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

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Keywords: Structure Activity Relationships (SARs), SOA yield, ozonolysis, alkene, oxygenated alkene, green leaf volatile

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 modelled 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 C₅-C₇ 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.

1.0 Introduction

Organic aerosol (OA) is a ubiquitous component of atmospheric 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.¹⁻³ Despite efforts to characterize the roles of these prevalent BVOCs, atmospheric models largely under-predict SOA mass as compared to field measurements,^{1,4-7} 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.⁸ 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,⁹⁻¹⁸ 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,^{19,20} but there is still considerable error associated with data calculated using this approach.²¹⁻²³ 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^{13,14,24-26} and alkyl-substituted alkenes.^{9,10,19} 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.⁵ We recently demonstrated that the 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.²⁷ 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.^{27,28} 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 behaviour.

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.^{12,19,20,29-34} 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 C₅-C₇ 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.

2.0 Experimental

All experiments were performed at ambient pressure and temperature (~23°C) in a 775 L Teflon chamber (**Figure 1**). Between experiments, the chamber was passivated overnight with 1-2 ppm O₃ and flushed with zero air to attain background aerosol mass loadings < 0.1 µg 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 S2 of

the supplemental material. Aerosol particle size distributions, as well as total aerosol mass loadings were measured continuously with a scanning mobility particle sizer (SMPS, model 3080, TSI Inc., Shoreview, MN). The vapor pressure of predicted ozonolysis products was estimated using structure based estimators courtesy of the US EPA Estimation Programs Interface Suite.³⁵

Reaction rate constants (k) for the ozonolysis of VOCs were determined using experimental protocol described by Grosjean et al.³⁶ (and references therein). Briefly, the rate of ozone decay was measured in the presence of at least a 10-fold initial molar excess of VOC (to ensure pseudo-first order conditions). VOCs were added to the chamber first followed by ozone, which was added as a quick burst (less than 45 seconds). Initial reaction conditions are summarized in S2 of the Supplemental Material. Ozone concentrations were monitored at 5 second intervals with an American Ecotech Serinus O₃ Monitor (model E020010). A plot of $\ln([O_3]_0/[O_3]_t)$, where $[O_3]_0$ and $[O_3]_t$ are the ozone concentrations at time zero and t , respectively, versus time (t , seconds) yields a straight line with slope k' (sec^{-1}). From the rate expression of the reaction, $k = k'/[VOC]_0$, where $[VOC]_0$ is the VOC concentration at time zero, we were able to determine k ($\text{cm}^3 \text{ sec}^{-1} \text{ molecule}^{-1}$). The loss of ozone, as well as the VOC, to chamber walls was measured and found to be negligible over the time scale of the kinetic experiments,²⁷ confirming that reaction with VOCs was the only significant removal process for ozone.

Separate experiments were used to calculate SOA yields, Y , according to equation (1),³⁷ where $\Delta[\text{SOA}]$ is the maximum, particle-loss corrected SOA concentration ($\mu\text{g m}^{-3}$) and $\Delta[\text{VOC}]$ is the total amount of VOC consumed ($\mu\text{g m}^{-3}$) at that SOA maximum:

$$Y = \frac{\Delta[\text{SOA}]}{\Delta[\text{VOC}]} * 100\% \quad (1)$$

Particle loss (to chamber walls, due to secondary reactions and/or phase transitions) was estimated by extrapolating decay trends in SOA mass loadings back to time zero of the

reaction (i.e., at time of ozone injection). A representative reaction profile can be found in S1 of the Supplemental Material. We report the average yield ($\pm$ standard deviation) from at least three experiments for each VOC. Student's T-tests were used to determine if averages were statistically different for different VOCs, at given confidence intervals, which are indicated with alpha- (α) values as they are discussed.

3.1 SOA Yield of Cyclic vs. Linear Alkenes.

Relationships between VOC molecular structure and SOA yield have been reported for a number of chemical systems. Some studies identify surrogates for naturally occurring VOCs,^{10,38} some catalog the SOA yield of several compounds,^{9,13,37,39} while others identify key molecular structures that influence SOA yield.^{10,14,24-26,40} Most studies to date have focused on linear, branched and cyclic alkanes or cycloalkenes. In the case of alkanes, it has been shown that SOA yield increases with carbon number and, given two compounds with the same number of carbon atoms, follows the trend of cyclic alkanes > linear alkanes > branched alkanes and decreases further with degree of branching. SOA yield in alkanes also increases if the oxidation results in oligomerization.^{24,26}

SOA yield for linear alkenes is also expected to increase with carbon number.¹⁰ For the series of linear VOCs studied in this work, we generally observed SOA yields increasing in the order of pentene < hexene < heptene. The position of the double bond, however, also plays an important role in the SOA yield, with the 1-alkene generally producing a greater SOA yield than the internally bonded analog. For example, 1-pentene resulted in a SOA yield of 1.8 ($\pm$ 0.2) %, which was greater ($\alpha = 0.05$) than that of 2-pentene (0.80 ($\pm$ 0.6) %).

