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Rapid Aqueous-phase Photooxidation of Dimers in α -Pinene SOA

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Abstract

Chemical complexity significantly hinders our understanding of the formation and evolution of secondary organic aerosol (SOA), known to have impacts on air quality and global climate. Dimeric substances present in SOA comprise a major fraction of extremely low-volatile organic compounds (ELVOCs) which are especially poorly characterized. Using on-line mass spectrometry, we have investigated the aqueous-phase OH oxidation of dimers present in the water-soluble fraction of SOA arising from ozonolysis of α -pinene. This study highlights very rapid OH oxidation of dimeric compounds. In particular, using pinonic acid as a reference compound, we obtained 2nd-order rate constants for the loss of 12 dimers, with an average value of $1.3 \pm 0.5 \times 10^9$ M⁻¹ s⁻¹ at room temperature. For the first time, this study demonstrates that rapid

loss of dimeric compounds will occur in cloudwater, and potentially also in aqueous aerosol.

Introduction

Secondary organic aerosol (SOA) refers to the organic fraction of suspended submicron particulate matter generated in the atmosphere via oxidation of volatile organic compounds (VOCs) of both anthropogenic and natural origins.¹ Due to the important role that SOA plays in air quality and global climate, the formation and evolution of SOA components have been a major area of interest in atmospheric chemistry in recent years. The chemical complexity of SOA, however, significantly hinders a molecular-level understanding of the composition and reactivity of SOA components. In particular, the chemistry of extremely low-volatile organic compounds (ELVOCs)² currently represents one of the largest gaps in our knowledge.

Dimers belong to an important class of ELVOCs and have been observed in laboratory-generated SOA³⁻⁹ ambient SOA¹⁰⁻¹³ as well as ambient fog water.¹⁴ Comprising a large number of trace compounds with highly variable structures and functionalities,¹¹ the separation and identification of individual dimers are highly challenging. Recent application of mass spectrometry has revealed the elemental composition and structures of a number of dimeric esters.^{6,8,12} During a typical atmospheric lifetime of SOA, dimers are subject to photochemical processing. While photochemical processing can also occur in the particle phase,^{15,16} when a particle is activated into a cloud droplet, the aerosol dimers can dissolve into the aqueous phase via nucleating scavenging¹⁷ and undergo aqueous-phase photochemistry.^{5,18-22} Despite an extensive database of the aqueous-phase OH reactivity of organic compounds,^{23,24} kinetic data for SOA dimers are lacking. Photochemistry of dimers has not been incorporated into cloudwater chemistry models, with one exception.²⁵ Analysis of dimers at the molecular-level is a prerequisite for understanding their chemistry. Whereas,

for atmospheric modeling, the concept of a generalized OH reactivity²⁶ that represents the wide diversity of dimers is essential, given that a complete speciation of dimers is infeasible.

Using an advanced mass spectrometric laboratory technique, we investigate for the first time the aqueous-phase photooxidation of dimers arising from α -pinene ozonolysis. This chemical system is an atmospherically-representative reaction system, and its dimers are the best documented.^{5,6,8,11,12} Our specific goals are to determine the OH reactivity of individual dimers, as well as to develop a generalized OH-dimer reactivity that can be used in photochemical models.

Materials and Methods

This work is based on experiments performed in Aljawhary et al.⁵ and a schematic view of the setup is shown in Figure 1. Briefly, SOA was generated by introducing α -pinene and O_3 to a 1 m³ Teflon chamber used as a continuously stirred tank reactor. The residence time of air in the chamber was 1.6 hours. The experiments were performed under the dry condition ($< 5\%$ RH) without an OH-scavenger so that the α -pinene oxidation proceeded mostly via ozonolysis with partial contribution from the OH radical. O_3 (600 ppb) and α -pinene (140 ppb) were continuously injected to the chamber, establishing a steady state at 500 and 40 ppb, respectively. Once the mass concentration of SOA reached its steady state (200 $\mu\text{g m}^{-3}$), particle samples were collected on a Teflon filter (47 mm diameter and 2 μm pore size) behind an O_3 denuder. The mass of SOA collected for each sample was 0.5 to 0.7 mg. After collection, the filter was immediately shaken in 50 mL of milliQ water for 15 min to extract the water-soluble organic compounds (WSOC) in SOA. The WSOC solutions were stored frozen at $-30\text{ }^\circ\text{C}$ until photooxidation experiments.

