ABSTRACT

SUDA, SARAH RAVENEL. Hygroscopicity Frequency Distributions of Secondary Organic Aerosols. (Under the direction of Markus D. Petters).

Atmospheric aerosol particles contribute to climate by changing the reflectivity and lifetime of clouds. An appreciable fraction of global ambient aerosol is secondary organic aerosol (SOA), which forms in the troposphere as a product of organic vapor oxidation. This study investigates the hygroscopicity of SOA as part of an ongoing effort to reduce uncertainty in the mechanisms and magnitude of the climatic effect of aerosol-cloud interaction. SOA was generated in an environmental chamber by the reaction of 24 different combinations of organic precursors and atmospheric oxidants. Cloud condensation nuclei (CCN) properties were measured for SOA generated inside a smog chamber. Filter samples from each experiment were chemically separated by high precision liquid chromatography, and CCN properties were measured for eluting compounds using a fast scanning method implemented for this study. The hygroscopicity parameter, κ , was calculated for each scan of the eluting material. Measured κ -values were matched with the quantity of simultaneously eluting material to show the underlying volume-weighted κ distribution for each sample. The κ -values of the constituent compounds in the SOA mixture varied more than the κ -values found for the samples measured online with the chamber reactions, showing that the overall κ -value is less sensitive to precursor composition than are the individual κ -values constituting the mixture. The volume-weighted average κ -values compared favorably to the online κ measurements. A number of targeted experiments were designed to examine the

change in the hygroscopicity distribution with the chemical reaction mechanisms. Observed shifts in the distribution were attributable to changes in the expected chemistry of aerosol formation, demonstrating the method's utility for studying chemical mechanisms.

Hygroscopicity Frequency Distributions of Secondary Organic Aerosols

by
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DEDICATION

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BIOGRAPHY

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TABLE OF CONTENTS

	<u>page</u>
LIST OF TABLES.....	viii
LIST OF FIGURES.....	xi
1. INTRODUCTION.....	1
1.1 Background.....	1
1.2 Objectives.....	2
1.3 References.....	3
2. LITERATURE REVIEW.....	6
2.1 Chemistry of secondary organic aerosol formation.....	6
2.2 Review of oxidation experiments conducted in environmental chambers.....	10
2.3 References.....	14
3. CLOUD CONDENSATION NUCLEI.....	18
3.1 CCN efficiency of aerosol.....	18
3.2 The effect of varying reaction conditions on aerosol hygroscopicity.....	23
3.3 Methods used in this study.....	29
3.4 References.....	29
3.5 Figures.....	33
4. A PAPER FOR JOURNAL SUBMISSION.....	35
Abstract.....	36
4.1 Introduction.....	37
4.2 Methods.....	40

	<u>page</u>
4.2.1 Köhler Theory.....	40
4.2.2 SOA generation.....	41
4.2.3 Measurement of CCN efficiency of total SOA.....	44
4.2.4 Measurement of CCN efficiency of HPLC-fractionated SOA.....	45
Generation of HPLC-fractionated SOA particles.....	45
Scanning flow cycle.....	46
Time series processing.....	46
Flow-to-supersaturation calibration.....	47
Envelope of resolvable κ -values.....	48
Reconstructing the κ -value of total SOA from component κ -values.....	48
Uncertainties and reproducibility of individual κ measurements.....	51
4.3 Results and discussion.....	52
4.4 Summary and conclusions.....	58
4.5 Acknowledgments.....	61
4.6 References.....	61
4.7 Figures.....	67
4.8 Tables.....	77
5. SUMMARY.....	78
5.1 References.....	80
APPENDICES.....	81
APPENDIX A: Tabulated results.....	82
APPENDIX B: Chromatograms for HPLC experiment pairs.....	135

	<u>page</u>
APPENDIX C: Chromatograms for individual HPLC experiments.....	143
APPENDIX D: Atomized droplet size distribution.....	155