The mechanisms leading to SOA formation from the ozonolysis of alkenes has been reviewed extensively.^{1,8,41,42} Following the very simplified ozonolysis mechanism in Scheme 1, 1-pentene is expected to produce C₁ and C₄ carboxylic acids and aldehydes, while 2-pentene is expected to result in the production of C₂ and C₃ carboxylic acids and aldehydes. These species

are relatively volatile, and will not nucleate to form SOA directly. Therefore, secondary oligomerization and/or condensation mechanisms are the likely route to SOA formation for these systems. In fact, secondary reactions of ozonolysis products, including oligomerization of stabilized Criegee Intermediates (CIs), are predominant drivers of SOA formation in the alkene-ozonolysis system.^{43,44} Oligomerization (and SOA yield) can be directly related to the fraction of CIs that exist in a peroxy-radical stabilized form, where a lower “stability fraction” results in lower SOA yields.⁴⁵⁻⁴⁷ It is possible that the enhanced stability of the C₁ and C₄ CIs in 1-pentene ozonolysis system allow it to undergo secondary oligomerization reactions more readily as compared to the less stable C₂ and C₃ CIs found in 2-pentene system, resulting in an enhanced SOA yield for 1-pentene.⁴⁵⁻⁴⁷

Based on observations made for 1- and 2- pentene, we would anticipate 1-hexene to have a greater SOA yield than 3-hexene, yet both species gave the SOA yield, within experimental error (3.0 (± 1.0)% for 1-hexene and 2.2 (± 1.6)% for 3-hexene). Reaction kinetics will be discussed in depth in the following sections, but it is worth noting that in addition to having an enhanced SOA yield, 3-hexene also has a much greater rate constant (k) than 1-hexene. It is possible that the kinetics of the 3-hexene ozonolysis reaction favour a pathway that leads to a greater degree of oligomerization and/or lower volatility products, ultimately leading to a greater SOA yield.

In the case of cycloalkenes, it has been shown that SOA yield increases with carbon number, with the number of endocyclic double bonds and with the presence of alkyl substitution at the double bond.^{9,10} One important trend that has not been explicitly reported in the literature is that of increasing SOA yield for cyclic alkenes as compared to their linear analogues. As shown in the abbreviated **Scheme 1**, the oxidative cleavage of linear alkenes produces several low molecular weight species that are expected to be found in the gas phase. The ozonolysis of cyclic alkenes, on the other hand, produces molecules with greater molecular weight and lower vapour

pressure, likely contributing to SOA more readily. Indeed, we observed an enhanced SOA yield for cyclopentene, cyclohexene and cycloheptene as compared to their linear analogs (Figure 2 and Table 1).

For unsubstituted C₅ – C₇ cyclic VOCs, we measured a SOA yield trend of cyclohexene < cyclopentene ≤ cycloheptene in contrast to the results of Keywood et al.,¹⁰ who found that SOA yield increased with carbon number for C₅-C₈ cycloalkenes. Although Keywood et al.¹⁰ worked at lower VOC concentrations and used ammonium sulfate seed particles, our yields for cyclohexene and cycloheptene are in good agreement with theirs. Our cyclopentene yield (19 ± 2.5%) however, was about twice that reported by Keywood et al.¹⁰ Again, it is worth noting that cyclopentene has the greatest rate constant (k) of these cyclic systems (See Table 2 and Section 3.2). It is possible that the enhanced k for cyclopentene contributes to its greater SOA yield. The reasons for the disparity between our measurements and those of Keywood et al.¹⁰ and for our deviation from the trend of increasing SOA yield with increasing carbon number are unclear.

Autoxidation reactions may also result in enhanced SOA yield. Autoxidation involves the incorporation of molecular oxygen into product structure after the initial oxidation by ozone and results in highly oxidized multifunction molecules (HOM) that contribute to SOA.⁴⁸⁻⁵³ It has been shown that cyclic alkenes undergo autoxidation more readily than their linear analogs,⁵³ which may contribute to the enhanced SOA yield we observed for cyclic vs linear alkenes. Autoxidation processes require available hydrogen atoms for H-shift rearrangements and is thus limited to ozonolysis intermediates with three or more carbon atoms,⁵³ which may contribute to our observation of equivalent yields for 1-hexene and 3-hexene. The ozonolysis of 1-hexene yields only one product that could undergo autoxidation while 3-hexene yields two. Without molecular-level characterization of resultant SOA, however, we cannot comment on the amount of HOM formed or the role of autoxidation in the formation of SOA herein. This additional analysis would be a logical next step in this research.

3.2 Ozonolysis rate constants (k) for linear and cyclic alkenes

Rate constants (k) for the ozonolysis of VOCs have been a predominant focus in the recent literature, especially with regard to the impact of VOC molecular structure.^{12,19,20,22,23,54,55} It is important, however, to distinguish between SOA yield (%Y) and reactivity (k), which are not *necessarily* related. As we show, a VOC may be highly reactive to atmospheric oxidants, yet contribute very little SOA or vice versa.