Aqueous-phase photooxidation was performed by exposing UVB radiation to the SOA extract contained in a glass bottle, with 1 mM of H_2O_2 (Sigma-Aldrich, TraceSelectTM) added as the OH precursor. The photon flux in the system has been reported by Badali

et al.²⁷ The OH steady state concentration was approximately 1.1×10^{-13} M, according to the decay rate of pinonic acid and its OH rate constant.²⁸ The length of each photooxidation experiment was typically 4 hours while the solution was continuously stirred and cooled by an external fan to keep the solution temperature at approximately 28 °C.

The solution composition was monitored in-situ by Aerosol Chemical Ionization Time of Flight Mass Spectrometry (Aerosol-ToF-CIMS) described in detail elsewhere.^{5,28-31} Briefly, the reaction solution was constantly atomized, and the generated particles were passed through a heated metal line (150°C) for thermo-desorption. Organic compounds volatilized in the heated line were introduced to an Aerodyne high-resolution time-of-flight CIMS for detection using three reagent ions: iodide ($\text{I}(\text{H}_2\text{O})_n^-$), acetate ($\text{CH}_3\text{C}(\text{O})\text{O}^-$) and protonated water clusters ($(\text{H}_2\text{O})_n\text{H}^+$). Iodide detects multi-functional organic compounds that can participate in hydrogen-bonding with iodide.^{32,33} Acetate detects organic and inorganic acids that possesses a larger gas-phase acidity than acetic acid.^{34,35} Water clusters detect organic compounds with a proton affinity larger than that of the water clusters.⁵ Overall, these three reagent ions detect overlapping yet distinct groups of species. Given that previous studies have shown that irradiation alone initiates chemical reactions of WSOC,^{5,20,21} a control experiment was performed for each of the reagent ions to investigate the effect of light without added H_2O_2 . Each OH-oxidation and control experiment employed a filter from an individual chamber experiment. In addition, positive matrix factorization (PMF) analysis was performed on the time resolved mass spectral observations from the iodide-OH experiment, as the iodide reagent ion detects a wide range of oxygenated compounds with a relatively uniform sensitivity. Please see SI Section S1.

Results and Discussion

Spectral Change during OH Oxidation

As described in our previous work,⁵ WSOC in α -pinene ozonolysis SOA is a highly complex mixture of organic compounds. The mass spectra of WSOC clearly exhibit a bimodal form, representing monomers and dimers (SI Figure S3). Significant changes of the mass spectra were observed in the OH oxidation experiments with all the three reagent ions. The OH oxidation resulted in a depletion of dimers and formation of monomers, confirming that dimers are not ion clusters forming in the instrument but independent chemical species. The PMF analysis of the overall, time-resolved mass spectrum resulted in three factors with, notably, the dimeric signals residing in the precursor factor (SI Section S1).

OH Reactivity of Individual Dimers

We focus on assigning specific peaks in the mass spectra to dimers in α -pinene SOA that have been previously identified.^{6,8,12} Assigning elemental compositions for dimers is challenging, as many possible combinations exist. The iodide reagent ion simplifies the process through the formation of iodide-analyte clusters where the heteroatom, iodine, adds unique mass signatures.³² We have successfully performed the high resolution mass fitting for 12 major dimers among which 10 have been reported previously (Table 1). The mass resolution of the iodide mode is approximately 4000 m/z m/z^{-1} at the dimer region, with a mass accuracy to within ± 6 ppm.

The time profiles of three well-documented compounds undergoing OH oxidation are shown in Figure 2, with the other nine in SI Figure S4a. All the dimers reacted away by the end of the experiment, with a few of them exhibiting a small degree of formation at short times. To quantify the net decay rates of an individual dimer (k_D^{II}), a relative kinetics method is employed, using pinonic acid (PIN) as the reference compound, where it is assumed that the ratio of PIN to other compounds in the atomizer output reflects that in the experimental

110 solution. A relative kinetic plot (Figure 2b) follows Eqn 1:

$$\ln \frac{[D]_0}{[D]_t} = \frac{k_D^{\text{II}}}{k_{\text{PIN}}^{\text{II}}} \ln \frac{[\text{PIN}]_0}{[\text{PIN}]_t}, \quad (1)$$

111 where $[D]_t$ and $[\text{PIN}]_t$ are the signals of a dimer and PIN at time t , respectively, and $k_{\text{PIN}}^{\text{II}}$
112 is the aqueous-phase OH rate constant of PIN: $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁸ As shown in Figure
113 2b, plotting $\ln([D]_0/[D]_t)$ against $\ln([\text{PIN}]_0/[\text{PIN}]_t)$ results in linear data passing through
114 the origin, with a slope equivalent to the ratio between k_D^{II} and $k_{\text{PIN}}^{\text{II}}$. The relative kinetics
115 plots for the other nine dimers are shown in SI Figure S4b, with the k_D^{II} values summarized
116 in Table 1. The OH oxidation of all the dimers is rapid, approaching the aqueous-phase
117 diffusion limit. We note that although each species assigned in Table 1 is arising from
118 one specific peak in the mass spectrum, it is possible that other isobaric compounds also
119 contribute to the observed peak intensity.