LIST OF TABLES

Table		page
Table 4.1	Summary of oxidation reactions performed. The number in column 1 is an identifier for experiments shown in Figure 4.8. V_{chamber} denotes the volume of the chamber used for the experiment.....	77
Table A.1a	1-Decene + O_3 : Detailed CN count for each particle dry diameter measured. CN at D_{ref} is calculated using Equation 4.6 with an exponential slope parameter $G = -2$. The number fraction is calculated including CN counted between flow scans, and the adjusted fraction excludes the first scan. The average κ calculation is shown in the corresponding table below (part b).....	82
Table A.1b	1-Decene + O_3 : Detailed κ measurements for each upscan and downscan, for each dry particle diameter. Each upscan and downscan produces a D_d - S_c data pair from which κ_{orig} is calculated. The critical supersaturation, s_c , is defined as $(S_c - 1) \times 100$. The final κ -value (κ_{final}) is adjusted based on the envelope of measurable κ -values. Values above the κ envelope are discarded, and values below the envelope are set to the envelope lower bound.....	84
Table A.2a	Ocimene + NO_3 : Similar to Table A.1a.....	85
Table A.2b	Ocimene + NO_3 : Similar to Table A.1b.....	86
Table A.3a	1,3-Cyclohexadiene + NO_3 : Similar to Table A.1a.....	87
Table A.3b	1,3-Cyclohexadiene + NO_3 : Similar to Table A.1b.....	88
Table A.4a	1,5-Cyclooctadiene + NO_3 A: Similar to Table A.1a.....	89
Table A.4b	1,5-Cyclooctadiene + NO_3 A: Similar to Table A.1b.....	90
Table A.5a	1,3,5,7-Cyclooctatetraene + NO_3 : Similar to Table A.1a.....	91
Table A.5b	1,3,5,7-Cyclooctatetraene + NO_3 : Similar to Table A.1b.....	92
Table A.6a	1,5-Cyclooctadiene + NO_3 B: Similar to Table A.1a.....	93
Table A.6b	1,5-Cyclooctadiene + NO_3 B: Similar to Table A.1b.....	94

<u>Table</u>		<u>page</u>
Table A.7a	Methyl furan + OH with NO _x : Similar to Table A.1a.....	95
Table A.7b	Methyl furan + OH with NO _x : Similar to Table A.1b.....	96
Table A.8a	1-Decene + O ₃ , RH 82%: Similar to Table A.1a.....	97
Table A.8b	1-Decene + O ₃ , RH 82%: Similar to Table A.1b.....	98
Table A.9a	<i>n</i> -Pentadecane + Cl (9 July A): Similar to Table A.1a.....	99
Table A.9b	<i>n</i> -Pentadecane + Cl (9 July A): Similar to Table A.1b.....	100
Table A.10a	<i>n</i> -Pentadecane + Cl (9 July B): Similar to Table A.1a.....	101
Table A.10b	<i>n</i> -Pentadecane + Cl (9 July B): Similar to Table A.1b.....	102
Table A.11a	<i>n</i> -Decane + Cl, 1 st irradiation: Similar to Table A.1a.....	103
Table A.11b	<i>n</i> -Decane + Cl, 1 st irradiation: Similar to Table A.1b.....	104
Table A.12a	<i>n</i> -Pentadecane + Cl (13 July): Similar to Table A.1a.....	105
Table A.12b	<i>n</i> -Pentadecane + Cl (13 July): Similar to Table A.1b.....	106
Table A.13a	<i>n</i> -Pentadecane + Cl (16 July B): Similar to Table A.1a.....	107
Table A.13b	<i>n</i> -Pentadecane + Cl (16 July B): Similar to Table A.1b.....	108
Table A.14a	Cyclodecane + OH with NO _x : Similar to Table A.1a.....	109
Table A.14b	Cyclodecane + OH with NO _x : Similar to Table A.1b.....	110
Table A.15a	<i>n</i> -Pentadecane + Cl (16 July A): Similar to Table A.1a.....	111
Table A.15b	<i>n</i> -Pentadecane + Cl (16 July A): Similar to Table A.1b.....	112
Table A.16a	1-Octene + O ₃ : Similar to Table A.1a.....	113
Table A.16b	1-Octene + O ₃ : Similar to Table A.1b.....	114
Table A.17a	<i>n</i> -Pentadecane + Cl (8 July B): Similar to Table A.1a.....	115
Table A.17b	<i>n</i> -Pentadecane + Cl (8 July B): Similar to Table A.1b.....	116

<u>Table</u>		<u>page</u>
Table A.18a	<i>n</i> -Pentadecane + Cl (8 July A): Similar to Table A.1a.....	117
Table A.18b	<i>n</i> -Pentadecane + Cl (8 July A): Similar to Table A.1b.....	118
Table A.19a	<i>m</i> -Xylene + OH with NO _x : Similar to Table A.1a.....	119
Table A.19b	<i>m</i> -Xylene + OH with NO _x : Similar to Table A.1b.....	120
Table A.20a	1,2-Dimethyl cyclohexene + O ₃ : Similar to Table A.1a.....	121
Table A.20b	1,2-Dimethyl cyclohexene + O ₃ : Similar to Table A.1b.....	122
Table A.21a	<i>n</i> -Decane + Cl, 2 nd irradiation: Similar to Table A.1a.....	123
Table A.21b	<i>n</i> -Decane + Cl, 2 nd irradiation: Similar to Table A.1b.....	124
Table A.22a	Cyclooctene + O ₃ : Similar to Table A.1a.....	125
Table A.22b	Cyclooctene + O ₃ : Similar to Table A.1b.....	126
Table A.23a	Cyclohexene + O ₃ : Similar to Table A.1a.....	127
Table A.23b	Cyclohexene + O ₃ : Similar to Table A.1b.....	128
Table A.24a	Cyclooctane + OH without NO _x : Similar to Table A.1a.....	129
Table A.24b	Cyclooctane + OH without NO _x : Similar to Table A.1b.....	130
Table A.25a	α -Pinene + O ₃ A: Similar to Table A.1a. This experiment was excluded from the study (see Figure B.7).....	131
Table A.25b	α -Pinene + O ₃ A: Similar to Table A.1b. This experiment was excluded from the study (see Figure B.7).....	132
Table A.26a	α -Pinene + O ₃ B: Similar to Table A.1a. This experiment was excluded from the study (see Figure B.7).....	133
Table A.26b	α -Pinene + O ₃ B: Similar to Table A.1b. This experiment was excluded from the study (see Figure B.7).....	134