We also measured and compared the ozonolysis rate constants (k) of the alkenes in this study. A representative reaction profile for the ozonolysis of HXL is given in **Figure 3**. For linear alkenes, our results (**Figure 4, Table 2**) support previous observations that terminal alkenes have a reduced k compared to internal alkenes.^{20,22,54} This trend may be explained by the inductive effect, wherein substituents near the double bond increase electron density at the reaction center, promoting electrophilic addition of ozone across the double bond. Terminal alkenes, which contain alkyl substituents on only one side of the double bond, experience a lower inductive effect and a correspondingly reduced k as compared to internal alkenes, which are substituted on both sides. Steric effects also impact the kinetics of the ozonolysis of internal vs terminal alkenes, whereby the approaching ozone molecule has easier access to the terminal species, which would enhance k over the internally double bonded analog. However, the marked increase in k that we observe for 3-hexene compared to 1-hexene indicates that, overall, the steric hindrance encountered in 3-hexene is outweighed by the enhancement of k due to the inductive effect (at least for these relatively small alkenes).

The interplay between the inductive effect and steric hindrance can be better appreciated with the Arrhenius equation,

$$k = Ae^{\frac{-Ea}{RT}} \quad (2)$$

The pre-exponential factor, A, is inversely related to steric effects and thus directly proportional to k. Activation energy, Ea, is inversely related to both the inductive effect and to k.^{19,20,56-58}

An increase in chain length from C₃ to C₆ results in a decrease in both E_a and A⁵⁶ and ultimately results in an increase in k for ozonolysis. Lengthening the carbon backbone also increases steric hindrance, but not enough to overcome inductive effects or to limit k. McGillen et al.²⁰ experimentally confirmed that k increases with carbon number for 1-hexene and 1-pentene, yet their SAR-predicted rate constants were identical for 1-heptene, 1-hexene and 1-pentene. Our measured rate constants for 1-hexene and 1-pentene were equal within error, confirming the modelled behaviour predicted by McGillen et al.,²⁰ but not experimental data as reported by their group or by others.⁵⁶ The reasons for the discrepancy are not clear, but the inconsistencies between modelled and measured k further support our supposition that additional, unknown nuances in molecular structure may exist that result in profound impacts on atmospheric SOA formation and reactivity. As shown in Table 2, we measured k values on the same order of magnitude as those reported by others, with the exception of 2-pentene, which was approximately one order of magnitude smaller than that measured and predicted by McGillen et al.^{20,35} The methods they used to measure k were analogous to those used herein, so the reason for this disparity is not clear.

We found no correlation between k and ring size. However our observed order of cyclohexene < cycloheptene < cyclopentene, was in accord with previously reported data.^{57,59} These variations in k-values for cycloalkenes could be related to differences in ring strain energies⁶⁰ wherein the oxidative cleavage of an endocyclic double bond relieves ring strain in cyclic molecules. In cyclopentene, the transition between cycloalkene to ozonide alleviates a considerable amount of ring strain, strongly favouring the reaction, whereas cyclohexene contains relatively little strain energy, resulting in a moderate k.⁶¹ Cycloheptene has been shown to experience a similar ring strain as cyclopentene,⁶¹ which could rationalize the enhanced k for cycloheptene over cyclohexene.

Both cyclopentene and cycloheptene had a greater k than their linear (internal/terminal)

analogs, further supporting the theory ring strain is a significant driver in these reactions. However, we measured the same k (within experimental error) for cyclohexene and 3-hexene. This observation suggests that ring strain in cyclohexene is not sufficient to enhance ozonolysis kinetics. Cyclohexene did, however, show a much greater k than 1-hexene, pointing back to the importance of the inductive effect; cyclohexene is more substituted at the double bond (two effective alkyl substituents) than 1-hexene (1 alkyl substituent), increasing the inductive effect and the overall k . **3.2. SOA Yield for Oxygenated Linear Alkenes**

Despite extensive research to establish the SARs for ozonolysis of alkyl substituted linear alkenes, there has been a limited effort to understand the relationship between reactivity (k) or SOA yield and oxygenated substituents or their proximity to the double bond. To shed light on this knowledge gap, we measured the SOA yields and ozonolysis reaction rates of a series of C₅-C₇ linear, oxygenated alkenes (Table 1).

