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Control of ozonolysis kinetics and aerosol yield by nuances in the molecular structure of volatile organic compounds

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HIGHLIGHTS

- We measure SOA yield and ozonolysis rate constants for a series of C_5–C_7 alkenes.
- SOA yields were greater for cyclic alkenes as compared to their linear analogs.
- Functional groups influence kinetics through both steric and electronic effects.
- We discuss relationships between VOC molecular structure and SOA yield/kinetics.

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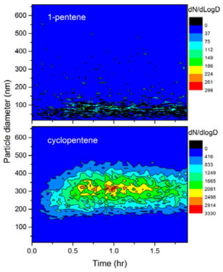
GRAPHICAL ABSTRACT



ABSTRACT

Secondary organic aerosol (SOA) plays integral roles in climate and human health, yet there remains a limited understanding of the mechanisms that lead to its formation and ultimate fate, as evidenced by a disparity between modeled atmospheric SOA loadings and field measurements. This disparity highlights the need for a more accurate representation of the molecular-level interactions between SOA sources and oxidative pathways. Due to the paucity of detailed chemical data for most SOA precursors of atmospheric relevance, models generally predict SOA loadings using structure activity relationships generalized to classes of SOA precursors. However, the kinetics and SOA forming potential of molecules are nuanced by seemingly minor structural differences in parent molecules that may be neglected in models. Laboratory chamber studies were used to measure SOA yields and rate constants for the ozonolysis of several linear, cyclic and oxygenated C_5–C_7 alkenes whose molecular structure vary in the site of unsaturation and/or the presence/position of functional groups and that represent atmospherically relevant classes of molecules. For the alkenes studied in this work, we found greater SOA yields for cyclic compounds compared to their linear analogs. For 1-alkenes, SOA yield increased with carbon number but was also dependent on the position of the double bond (internal vs terminal). Both the identity and position of oxygenated functional groups influenced SOA yield and kinetics through steric and electronic effects. Additionally, terminal alkenes generally resulted in a greater SOA yield than analogous internal alkenes, indicating that the position of the double bond in alkenes plays an important role in its atmospheric fate. Herein, we demonstrate the nuanced behavior of these ozonolysis reactions and discuss relationships between parent compound molecular structure and SOA yield and kinetics.

1. Introduction

Organic aerosol (OA) is a ubiquitous component of atmospheric

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particulate matter that influences both human health and global climate. A large fraction of OA is secondary in nature (SOA), being produced by the oxidation of volatile organic compounds (VOCs) emitted by anthropogenic (AVOCs) and biogenic sources (BVOCs). Despite the integral role of SOA in atmospheric processes, there remains a limited understanding of its formation and fate in the atmosphere. This challenge is rooted not only in identifying the sources of SOA but also in understanding the fundamental chemical processes that lead to SOA formation and transformation.

In spite of the breadth of atmospheric A/BVOCs, an extensive amount of work has focused primarily on biogenically emitted terpenes and monoterpenes (Hallquist et al., 2009; Ng et al., 2006; Lee et al., 2006a). Despite efforts to characterize the roles of these prevalent BVOCs, atmospheric models largely under-predict SOA mass as compared to field measurements (Hallquist et al., 2009; Heald et al., 2005; Kanakidou et al., 2005; Jo et al., 2013; Goldstein and Galbally, 2007), due in part to uncertainties in measured VOC emissions, omission of key VOCs, missing chemical and physical processes that contribute to SOA, errors associated with extrapolating laboratory-derived data to the atmosphere and uncertainties in ambient OA measurements (Carlton et al., 2009). Herein, we propose that another contributor to the disparity between field measurements and atmospheric models may lie in the coarse level of chemical assumptions and approximations that must be made by modelers due to a lack of chemical data for the majority of compounds of interest. We highlight this recognized need for a more complete understanding of VOC reactivity and SOA formation at the molecular level by examining the ozonolysis rates and SOA formation yields for a number of compound classes of atmospheric relevance, demonstrating the dramatic impact of small nuances in molecular structure on these chemical parameters.