LIST OF FIGURES

<u>Figure</u>		<u>page</u>
Figure 3.1	The Köhler equation, plotted for a droplet of variable diameter in an environment of variable water vapor pressure. The dissolved solute is constant and equivalent to a dry particle of diameter D_d . Plot a: the equilibrium droplet size as a function of the ambient molecular flux of water to the droplet (bottom axis), or as a function of the ambient saturation ratio (top axis). Molecular flux is proportional to vapor pressure. Dissolved solute is held constant and is equivalent to $D_d = 50$ nm for both sodium chloride (NaCl) and ammonium sulfate ((NH ₃) ₂ SO ₄). Dotted lines indicate regions of unstable equilibrium. Droplets whose sizes are not in equilibrium with ambient conditions at points <i>a</i> and <i>d</i> will evaporate until reaching equilibrium; droplets at points <i>b</i> will grow until reaching equilibrium; and droplets at points <i>c</i> and <i>e</i> will grow indefinitely. In the upper righthand corner is indicated the range in saturation ratio achievable by the measurement setup used in this study. Plot b: the classical representation of the Köhler curve, showing the molecular flux of water molecules evaporating from a droplet as a function of the droplet diameter. The dissolved solute, (NH ₃) ₂ SO ₄ , is equivalent to $D_d = 10, 50$ and 100 nm.....	33
Figure 4.1	Schematic of the instrument setup.....	67
Figure 4.2	Left plot: example duty cycle illustrating the flow rate (grey line), CCN (solid black line) and CN (dashed line) time series. Right plot: Inferred CCN activation curve for the upscan (black circles) and downscan (red circles). Each circle represents a 4 s average. Lines represent a fit to the data from which the flow at 50% activation is inferred.....	68
Figure 4.3	Relationship between CCNC flow rate at 50% activated fraction and calculated supersaturation percent for size selected ammonium sulfate particles.....	69
Figure 4.4	Size distribution of particles from the HPLC CCN measurement system for SOA from an <i>n</i> -pentadecane + Cl experiment, as measured by the online CCN measurement setup. Times reported are the start times for the 11 min scans. The stepped lines show the measured size distribution over the scan, and the dotted lines show a fit to the data. The integrated total count over the fit, N_{tot} , the mode diameter, D , and the standard deviation, σ , are noted in a table below the distributions	70

<u>Figure</u>		<u>page</u>
Figure 4.5	CN (black lines) and CCN (grey lines) concentrations vs. HPLC retention time, for the SOA from 1,5-cyclooctadiene + NO ₃ A (top) and B (middle) using the same filter extract. Bottom timeseries: κ -values (symbols) and envelope of measurable κ -values (grey lines) vs. HPLC retention time for 1,5-cyclooctadiene + NO ₃ A (circles) and B (triangles). The selected dry diameter is indicated below the symbols. Scan A was terminated prematurely due to erroneous software settings.....	71
Figure 4.6	Kappa frequency distributions of pairs of repeated HPLC experiments using the same filter extract. Experiment A in the pair is in the first row, and experiment B is in the second row. The oxidant:precursor ratio for each pentadecane + Cl chamber experiment is indicated on the plot as Cl : C ₁₅ . The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value.....	72
Figure 4.7	The HPLC eluate hygroscopicities for all experiments as a function of their retention time.....	73
Figure 4.8	Kappa frequency distributions of selected SOA systems. The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value.....	74
Figure 4.9	Scatter plot of reconstructed HPLC eluate κ -values versus κ -values measured for SOA sampled directly from the chamber. The 1:1 line is printed in grey behind the data. Numbers on the graph correspond to the experiment number given in Table 4.1. Horizontal bars indicate the sensitivity of the HPLC κ -value to the choice of exponent G in the size correction. Vertical bars indicate the uncertainty in the online κ -value determined from the reproducibility of the calibration.....	75
Figure 4.10	Kappa frequency distributions of SOA from the 1-decene + O ₃ and <i>n</i> -decane + Cl chamber experiments. The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value....	76
Figure B.1	1,5-Cyclooctadiene + NO ₃ : timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). Two HPLC experiments, A and B, were performed for the same filter extract. The bottom plot shows measured κ -values (circle for experiment A, triangle for experiment B) and the envelope of measureable κ -values during the experiments (dotted lines; lavender for experiment A, grey for experiment B). The particle dry diameter is noted below the symbol for each κ -value...	135