The SOA yield for 1-penten-3-ol (PTL) (3.3 ± 0.7 %) was greater than that measured for its non-oxygenated analog, 1-pentene (1.7 ± 0.2 %) ($\alpha = 0.05$). The ozonolysis of 1-pentene is expected to produce C₁ and C₄ products, which can undergo secondary oligomerization reactions (including hemi-acetal, aldol and ester condensation reactions) to form SOA. The ozonolysis of 1-PTL will produce the same C₁ products but its C₄ products will also contain an additional hydroxyl functionality, which (in addition to lowering the overall vapour pressure of the products) can undergo additional secondary reactions that are known to form SOA²⁸. Analogously, HXL ($6.5 \pm 2.6\%$) and HXNDL ($9.3 \pm 0.4\%$) have greater SOA yield than 3-hexene ($2.2 \pm 1.6\%$). CHA was found to have the same SOA yield as HXL ($3.9 \pm 2.4\%$) despite the fact that its methyl ester substituent shuts down the additional oligomerization pathway.²⁸ The reasons for this deviation from expected trends are unclear, but the large error associated with these measurements may be masking a general trend for HXL having a greater yield than CHA.

3.3 Ozonolysis Kinetics for Oxygenated Linear Alkenes

As stated above, electron donating substituents at the site of a double bond can promote the electrophilic addition of ozone, enhancing reactivity through the inductive effect.^{12,19,20,22,54} Hydroxyl groups are strongly electron donating and may therefore be predicted to enhance reactivity to an even greater degree than alkyl substituents. However, as we observed, HXNDL and HXL had *lower* reaction rates than their unsubstituted analogs. The hydroxyl substitution(s) at the beta (HXNDL) or gamma (HXL) position may be too distant from the double bond to enhance reactivity via the inductive effect, and actually seem to inhibit reactivity, likely due to steric interference. This interference is particularly strong for HXNDL, which has two hydroxyl groups in very close proximity to the double bond.

Analogous to the case of non-oxygenated alkenes, the reactivity of oxygenated molecules is a trade-off between both steric hindrance and inductive enhancement.^{19,20,22,54} Though it may seem intuitive, it has been well established that the steric effect diminishes with increasing distance from the reactive site.^{19,20,22,54,64} Aschmann and Atkinson²³ measured the steric effect for methyl-substituted alkenes and found no difference between that measured for 1-hexene and 5-methyl-1-hexene, yet as the methyl substituent moved closer to the double bond, steric effects increased, and the (NO₃) oxidation rate constant decreased, though the trend was not statistically significant. Since steric effects are expected to be more pronounced in ozone-alkene reactions than in corresponding NO₃-alkene reactions,²³ the trend in ozonolysis rate constant is expected to follow to a more significant degree. Based on our results, it appears that the steric hindrance provided by the hydroxyl substituents in HXL and HXNDL out-competes any reactivity enhancement they may contribute via the inductive effect, resulting in a lower ozonolysis rate constant as compared to 3-hexene.

Alternatively, we observed a slight enhancement in the ozonolysis rate constant for PTL as compared to 1-pentene, echoing results from O'Dwyer et al.,¹² and suggesting that the terminal position of the double bond in PTL offers sufficient room for an approaching ozone molecule so

the inductive effect associated with the hydroxyl substituent enhances reactivity overall. Using 3-methyl-1-pentene, we found a diminished k as compared to 1-pentene, suggesting that the methyl substituent provides significant steric hindrance to ozone to overcome any inductive enhancement it may also provide. 3-methyl-1-pentene has slightly less steric hindrance than PTL, suggesting that (if steric effects alone were considered) the methylated 1-pentene might have a greater k than PTL.^{19,20} However, we measure a much greater k for PTL than what has been reported for 3-methyl-1-pentene.^{19,20} Although steric hindrance due to the hydroxyl group is large for PTL, it enhances k overall as compared to the methylated analog due to the inductive effect.

Acetate esters are also electron donating, although not as strongly as hydroxyl groups, and would therefore be expected to enhance k . In fact, ester groups β to the alkene are predicted to enhance the inductive effect over unsubstituted alkenes by about 1.5 times.¹⁹ However, we found that CHA has a slightly (albeit not significantly) *smaller* rate constant than the 3-hexene. We would also expect CHA to have a smaller rate constant than HXL, since β -hydroxyl groups are estimated to increase the inductive effect over β -esters by a factor of about three.¹⁹ We also predict methyl esters to provide more steric hindrance than hydroxyl groups, which would also result in a smaller k . However, we observed a slightly greater k for CHA compared to HXL. Transition state theory could be used to shed further light on the factors affecting these systems. Nonetheless, our data clearly demonstrate that the presence, position and identity of substituents are all key to predict ozonolysis reaction kinetics.