120 In addition to kinetic information, the current work provides tentative mechanistic in-
121 formation for the dimer chemistry. Extracting exclusive mechanisms from each individual
122 dimer in such a complex chemical system is challenging. In SI Section S3, we have performed
123 a case study for pinyl-diaterpenyl ester, the most dominant dimer observed. We have em-
124 ployed a structure-activity relationship^{36,37} to evaluate the most likely reaction pathway and
125 have investigated products from both fragmentation and functionalization reactions.

126 OH Reactivity of the Total Dimer Content

127 Due to the infeasibility of performing high resolution peak fitting for all the dimers, we
128 have lumped unit mass resolution signals across the entire dimer region to represent the
129 total dimer content of the SOA. For the iodide experiment, peaks from 450 to 600 m/z
130 were summed to cover as much of the dimer region as possible without overlapping with the
131 monomer region (Figure S3a). Similarly, the mass range of 300 to 450 m/z was selected for
132 the acetate and water clusters experiments.

A rapid decay of the total dimer signal is seen in OH-oxidation experiments using all the three reagent ions. The results of the iodide experiment are shown in Figure 2c as an example, and those of the other two reagent ions are shown in SI Figure S5. The relative kinetics plots of the three experiments are shown in Figure 2d. An averaged dimer OH reactivity ($k_{\text{Davg}}^{\text{II}}$) is determined from each of the three OH-oxidation experiments (Table 1) and three $k_{\text{Davg}}^{\text{II}}$ values agree to within a factor of two. Since the three reagent ions detect different populations of organic compounds, we propose that the average of the three $k_{\text{Davg}}^{\text{II}}$, $1.3 \pm 0.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, can be employed as a generic OH rate constant of dimers arising from α -pinene ozonolysis.

We note that the second-order rate constant for the decay of the precursor factor (Factor 1) in the PMF solution is $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, obtained using the relative kinetics method mentioned above. Although containing the dimeric signals, Factor 1 is largely driven by intense monomeric peaks. The fact that the rate constants for decay of both dimers (i.e. $k_{\text{Davg}}^{\text{II}}$) and Factor 1 are similar to those of a large variety of atmospherically-relevant organic compounds²³ demonstrates uniform reactivity for a wide range of species, i.e. the dimers are inherently neither more reactive nor more stable with respect to OH oxidation than monomeric species in solution.

Currently, the aqueous-phase OH reactivity of dimers is poorly constrained. Ervens et al.²⁵ have reported the OH reactivity of methylvinyl ketone oligomers ($1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), obtained by fitting experimental observations in a chemical system in which dimers formed and reacted simultaneously. The strength and novelty of this work lie in the in-situ measurement of the decaying dimers that are actually extracted from α -pinene SOA. The $k_{\text{Davg}}^{\text{II}}$ value determined in this work provides a significant experimental constraint to the aqueous-phase OH reactivity of dimers.

One experimental uncertainty in this work arises from the potential for direct photolysis of dimers with UVB light. Direct photolysis of aqueous dimers has been observed.¹⁸⁻²¹ Nevertheless, our best estimate is that direct photolysis contributes at most a few % of

the dimer decay observed during the OH oxidation experiments. See SI Section S4 for details. We also note that chemical processes occurring in the irradiated WSOC solution are highly complex, making the decoupling of direct photolysis and OH oxidation difficult. In particular, studies have shown that WSOC of SOA itself can generate OH radicals.^{27,38} Meanwhile, the aqueous-phase formation of oligomers has also been reported,^{39–43} as was observed to a minor degree at early times for a couple of dimers in this work (see Figure S4 and Section S3.3). Thus, the kinetic information reported in the current work should be considered as an effective OH-oxidation rate coefficient, representing the net decay of dimers upon exposure to OH in aqueous media (e.g., cloudwater).

Environmental Implications

On-line mass spectrometry was applied to investigate the aqueous-phase OH reactivity of the water-soluble fraction of SOA arising from α -pinene ozonolysis, with a specific focus on dimers present in this complex system. By directly observing the decay of specific dimeric species, and supported by positive matrix factorization analysis of the full CIMS spectrum, we demonstrate that dimeric compounds undergo aqueous-phase photochemical processing and contribute to monomeric products.