<u>Figure</u>		<u>page</u>
Figure B.2	<i>n</i> -Pentadecane + Cl (8 July): similar to Figure B.1. The ratio of Cl atoms to <i>n</i> -pentadecane molecules determines the extent of oxidation.....	136
Figure B.3	<i>n</i> -Pentadecane + Cl (9 July): timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). Two HPLC experiments, A and B, were performed for the same filter extract. The bottom plot shows measured κ -values (circle for experiment A, triangle for experiment B) and the envelope of measureable κ -values during the experiments (dotted lines; lavender for experiment A, grey for experiment B). The particle dry diameter is centered above (experiment B) or below (experiment A) the set of κ envelopes associated with each upscan-downscan cycle. The ratio of Cl atoms to <i>n</i> -pentadecane molecules determines the extent of oxidation.....	137
Figure B.4	<i>n</i> -Pentadecane + Cl (16 July): similar to Figure B.3.....	138
Figure B.5	1-Decene + O ₃ : timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (first and third plots). The second and fourth plots show measured κ -values (circle for RH = 20%, triangle for RH = 82%) and the envelope of measureable κ -values during the experiments (dotted lines). The particle dry diameter is noted near the symbol for each κ -value. The fifth plot shows a comparison between both experiments of the timeseries of κ -values (circle for RH = 20%, triangle for RH = 82%). Two experiments were performed for the 1-decene + O ₃ system with different relative humidity present during the chamber reaction.....	139
Figure B.6	<i>n</i> -Decane + Cl: similar to Figure B.5. The <i>n</i> -decane + Cl system was irradiated twice, and a filter sample was taken after each irradiation.....	141
Figure B.7	α -Pinene + O ₃ : similar to Figure B.5. Two HPLC experiments, A and B, were performed for the same filter extract. This data was excluded from the study – some of the CCN measured in experiment A seem to be multiply charged particles, which are larger than the prescribed D_d and thus would be expected to have a higher κ -value. The κ -value was lower for experiment A than for experiment B, throughout all retention times, despite multiply charged particles. Experiment A was the first experiment performed during the study.....	142

<u>Figure</u>	<u>page</u>
Figure C.1 1,2-Dimethyl cyclohexene + O ₃ : timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). The bottom plot shows measured κ -values and the envelope of measureable κ -values during the experiments (dotted lines). The particle dry diameter is noted above the symbol for each κ -value. The fraction of total eluting material is plotted vs. its associated κ -value, for each dry diameter measured (inset bar plot). The volume-weighted average κ -value is noted above the bars....	143
Figure C.2 1,3,5,7-Cyclooctatetraene + NO ₃ : similar to Figure C.1.....	144
Figure C.3 1,3-Cyclohexadiene + NO ₃ : similar to Figure C.1.....	145
Figure C.4 1-Octene + O ₃ : similar to Figure C.1.....	146
Figure C.5 Cyclodecane + OH with NO _x : similar to Figure C.1.....	147
Figure C.6 Cyclohexene + O ₃ : similar to Figure C.1.....	148
Figure C.7 Cyclooctane + OH with NO _x : similar to Figure C.1.....	149
Figure C.8 Cyclooctene + O ₃ : similar to Figure C.1.....	150
Figure C.9 Methyl furan + OH with NO _x : similar to Figure C.1.....	151
Figure C.10 <i>m</i> -Xylene + OH with NO _x : similar to Figure C.1.....	152
Figure C.11 Ocimene + NO ₃ : similar to Figure C.1.....	153
Figure C.12 <i>n</i> -Pentadecane + Cl (13 July): similar to Figure C.1.....	154
Figure D.1 (left) Lognormal size distribution of atomized droplets with a mode diameter of 300 nm, and the size distributions of residual particles for three concentrations of solute. The standard deviation is 1.58, which was obtained from the pentadecane size distribution in Figure 4.4. Mode diameters of the residual size distributions are noted above the distributions. (right) The number concentration of particles as a function of the solute concentration, for four different diameters within the range of diameters selected in this study. Note that the mode diameter axis is not monotonically spaced.....	156