4.0 Atmospheric Implications

The marked disparity between predicted SOA mass loadings and those measured in the field highlights the need for more accurate representation of the molecular level interactions between VOCs and oxidants. Some SARs have been shown to match chamber studies well,^{19,20,54} but chamber studies rarely match atmospheric conditions (with chamber studies working at unrealistically high VOC concentrations and mass loadings) and experimental results are often

irreproducible between (and even within) laboratories.^{10,65} We recently reported the SOA yield of several green leaf volatiles using an experimental design analogous to that used by Hamilton et al.,⁶⁶ yet measured very different SOA yields with a high degree of uncertainty.²⁷ Keywood et al.¹⁰ also demonstrated the large degree of variability in making SOA yield measurements, reporting yields ranging from 0% to 19% for a single VOC in a single laboratory. Herein, we also report rather large ranges in SOA yield for replicate experiments (between 5% and 75% relative error). The reasons for the disparity in yield measurements made for the same chemical systems under the same nominal conditions are unclear, but there is growing evidence to suggest that inconsistencies in the instrumental parameters used by different laboratories play a role.⁶⁷ For a laboratory where instrumental parameters are not a variable, like ours for example, differences in SOA mass measurements may suggest a degree of chaos during the initial reaction steps that have yet to be understood, making them all but impossible to predict or model.

We have shown that the mechanisms and product yields of VOC oxidation are impacted by subtleties in molecular structure. Due to computational costs and limited kinetic data available, these relationships are not always incorporated into atmospheric models. We have shown that both the aerosol yield and the rate constant of structural isomers (cyclic vs linear, internally unsaturated vs terminally unsaturated and presence, type and position of substituents) vary significantly. It is in these seemingly minor (and rarely considered) molecular variations where error can be born, which can then be extrapolated in models and may result in the large disparities between modelled and measured atmospheric aerosol levels and properties. Ultimately, advances in computing power and our state of knowledge will permit models to evolve to incorporate much of this nuanced chemistry. Until such time, we offer this glimpse of the dramatic impact of seemingly small variations in molecular structure on reactivity and SOA formation. These initial steps will serve to further inform the atmospheric chemistry community on considerations that must be taken in order to harmonize laboratory findings with field studies

and model outputs.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. CHE-1213632.

References

- (1) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T. F.; Monod, A.; Prévôt, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. *Atmos. Chem. Phys.* **2009**, *9*, 5155.
- (2) Ng, N. L.; Kroll, J. H.; Keywood, M. D.; Bahreini, R.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H.; Lee, A.; Goldstein, A. H. *Environ Sci Technol* **2006**, *40*, 2283.
- (3) Lee, J. D.; Lewis, A. C.; Monks, P. S.; Jacob, M.; Hamilton, J. F.; Hopkins, J. R.; Watson, N. M.; Saxton, J. E.; Ennis, C.; Carpenter, L. J.; Carslaw, N.; Fleming, Z.; Bandy, B. J.; Oram, D. E.; Penkett, S. A.; Slemr, J.; Norton, E.; Rickard, A. R.; Whalley, L. K.; Heard, D. E.; Bloss, W. J.; Gravesstock, T.; Smith, S. C.; Stanton, J.; Pilling, M. J.; Jenkin, M. E. *Atmos Environ* **2006**, *40*, 7598.
- (4) Heald, C. L.; Jacob, D. J.; Park, R. J.; Russell, L. M.; Huebert, B. J.; Seinfeld, J. H.; Liao, H.; Weber, R. J. *Geophysical Research Letters* **2005**, *32*, L18809.
- (5) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. *Atmos. Chem. Phys.* **2005**, *5*, 1053.
- (6) Jo, D. S.; Park, R. J.; Kim, M. J.; Spracklen, D. V. *Atmos Environ* **2013**, *81*, 230.
- (7) Goldstein, A. H.; Galbally, I. E. *Environ Sci Technol* **2007**, *41*, 1514.
- (8) Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. *Atmos. Chem. Phys.* **2009**, *9*, 4987.
- (9) Lee, A.; Goldstein, A. H.; Keywood, M. D.; Gao, S.; Varutbangkul, V.; Bahreini, R.; Ng, N. L.; Flagan, R. C.; Seinfeld, J. H. *Journal of Geophysical Research: Atmospheres* **2006**, *111*, D07302.
- (10) Keywood, M. D.; Varutbangkul, V.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H. *Environ Sci Technol* **2004**, *38*, 4157.
- (11) Kroll, J. H.; Seinfeld, J. H. *Atmos Environ* **2008**, *42*, 3593.
- (12) O'Dwyer, M. A.; Carey, T. J.; Healy, R. M.; Wenger, J. C.; Picquet-Varrault, B.; Doussin, J. F. *Z Phys Chem* **2010**, *224*, 1059.
- (13) Loza, C. L.; Craven, J. S.; Yee, L. D.; Coggon, M. M.; Schwantes, R. H.; Shiraiwa, M.; Zhang, X.; Schilling, K. A.; Ng, N. L.; Canagaratna, M. R.; Ziemann, P. J.; Flagan, R. C.; Seinfeld, J. H. *Atmos. Chem. Phys.* **2014**, *14*, 1423.

