactions was obtained from the slopes of the lines fitted to the experimental data (Figure 2). The calculated ϵ values, representing $(KIE-1)\cdot 1000$, were 1.87 ± 0.27‰ and 2.29 ± 0.18‰, respectively, showing good agreement within the error ranges. Moreover, both ϵ values agree fairly well with the value predicted from the inverse dependence of the kinetic isotope effect on carbon number (N_C) for alkanes [*Rudolph*, 2007]. Thereupon, a ϵ value of 2.77‰ is derived for $N_C=6$.

From the exponential decay of levoglucosan concentration with irradiation time, *Zhao et al.* [2014] determined the rate constant of the aqueous-phase reaction with OH radicals to be $(1.08\pm0.16)\cdot10^9$ M^{-1} s^{-1} at room temperature, showing good agreement with *Hoffmann et al.* [2010]. For the heterogeneous oxidation of

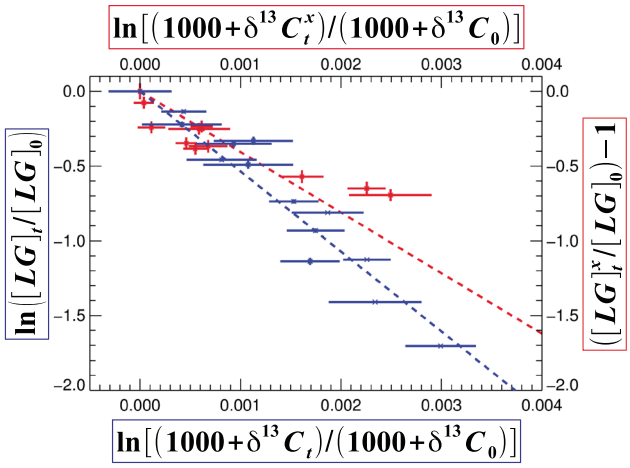

Figure 2. Experimental KIE determination for the oxidation reaction in aqueous (blue crosses) and particle phase (red crosses).

levoglucosan by OH an effective rate coefficient of $(2.67 \pm 0.03) \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} was calculated from the linear least squares analysis of the experimental data (see equation (S5)). This value is 1 order of magnitude lower than that reported by *Hennigan et al.* [2010] and 1 order of magnitude higher than that reported by *Kessler et al.* [2010]. Here it should be mentioned that the levoglucosan aerosol particles produced for this study had a surface area-weighted diameter three times smaller than those used by *Hennigan et al.* [2010]. Correspondingly, less reacting surface leads to lower reaction rates for the levoglucosan oxidation in particle phase by gaseous OH. On the contrary, *Kessler et al.* [2010] used a much lower relative humidity during their flow tube experiments. This might enhance the viscosity of the particles, thus creating kinetic hindrance for the heterogeneous reaction and lowering the rate of oxidation.

Using the observed effective reaction rate constant, an uptake coefficient of 1.93 was derived for levoglucosan heterogeneous OH oxidation (see supporting information equation (S8)). Uptake coefficients higher than unity were already reported in the literature [*Hennigan et al.*, 2010; *Kessler et al.*, 2010], indicating the possibility of reaction of gas-phase levoglucosan or secondary chemistry occurring inside particles.

The proven chemical reactivity of levoglucosan certainly calls into question its use as a molecular marker of biomass burning emissions in aerosol. *Hennigan et al.* [2010] already discussed the necessity to combine levoglucosan with other tracers, in order to constrain the source apportionment of biomass smoke. Here it is noteworthy mentioning the general requirements for such an additional tracer. The emission factors of the coemitted species must be known, as well as their relative loss rates. Furthermore, their reactivity has to be comparable to ensure a wide range of conversion extent being covered for both compounds. Using stable isotope ratios ideally fulfils these requirements. We suggest that levoglucosan δ^{13}C measurements in ambient samples can be used to quantify the extent of the aerosol processing when homogeneous source conditions are met. Levoglucosan was previously shown to have source-specific isotopic composition in biomass burning source aerosol [*Sang et al.*, 2012]. Notably for the applicability in isotopic ambient studies, the enrichment in ^{13}C relative to the parent holocellulose was consistent among all samples, being independent of firing type. Further, due to the KIE, the highest sensitivity of chemical aging isotopic calculations will be attained for levoglucosan conversions above 80%, conditions at which the consideration of concentration as sole constraint for biomass mass source strength is prone to induce the largest errors.

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Erratum

In the originally published version of this article, in the third key point, the greek delta symbol was incorrectly presented as "d". Also, in the abstract, "cm^3 $molecule^{-1}$ s^{-1}" was missing "s^{-1}". These errors have since been corrected and this version may be considered the authoritative version of record.