1. INTRODUCTION

1.1 Background

Solid or liquid aerosol particles suspended in the atmosphere affect the terrestrial radiation budget by scattering or absorbing sunlight, changing the atmospheric temperature profile and influencing the climate (Charlson et al., 1992; Koren et al., 2004). Cloud droplets form in supersaturated air on the subset of aerosols that serve as cloud condensation nuclei (CCN) (e.g., Andreae and Rosenfeld, 2008). Aerosols serving as CCN indirectly affect climate by changing cloud albedo (Twomey, 1974; Lohmann and Feichter, 2005) and lifetime (Albrecht, 1989; Khain et al., 2008; Rosenfeld et al., 2008). Organic matter is often a large fraction of fine aerosol composition (Sardar et al., 2005; Zhang et al., 2007), and uncertainties in the composition and formation mechanisms of this organic material limit the current understanding of the effects of aerosol on climate (e.g., Lohmann and Feichter, 2005).

Organic aerosols have both primary and secondary sources. Primary particles are emitted directly into the atmosphere, while secondary organic aerosol (SOA) is formed when volatile organic compounds (VOCs) are oxidized and subsequently condense onto preexisting particles or form new particles during a nucleation event (e.g., Kroll and Seinfeld, 2008). The CCN properties of SOA are determined by measuring the number fraction of SOA particles that serve as CCN in supersaturated air (e.g., Engelhart et al., 2008) or by measuring the particle water uptake at high relative humidity (e.g., Poulain et al., 2010). One

way to express the CCN efficiency of an aerosol, independent of the experimental conditions, is by the hygroscopicity parameter, κ , defined by Petters and Kriedenweis (2007). Several studies have determined κ for SOA formed by different VOC and oxidant systems (e.g., Duplissy et al., 2008; Engelhart et al., 2008; King et al., 2009; Poulain et al., 2010).

SOA formed under different reaction conditions has different chemical properties – SOA is a mixture of compounds resulting from a subset of the products of generations of oxidation reactions (e.g., Aumont et al., 2005). Typically, the bulk κ -value of SOA has been measured. Here the bulk value refers to the net CCN activity of the mixture of compounds, not accounting for the underlying chemical complexity of the mixture. One way to characterize SOA mixture components is to collect the aerosol on a filter, extract the compounds in to a solvent and chemically separate the components using liquid chromatography. Here, we have separated SOA using liquid chromatography and measured the κ -value of the component compounds to obtain a high-resolution κ frequency distribution. These distributions may be useful to the study of the mechanisms of SOA formation.

1.2 Objectives

This thesis is part of an ongoing effort to measure and understand CCN properties of SOA. SOA was generated inside an environmental chamber and collected on filters. The SOA CCN properties were measured using a newly developed technique that couples high-performance liquid chromatography (Matsunaga and Ziemann, 2010) with scanning flow CCN analysis (Moore and Nenes, 2009). The main objectives of these experiments were

1. Determine if the newly developed technique satisfactorily separates SOA mixture components and measures its CCN properties
2. Test if SOA mixture component CCN properties manifest themselves in a predictable manner in the SOA bulk CCN properties
3. Associate changes in underlying κ distributions of SOA generated under different conditions with changes in SOA formation mechanisms

The remainder of this thesis is structured as follows: Chapter 2 provides an in-depth literature review of the chemistry of SOA formation and the methods of generating SOA in environmental chambers. Chapter 3 provides a review of Köhler theory, CCN measurement techniques, and current CCN studies characterizing SOA. Chapter 4 includes a manuscript for submission to the Journal of Geophysical Research that describes the main method and results from the environmental chamber experiments. Chapter 5 provides a summary of the thesis. Appendices A through C include all of the collected data on which the manuscript is based, in both tabular and graphical forms.

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2. LITERATURE REVIEW

2.1 Chemistry of secondary organic aerosol formation

The atmospheric oxidation of VOCs can be initiated by the hydroxyl radical (OH), ozonolysis (reaction with ozone, O₃), the nitrate radical (NO₃), or the Cl atom (Hallquist et al., 2009). Hydroxyl radicals are produced in the daytime by the photolysis of O₃ in the presence of water vapor, and are the main tropospheric oxidant in terms of concentration and reactivity (Seinfeld and Pandis, 2006). Atmospheric OH concentrations are not immediately depleted by reaction with VOCs because OH is often regenerated in the process, and can also be generated as a product of VOC ozonolysis (Atkinson, 2000; Lelieveld et al., 2008). Ozone is produced in the daytime by the photolysis of NO₂ and removed by its reaction with NO in a catalytic NO₂-O₃-NO cycle. In the absence of an alternative pathway, the NO + O₃ reaction destroys O₃ as quickly as it is produced – O₃ accumulates in the presence of VOCs, whose oxidation products are an alternative sink for NO (Atkinson, 2000). The photolytic production of oxidants ceases after nightfall, resulting in the slow depletion of OH and O₃ concentrations. VOC oxidation can continue by reaction with NO₃ radicals, which are both reactive and abundant after dark (Winer et al., 1984). Nitrate radicals are produced by the reaction of O₃ with NO₂ and destroyed rapidly in the presence of sunlight (Atkinson, 2000). The nighttime NO₃ concentration can be depleted by high VOC concentrations in an urban location, but may persist until sunrise in a low-VOC location (Winer et al., 1984). Chlorine atoms are strong oxidants, but contribute little to global VOC oxidation because they are only

formed in appreciable concentration under certain marine conditions (Atkinson, 2000), probably by the aqueous oxidation of seasalt solutions in the presence of O_3 (Oum et al., 1998).