- (14) Tkacik, D. S.; Presto, A. A.; Donahue, N. M.; Robinson, A. L. *Environ Sci Technol***2012**, 46, 8773.
- (15) Atkinson, R.; Arey, J.; Aschmann, S. M.; Corchnoy, S. B.; Shu, Y. *Int J Chem Kinet***1995**, 27, 941.
- (16) Khamaganov, V. G.; Hites, R. A. *The Journal of Physical Chemistry A***2001**, 105, 815.
- (17) Papagni, C.; Arey, J.; Atkinson, R. *Int J Chem Kinet***2001**, 33, 142.
- (18) Cusick, R. D.; Atkinson, R. *Int J Chem Kinet***2005**, 37, 183.
- (19) McGillen, M. R.; Archibald, A. T.; Carey, T.; Leather, K. E.; Shallcross, D. E.; Wenger, J. C.; Percival, C. J. *Phys Chem Chem Phys***2011**, 13, 2842.
- (20) McGillen, M. R.; Carey, T. J.; Archibald, A. T.; Wenger, J. C.; Shallcross, D. E.; Percival, C. J. *Phys Chem Chem Phys***2008**, 10, 1757.
- (21) Pfrang, C.; King, M. D.; Canosa-Mas, C. E.; Wayne, R. P. *Atmos Environ***2006**, 40, 1180.
- (22) McGillen, M. R.; Crosier, J.; Percival, C. J.; Sanchez-Reyna, G.; Shallcross, D. E. *Chemosphere***2006**, 65, 2035.
- (23) Aschmann, S. M.; Atkinson, R. *The Journal of Physical Chemistry A***2011**, 115, 1358.
- (24) Lim, Y. B.; Ziemann, P. J. *Environ Sci Technol***2009**, 43, 2328.
- (25) Aumont, B.; Camredon, M.; Mouchel-Vallon, C.; La, S.; Ouzebidour, F.; Valorso, R.; Lee-Taylor, J.; Madronich, S. *Faraday Discuss***2013**, 165, 105.
- (26) Yee, L. D.; Craven, J. S.; Loza, C. L.; Schilling, K. A.; Ng, N. L.; Canagaratna, M. R.; Ziemann, P. J.; Flagan, R. C.; Seinfeld, J. H. *Atmos. Chem. Phys. Discuss.***2013**, 13, 10859.
- (27) Harvey, R. M.; Zahardis, J.; Petrucci, G. A. *Atmos. Chem. Phys.***2014**, 14, 797.
- (28) Jain, S.; Zahardis, J.; Petrucci, G. A. *Environ Sci Technol***2014**.
- (29) Boyd, A. A.; Villenave, E.; Lesclaux, R. *Atmos Environ***2003**, 37, 2751.
- (30) Peeters, J.; Boullart, W.; Pultau, V.; Vandenberg, S.; Vereecken, L. *J Phys Chem A***2007**, 111, 1618.
- (31) Peeters, J.; Boullart, W.; Pultau, V.; Vandenberg, S.; Vereecken, L. *The Journal of Physical Chemistry A***2007**, 111, 1618.
- (32) Al Mulla, I.; Viera, L.; Morris, R.; Sidebottom, H.; Treacy, J.; Mellouki, A. *Chemphyschem***2010**, 11, 4069.
- (33) Vereecken, L.; Francisco, J. S. *Chem Soc Rev***2012**, 41, 6259.
- (34) Stewart, D. J.; Altabrok, S. H.; Lockhart, J. P.; Mohamed, O. M.; Nutt, D. R.; Pfrang, C.; Marston, G. *Atmos Environ***2013**, 70, 227.
- (35) Agency, U. S. E. P.; 4.11 ed. Washington DC, USA, 2014.
- (36) Grosjean, E.; Grosjean, D. *Int J Chem Kinet***1994**, 26, 1185.
- (37) Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. *Environ Sci Technol***1996**, 30, 2580.
- (38) Epstein, S. A.; Donahue, N. M. *The Journal of Physical Chemistry A***2010**, 114, 7509.
- (39) Gao, S.; Keywood, M.; Ng, N. L.; Surratt, J.; Varutbangkul, V.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H. *The Journal of Physical Chemistry A***2004**, 108, 10147.
- (40) Jathar, S. H.; Miracolo, M. A.; Tkacik, D. S.; Donahue, N. M.; Adams, P. J.; Robinson, A. L. *Environ Sci Technol***2013**, 47, 12886.
- (41) Atkinson, R.; Arey, J. *Chem Rev***2003**, 103, 4605.
- (42) Zahardis, J.; Petrucci, G. A. *Atmos. Chem. Phys.***2007**, 7, 1237.
- (43) Tolocka, M. P.; Jang, M.; Ginter, J. M.; Cox, F. J.; Kamens, R. M.; Johnston, M. V. *Environ Sci Technol***2004**, 38, 1428.
- (44) Sakamoto, Y.; Inomata, S.; Hirokawa, J. *The Journal of Physical Chemistry A***2013**, 117, 12912.