Reaction rate constants and SOA yield data for input to atmospheric models have been measured experimentally for a number of key VOCs (Lee et al., 2006b; Keywood et al., 2004; Kroll and Seinfeld, 2008; O'Dwyer et al., 2010; Loza et al., 2014; Tkacik et al., 2012; Atkinson et al., 1995; Khamaganov and Hites, 2001; Papagni et al., 2001; Cusick and Atkinson, 2005), yet the list of studied compounds is far from exhaustive. In order to circumvent the paucity of kinetic data, structure activity relationships (SARs) have been developed to estimate oxidation rate constants based on molecular structure of parent compounds. In some cases, SARs have been shown to follow experimental data well (McGillen et al., 2011a, 2008), but there is still considerable error associated with data calculated using this approach (Pfrang et al., 2006; McGillen et al., 2006; Aschmann and Atkinson, 2011). In addition to SARs, which marry structure and (re)activity, several studies have demonstrated correlations between VOC structure and SOA mass yield, although this discussion has been predominantly limited to alkanes (Loza et al., 2014; Tkacik et al., 2012; Lim and Ziemann, 2009; Aumont et al., 2013; Yee et al., 2013) and alkyl-substituted alkenes (Lee et al., 2006b; Keywood et al., 2004; McGillen et al., 2011a). SARs and SOA yield correlations have, by necessity, been used in lieu of experimental data in atmospheric models to predict large scale air quality and climate trends. Inaccuracies or incompleteness in SARs/yield correlations will be reflected in model outputs.

The omission of many VOCs from atmospheric models may also prove to be an important source of error. Semi-volatile organic compounds (SVOCs) and other reactive VOCs (ORVOCs) have received growing attention as potential SOA precursors (Kanakidou et al., 2005). We recently demonstrated that lawn mowing results in the emission of ORVOCs (cis-3-hexenol, HXL, cis-3-hexenyl acetate, CHA and 1-penten-3-ol, PTL) that, upon ozonolysis, contribute to SOA formation at levels approaching those of predominant terpenes (Harvey et al., 2014). Interestingly, despite having similar molecular backbones consisting of 3-hexene, the SOA forming potential of HXL was found to be much greater than CHA, despite HXL being emitted at a 5x lower rate. This disparity was attributed to the molecular structure of each ORVOC (Harvey et al., 2014; Jain et al., 2014). Similarly, although PTL has a similar molecular structure to HXL (oxygenated internal alkene), it was found to have limited reactivity to ozone and a negligible SOA yield. These observations led us to posit that the chemical processes leading to SOA formation from the oxidation of VOCs are quite nuanced; that a seemingly small change in molecular structure has a profound impact on the molecule's atmospheric behavior.

Several recent studies have expanded our understanding of SARs by describing mechanisms by which certain molecular features impact reaction kinetics and/or SOA forming potential (O'Dwyer et al., 2010; McGillen et al., 2011a, 2008; Boyd et al., 2003; Peeters et al., 2007a, 2007b; Mulla et al., 2010; Vereecken and Francisco, 2012; Stewart et al., 2013). The discussion thus far has focused on unsaturated hydrocarbons, with little work reported with regard to oxygenated species, which contribute a significant fraction of atmospheric reactive VOCs. A more complete understanding of the chemical basis of SARs in oxygenated alkenes may allow for the development of more accurate atmospheric models. In the present work, rate constants for the ozonolysis of a series of cyclic and linear C_5–C_7 unsaturated methyl esters and alcohols are measured and discussed with respect to molecular structure. We add to the discussion of SARs of VOCs by focusing on the effect of oxygenated substituents.

2. Experimental

All experiments were performed at ambient pressure and temperature (~23 °C) in a 775 L Teflon chamber (Fig. 1). Between experiments, the chamber was passivated overnight with 1–2 ppm O_3 and flushed with zero air to attain background aerosol mass loadings $<0.1\ \mu g\ m^{-3}$.

1-pentene, 1-pentene-3-ol (PTL), 2-pentene, 1-hexene, cis-3-hexenyl acetate (CHA), cis-3-hexenol (HXL), cyclohexene, 3-hexene-2,5-diol (HXNDL), 3-heptene (racemic), and cycloheptene were purchased from Sigma Aldrich. Cyclopentene and cis-3-hexene were purchased from Alfa Aesar. Reagents (all > 95%) were used without further purification. Dry, zero air was produced by passing compressed air sequentially through silica, activated carbon and HEPA filters. This zero air was also used to generate ozone using a commercial corona discharge ozone generator (OLSOA/DLS OzoneLab).

Thermal desorption gas chromatography mass spectrometry (TD-GC/MS) was used to monitor VOC consumption. A detailed description of the TD-GC/MS used can be found in S1 of the

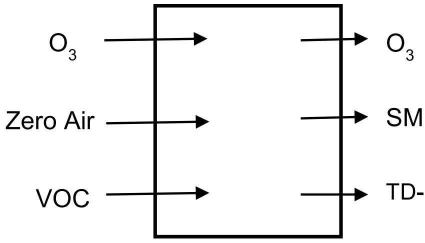

Fig. 1. All experiments were carried out in a 775 L Teflon pillow–style reaction chamber. VOCs were injected via a heated bulb under a steady flow of zero air and mixed by gentle rocking. Once VOC concentrations were stable (15 min), ozone was injected as a short burst and monitored along with particle mass distributions throughout experiments.