Volatile organic compounds are emitted into the atmosphere in excess of 1000 Tg Carbon per year (Guenther et al., 1995). Global biogenic VOC emissions are ~10 times greater than anthropogenic VOC emissions, although anthropogenic compounds can be more concentrated than biogenic compounds in urban air (Goldstein and Galbally, 2007; Atkinson and Arey, 2003). Different plant species emit different combinations of VOCs – global vegetative emissions are primarily of isoprene, the C_5 base unit of terpenoid alkenes, and monoterpene isomers, which are composed of two isoprene units each and vary in structure and properties (Guenther et al., 1995; Geron et al., 2000). Plants also emit $C_2 - C_6$ alcohols and aldehydes, often in response to drought stress or tissue damage (Kesselmeier and Staudt, 1999; Fuentes et al., 2000). Anthropogenic VOCs present in urban air include mostly $C_2 - C_6$ alkanes and $C_6 - C_9$ aromatic compounds, with smaller contributions from alkenes and from ethyne (Seila et al., 1989; Lurmann et al., 1992; Derwent et al., 1995). Over half of the anthropogenic VOC emissions come from gasoline combustion (Watson et al., 2001). Emission from the combustion of gasoline is followed closely in magnitude by a large contribution from gasoline leakage and evaporation, followed by the use of solvents and coatings, which is the largest stationary contributor to urban VOC concentrations (Watson et al., 2001).

Alkane oxidation is initiated by OH, NO_3 , or Cl atoms, which abstract a hydrogen atom from the alkane molecule to form an alkyl radical and H_2O , HNO_3 , or HCl,

respectively. The by-products H_2O and HCl do not participate in aerosol formation, so Cl atoms can be used interchangeably with OH radicals in the laboratory to initiate the oxidation of alkanes, with the advantage that Cl atom concentration is easier to control than OH radical concentration. The alkyl radical quickly reacts with oxygen (O_2) to form an alkyl peroxy radical, RO_2 (Atkinson, 2000). Alkenes are more reactive than alkanes because they have a carbon double bond ($\text{R}=\text{R}'$, where R and R' represent alkane structures and = represents a double bond). Typically the oxidant substitutes itself into the carbon double bond by an addition reaction, resulting in a radical alkane structure with the attached oxidant as a functional group, $\text{R}(\text{Oxidant})\text{R}'$. The radical then reacts with O_2 to form a peroxy radical, $\text{R}(\text{Oxidant})\text{R}'\text{O}_2$ (Atkinson, 2000). Oxidation by OH results in a β -hydroxyalkyl peroxy radical, which is an alkane with an OH functional group and a peroxy functional group, $\text{R}(\text{OH})\text{CH}_2\text{O}_2$ (Atkinson, 2000). Oxidation by NO_3 results in β -nitrooxyalkyl peroxy radicals, or $\text{R}(\text{ONO}_2)\text{CH}_2\text{O}_2$ (Atkinson, 2000).

Oxidation by O_3 , or ozonolysis, follows the Criegee mechanism. The original mechanism for ozonolysis proposed by R. Criegee in 1975 followed three steps: O_3 substitutes itself into the alkene double bond, bridging the two carbons and forming a primary ozonide. This ozonide breaks asymmetrically into a carbonyl molecule and a zwitterionic carbonyl oxide molecule, which is now known as the Criegee Intermediate and has a biradical structure (Criegee, 1975; Wadt and Goddard, 1975; Harding and Goddard, 1978). The Criegee Intermediate can then bond to the carbonyl, forming a secondary ozonide molecule (Criegee, 1975). Several pathways exist for the Criegee Intermediate – it can form a secondary ozonide; it can isomerize and decompose into products such as OH and organic

acids (Jacobson, 2005; Kroll and Seinfeld, 2008); or it can be stabilized and react with water to form α -hydroxy-hydroperoxides, $R(OH)R'OOH$ (Kroll and Seinfeld, 2008).