- (45) Sadezky, A.; Chaimbault, P.; Mellouki, A.; Römp, A.; Winterhalter, R.; Le Bras, G.; Moortgat, G. K. *Atmos. Chem. Phys.* **2006**, *6*, 5009.
- (46) Sadezky, A.; Winterhalter, R.; Kanawati, B.; Römp, A.; Spengler, B.; Mellouki, A.; Le Bras, G.; Chaimbault, P.; Moortgat, G. K. *Atmos. Chem. Phys.* **2008**, *8*, 2667.
- (47) Donahue, N. M.; Drozd, G. T.; Epstein, S. A.; Presto, A. A.; Kroll, J. H. *Phys Chem Chem Phys* **2011**, *13*, 10848.
- (48) Ehn, M.; Kleist, E.; Junninen, H.; Petäjä, T.; Lönn, G.; Schobesberger, S.; Dal Maso, M.; Trimborn, A.; Kulmala, M.; Worsnop, D. R.; Wahner, A.; Wildt, J.; Mentel, T. F. *Atmos. Chem. Phys.* **2012**, *12*, 5113.
- (49) Crounse, J. D.; Nielsen, L. B.; Jørgensen, S.; Kjaergaard, H. G.; Wennberg, P. O. *The Journal of Physical Chemistry Letters* **2013**, *4*, 3513.
- (50) Jokinen, T.; Sipilä, M.; Richters, S.; Kerminen, V.-M.; Paasonen, P.; Stratmann, F.; Worsnop, D.; Kulmala, M.; Ehn, M.; Herrmann, H.; Berndt, T. *Angewandte Chemie International Edition* **2014**, *53*, 14596.
- (51) Rissanen, M. P.; Kurtén, T.; Sipilä, M.; Thornton, J. A.; Kangasluoma, J.; Sarnela, N.; Junninen, H.; Jørgensen, S.; Schallhart, S.; Kajos, M. K.; Taipale, R.; Springer, M.; Mentel, T. F.; Ruuskanen, T.; Petäjä, T.; Worsnop, D. R.; Kjaergaard, H. G.; Ehn, M. *J Am Chem Soc* **2014**, *136*, 15596.
- (52) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I.-H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurten, T.; Nielsen, L. B.; Jørgensen, S.; Kjaergaard, H. G.; Canagaratna, M.; Maso, M. D.; Berndt, T.; Petaja, T.; Wahner, A.; Kerminen, V.-M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.; Mentel, T. F. *Nature* **2014**, *506*, 476.
- (53) Mentel, T. F.; Springer, M.; Ehn, M.; Kleist, E.; Pullinen, I.; Kurtén, T.; Rissanen, M.; Wahner, A.; Wildt, J. *Atmos. Chem. Phys.* **2015**, *15*, 6745.
- (54) McGillen, M. R.; Ghalaieny, M.; Percival, C. J. *Phys Chem Chem Phys* **2011**, *13*, 10965.
- (55) Johnson, D.; Rickard, A. R.; McGill, C. D.; Marston, G. *Phys Chem Chem Phys* **2000**, *2*, 323.
- (56) Treacy, J.; Elhag, M.; Ofarrell, D.; Sidebottom, H. *Ber Bunsen Phys Chem* **1992**, *96*, 422.
- (57) Treacy, J.; Curley, M.; Wenger, J.; Sidebottom, H. *Journal of the Chemical Society, Faraday Transactions* **1997**, *93*, 2877.
- (58) Leather, K. E.; McGillen, M. R.; Percival, C. J. *Phys Chem Chem Phys* **2010**, *12*, 2935.
- (59) Sidebottom, H.; Tracy, J. In *Chemical Processes in Atmospheric Oxidation*; Le Bras, G., Ed.; Springer Berlin Heidelberg: 1997; Vol. 3, p 218.
- (60) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Pitts, J. N. *Int J Chem Kinet* **1983**, *15*, 721.
- (61) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1966.
- (62) Greene, C. R.; Atkinson, R. *Int J Chem Kinet* **1992**, *24*, 803.
- (63) Kirstine, W. V.; Galbally, I. E. *J Air Waste Manage* **2004**, *54*, 1299.
- (64) Taft, R. *Steric Effects in Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1956.
- (65) Bahreini, R.; Ervens, B.; Middlebrook, A. M.; Warneke, C.; de Gouw, J. A.; DeCarlo, P. F.; Jimenez, J. L.; Brock, C. A.; Neuman, J. A.; Ryerson, T. B.; Stark, H.; Atlas, E.; Brioude, J.; Fried, A.; Holloway, J. S.; Peischl, J.; Richter, D.; Walega, J.; Weibring, P.; Wollny, A. G.; Fehsenfeld, F. C. *J Geophys Res-Atmos* **2009**, *114*.
- (66) Hamilton, J. F.; Lewis, A. C.; Carey, T. J.; Wenger, J. C.; Borrás i Garcia, E.; Muñoz, A. *Atmos. Chem. Phys.* **2009**, *9*, 3815.