Building upon recent studies that have identified dimers in the α -pinene system, we have quantified for the first time the effective second-order rate constants (k_D^{II}) of 12 individual dimers. As well, the rate coefficients of the total dimer ($k_{\text{Davg}}^{\text{II}}$), measured using three different reagent ions of the CIMS agree to within a factor of two. We propose that the average value ($1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) can be used in multi- and aqueous-phase models as a generic rate constant for OH oxidation of dimers in biogenic SOA dominated by reactions of monoterpenes. While this study focused on a specific category of dimers from α -pinene, future studies should investigate the reactivity of a wider spectrum of extremely low-volatile organic compounds (ELVOCs) arising in both laboratory experiments and the ambient atmosphere.

More generally, the environmental significance of this result is that it further illustrates that OH oxidation in cloudwater can be an efficient sink of a number of organic species.⁴⁴ These include not only monomeric tracer compounds (such as levoglucosan and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA))^{28,31} and brown carbon species,⁴⁵ but also dimers. The $k_{\text{Davg}}^{\text{II}}$ value from this work can be translated into an e-fold lifetime of 2.1 hours in cloudwater, assuming an OH concentration of 1×10^{-13} M.²³ The ratio of dimers to monomers in SOA may represent an unique tracer for condensed-phase processing and should be investigated in the future. Our results imply an important role of the aqueous phase in removing organic compounds in the atmosphere, as it has been previously shown that aging of SOA particles under dry conditions did not remove dimers efficiently.⁴⁶ While the current work simulates dilute cloudwater-relevant conditions, aqueous-phase OH oxidation can be potentially important in aerosol liquid water, where the concentrations of both reactants and oxidants are highly uncertain.²⁶

Investigation of the identity and formation pathways of dimers in SOA is a major current priority in atmospheric chemistry, as dimers may constitute a sizable fraction of SOA mass.^{8,12} The dimers investigated in this work represent a poorly characterized fraction of SOA component, e.g., ELVOCs, and the reactive sink evaluated in this work is one of the first studies of the dimer chemistry. Overall, aqueous-phase sinks should be taken into consideration when the environmental fate of ELVOCs and related highly-oxygenated compounds is assessed.

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Supporting Information Available

Additional information for the PMF analysis and kinetic data are available.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Table 1: A list of individual dimers and their OH rate constant (k_D^{II}), as well as the average OH reactivity of SOA dimer content ($k_{\text{Davg}}^{\text{II}}$). The three compounds highlighted in colors are those presented in Figure 2a and b

Observed m/z	Dimer Nominal Mass (g mol ⁻¹)	Proposed Dimer Formula	k_D^{II} (M ⁻¹ s ⁻¹) ^a	Ref.
453	326	C ₁₆ H ₂₂ O ₇	1.5×10^9	n.a.
455	328	C ₁₆ H ₂₄ O ₇	1.6×10^{9b}	12,47
467	340	C ₁₈ H ₂₈ O ₆	2.4×10^9	12,47,48
469	342	C ₁₇ H ₂₆ O ₇	2.8×10^9	12,47,49
471	344	C₁₆H₂₄O₈ (pinyl-diaterbyl ester)	9.5×10^8	6,8,12,47
485	358	C₁₇H₂₆O₈ (pinyl-diaterpenyl ester)	2.6×10^9	6-8,12,47,50
495	368	C₁₉H₂₈O₇ (pinonyl-pinyl ester)	4.8×10^9	4,6-8,12,47,49-51
501	374	C ₁₇ H ₂₆ O ₉	1.2×10^{9b}	12
511	384	C ₁₉ H ₂₈ O ₈	3.6×10^9	12
515	388	C ₁₈ H ₂₈ O ₉	2.0×10^9	6,12
527	400	C ₁₉ H ₂₈ O ₉	3.2×10^9	8,12
529	402	C ₁₉ H ₃₀ O ₉	1.9×10^9	n.a.
Expt.			$k_{\text{Davg}}^{\text{II}}$ (M ⁻¹ s ⁻¹)	
Iodide			1.6×10^9	
Acetate			1.5×10^9	
Water cluster			7.0×10^8	
Average			$(1.3 \pm 0.5) \times 10^9$	

^a Derived from the OH oxidation experiment using the iodide reagent ion.

^b This compound exhibits an initial formation, and the k_D^{II} value is derived from the later decay.

Figure 1: Experimental apparatus.

Figure 2: The time series (a) and relative kinetics plots (b) of three individual dimers, as well as those of the lumped total dimer signals (c and d). For clarity, only the total dimer signal from the iodide experiment is shown in (c) along with the decay profile of pinonic acid (PIN) as a reference. The dashed line presents the mass spectral background of the total dimer signal. The solid lines in (b) and (d) are the linear fit curves.

Figure 3: This is the TOC graphic.