After their formation in the initial steps of oxidation, peroxy radicals (RO_2) react with oxidants, NO_x , or other peroxy radicals. In the presence of NO_x , peroxy radicals can participate in the catalytic ozone cycle by removing NO to produce NO_2 and an alkoxy radical (RO) (Jacobson, 2005; Kroll and Seinfeld, 2008). In the absence of NO , peroxy radicals can react with other peroxy radicals, resulting in higher molecular weight compounds with lower vapor pressure. This low- NO_x pathway seems to promote the condensation of reaction products, raising the SOA yield from the oxidation of low molecular weight VOCs, but seems to suppress SOA formation from the oxidation of larger VOCs (Kroll and Seinfeld, 2008).

After the oxidation has begun, the first generation oxidation products continue to evolve by a series of reactions similar to the initial oxidation sequence (Kroll and Seinfeld, 2008; Aumont et al., 2005). The number of possible molecular isomers increases exponentially with the number of carbon atoms in each compound, making the intermediate steps between first generation products and end products difficult to catalogue (Goldstein and Galbally, 2007). In general, an oxidation reaction can cleave the VOC molecule or add a molecular functional group, or both. Products with low molecular weight are typically more volatile and remain in the gas phase, and the stable gas-phase end product of VOC oxidation is CO_2 (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Products with more functional groups or higher molecular weight tend to be less volatile. The addition of functional groups lowers a compound's vapor pressure by increasing intermolecular attraction, and oxygenated

functional groups such as hydroxyl or carbonyl groups contribute more strongly to intermolecular attraction than do hydrocarbon groups such as CH, CH₂, or CH₃ (Joback and Reid, 1987). Thus, large oxygenated compounds tend to have low vapor pressure and may condense, forming secondary organic aerosol.

As SOA forms, some of the condensing material remains in the gas phase. The fraction of a reaction product that condenses is controlled by its gas phase concentration and the mass concentration of existing particles (Pankow, 1994a). Compounds are absorbed rather than adsorbed by existing particles under typical conditions – the temperature must be high enough that the particles are in a liquid or amorphous solid state (Pankow, 1994b). Over the entire oxidation reaction, the fraction of VOC that results in condensed aerosol phase products is known as the aerosol yield (Odum et al., 1996). In calculating yield, the non-carbon mass added to aerosol by oxidant species is not subtracted; yield is the mass ratio of aerosol formed and the reacting amount of VOC precursor. The measurement of aerosol yield has been one of the primary goals of SOA experiments in the laboratory (Hallquist et al., 2009).

2.2 Review of oxidation experiments conducted in environmental chambers

Environmental chambers allow the study of secondary organic aerosol formed under controlled conditions using a limited subset of initiating oxidants and precursor VOCs. Chamber studies have been done as early as the 1970s in an effort to determine aerosol yield from the oxidation of various compounds or to determine the chemical mechanisms involved with the oxidation of specific compounds (Hallquist et al., 2009). Environmental chamber

experiments are the main method by which SOA is studied (Hallquist et al., 2009), even though physical limitations such as the chamber material and irradiation source or the reactants' concentration and mixing state prevent the chamber conditions from imitating the ambient environment.

The chamber material is chosen to avoid interaction between the reactants and the chamber walls, minimize hydrocarbon volatilization from the walls, and to maximize the transmission of the applied irradiation to the reactants inside the bag (Paulsen et al., 2005). Teflon is often used: commonly used Teflons are fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) (Hallquist et al., 2009). A slight electrostatic charge builds up on the Teflon material, accelerating the loss of particles to the chamber walls (Paulsen et al., 2005); gas-phase compounds of intermediate volatility are also lost as they are absorbed by the polymer structure of the material (Matsunaga and Ziemann, 2010). The buildup of organic reaction products is removed in between experiments by filling and emptying the chamber with clean air, and in some cases blacklights are also used to remove contaminants (e.g., Paulsen et al., 2005; King et al., 2009). Irradiation by blacklights in clean air or with O₃ removes organic compounds, NO_x, and CO that may be released by the Teflon material, especially when the chamber is new (Kelly et al., 1982).

Sunlight is a key ingredient in ambient air chemistry because it provides energy to cleave molecules and change their reactivity. To better constrain the reaction pathways of reactants, chamber experiments are conducted either by irradiating the chemical mixture or by injecting oxidants in the absence of light. The reaction chambers can be placed outdoors to use the full spectrum of natural sunlight (e.g., Grosjean, 1984; Rohrer et al., 2005) or

indoors with an array of blacklights (e.g., Lim and Ziemann, 2005). The addition of blacklights to an indoor reaction chamber provides greater control over the intensity and duration of the radiation than is possible with an outdoor photoreactor, but it limits the light spectrum. Dark reactions including ozonolysis or reaction with NO_3 radicals can be conducted indoors without blacklights (e.g., Prenni et al., 2007; King et al., 2007). The absence of light prevents photochemical generation or destruction of oxidants, such that their concentrations can be better constrained.