(67) Wiedensohler, A.; Birmili, W.; Nowak, A.; Sonntag, A.; Weinhold, K.; Merkel, M.; Wehner, B.; Tuch, T.; Pfeifer, S.; Fiebig, M.; Fjåraa, A. M.; Asmi, E.; Sellegri, K.; Depuy, R.; Venzac, H.; Villani, P.; Laj, P.; Aalto, P.; Ogren, J. A.; Swietlicki, E.; Williams, P.; Roldin, P.; Quincey, P.; Hüglin, C.; Fierz-Schmidhauser, R.; Gysel, M.; Weingartner, E.; Riccobono, F.; Santos, S.; Gruning, C.; Faloon, K.; Beddows, D.; Harrison, R.; Monahan, C.; Jennings, S. G.; O'Dowd, C. D.; Marinoni, A.; Horn, H. G.; Keck, L.; Jiang, J.; Scheckman, J.; McMurry, P. H.; Deng, Z.; Zhao, C. S.; Moerman, M.; Henzing, B.; de Leeuw, G.; Löschau, G.; Bastian, S. *Atmos. Meas. Tech.* **2012**, *5*, 657.

Figure Captions:

Figure 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.

Figure 2. SOA Yield of C₅-C₇ linear and cycloalkenes. In all cases, the cycloalkene has a greater SOA yield than its linear analog. Terminally unsaturated alkenes showed an enhanced SOA yield over internal, linear alkenes.

Figure 3. A representative reaction profile for the ozonolysis of HXL used to determine the rate constant *k*. In all rate experiments, ozone decay was measured in the presence of at least a 10-fold excess of VOC (to ensure pseudo-first order conditions). Although SOA mass distribution was monitored, these experiments were not used to determine SOA yield because they contained such a large excess of VOC.

Figure 4. Plots of $\ln([O_3]_0/[O_3]_t)$ vs time yielded a linear decay, confirming reactions were pseudo-first order for the VOC. *k'* (sec⁻¹) for the ozonolysis of each alkene was found from the slope of the linear regression, which is given in Supplemental Material S3.

Scheme 1. Abbreviated ozonolysis schemes for cyclic and linear C₆ alkenes, showing the formation of higher volatility products in the linear case, which leads to lower SOA yields, especially for internal, linear alkenes.

Table 1. SOA yield of linear, cyclic and oxygenated alkenes. Initial concentrations of the parent hydrocarbon and ozone in each experiment were 1000 ± 100 ppbv. N=3 for all reported values.

Table 2. Ozonolysis rate constants (*k*, $\times 10^{-17}$ cm³ sec⁻¹ molecule⁻¹) of alkenes are reported $\pm$ the standard deviation of replicate experiments. Individual experimental conditions can be found in Table S2 of the Supplemental Material (* indicates a predicted/modelled value). N = 3 for all reported values.

Table 1

Chemical System	SOA % Yield (average ± standard deviation)
1-pentene	1.77 ± 0.22
2-pentene	0.79 ± 0.57
PTL	3.28 ± 0.7
cyclopentene	19 ± 2.5
3-hexene	2.17 ± 1.6
1-hexene	3.0 ± 1.0
cyclohexene	15.7 ± 0.8
CHA	3.9 ± 2.4
HXL	6.5 ± 2.6
HXNDL	9.3 ± 0.4
3-heptene	3.9 ± 1.6
cycloheptene	22.4 ± 5.4

Table 2

Table 2. Ozonolysis rate constants (k , $\times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ molecule}^{-1}$) of alkenes are reported $\pm$ the standard deviation of replicate experiments. Individual experimental conditions can be found in Table S2 of the Supplemental Material (* indicates a predicted/modelled value). $N = 3$ for all reported values.

VOC	k	Reference	VOC	k	Reference
1-pentene-3-ol (PTL)	1.7 ± 0.1	This work	3-hexene	5.9 ± 0.5	This work
	1.64	12		15.0	36
	1.79	36		14.4	20
1-pentene	1.2 ± 0.4	This work		12.2	20*
	0.92	56	cyclohexene	6.8 ± 0.1	This work
	0.99	58		7.00	62
	1.20	35		8.50	57
	0.753	20*		7.90	41

2-pentene	1.7 ± 0.9	This work	cis-3-hexenol (HXL)	5.8 ± 0.9	This work
cis-2-pentene	13.0	35		10.5	36
	20.9	20		6.14	15
trans-2-pentene	20.0	35		6.47	63
	31.6	20	cis-3-hexenyl acetate (CHA)	5.8 ± 0.1	This work
cyclopentene	24 ± 11	This work		5.40	15
	20.0	35		5.90	62
	61.0	62	hex-3-ene-2,5-diol (HXNDL)	0.9 ± 0.8	This work
	67	41	3-heptene	6.6 ± 0.3	This work
1-hexene	1.4 ± 0.3	This work	cycloheptene	12.8 ± 4.6	This work
	1.42	58		22.6	62
	1.01	20		23.7	57

Figure 1

Figure 2

Figure 3

Figure 4