Precursors and oxidants are blown into the chamber individually from a port in the wall and allowed to mix together; different chamber volumes and modes of operation result in different mixing times. Larger chambers require, on average, a longer reaction time and cleaning time. Currently, chambers range in volume from 270 m^3 to $< 1 \text{ m}^3$, although those equipped with blacklights are $< 100 \text{ m}^3$ in volume (Hallquist et al., 2009; Wex et al., 2009). If the chamber air is not replaced or the reactants re-injected during an experiment, the reactants evolve in the chamber, and their original concentrations are lost. This is the “batch” mode of operation, in which reactant concentrations change as the composition evolves and aerosol forms (e.g., Lim and Ziemann, 2005; Stanier et al., 2007; Paulsen et al., 2005; Cocker et al., 2001). An alternative mode of operation is the “continuous flow” mode, in which air and reactants flow continuously through the chamber at controlled concentrations (e.g. King et al., 2007; Wex et al., 2009). In either mode of operation, reaction products can be continuously siphoned away for analysis.

Precursors to SOA formation are purchased and blown into the chamber as they evaporate from a container. Oxidants are more difficult to add to an experiment because they

are difficult to store. Some oxidants are synthesized on-site and blown into the chamber shortly thereafter; some experiments are designed such that the desired oxidant forms in the chamber after the reaction has begun. Ozone is generated by a commercial ozone generator in low concentrations with oxygen gas (e.g., Welsbach T-408 ozone generator, Prenni et al., 2007; Azcozon ozone generator, Engelhart et al., 2008). Ozonolysis of VOCs often produces OH radicals; to isolate the effect of ozonolysis, the OH radicals can be removed by a scavenger (Atkinson and Arey, 2003). An OH scavenger such as 1-butanol reacts with OH but not with O₃ because it has no carbon double bonds for O₃ to break. The OH scavenger has a low molecular weight and high vapor pressure such that its products stay in the gas phase and will not change the aerosol chemistry. Likewise, to generate OH radicals, the ozonolysis of an alkene can be used. Since this method of generating OH includes both OH and O₃ as oxidants, a VOC that does not react with O₃ may be oxidized to constrain the reaction pathways to OH oxidation. Alkanes do not react with O₃, and are good candidates for reaction with OH that has been generated by ozonolysis. A second method of generating OH radicals is by the photolysis of methyl nitrite (CH₃ONO) (Atkinson et al., 1981; Prenni et al., 2007). This method, because it involves nitrogen and irradiation, leads to the generation of O₃ and NO₃ radicals; NO can be added to the chamber to scavenge these extra oxidants (e.g., Prenni et al., 2007). To generate NO₃ in the absence of additional oxidants, N₂O₅ is added to the chamber in the absence of light and thermally dissociates into NO₂ and NO₃ radicals (Atkinson, 2000).

2.3 References

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3. CLOUD CONDENSATION NUCLEI

3.1 CCN efficiency of aerosol

The equilibrium vapor pressure of water, e_s , is strongly dependent on temperature, T , as described by the Clausius-Clapeyron equation:

$$e_s = e_{s,0} \exp \left(\frac{L_v}{R_w} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right) \quad (3.1)$$

where R_w is the specific gas constant for water vapor, $e_{s,0}$ is the equilibrium vapor pressure measured at temperature T_0 , and L_v is the latent heat of vaporization at T (Fleagle and Businger, 1980; North and Erukhimova, 2009). This equation describes the flux of evaporating water molecules with empirical constants L_v and $e_{s,0}$ measured at T_0 for a flat water surface. This flux is balanced by an equal flux of condensing molecules at equilibrium.

The Clausius-Clapeyron equation does not contain a surface tension term, because the surface area of water is constant as water evaporates from a beaker. Surface tension can be described as either the energy required to change the surface area of a liquid (Fleagle and Businger, 1980) or the restoring force when a surface is disturbed. Surface tension affects the evaporation rate from a droplet because the droplet's surface area shrinks as water evaporates. The reduction in surface area lowers the droplet's potential energy, as is demonstrated by its area-minimizing spherical shape (Bohren, 1987). Evaporation occurs faster from a droplet surface than from a flat surface at the same temperature because depleting the surface area makes additional energy available. The Kelvin equation describes

the effect of surface tension on the equilibrium vapor pressure of a pure liquid water in the presence of pure water vapor, e_c :

$$e_c = e_{s,0} \exp\left(\frac{L_v}{R_w} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \exp\left(\frac{2\sigma}{R_w T \rho_w r}\right) = e_s \exp\left(\frac{2\sigma}{R_w T \rho_w r}\right) \quad (3.2)$$

where σ is the surface tension of pure water, ρ_w is the density of liquid water, and r is the droplet radius (Fleagle and Businger, 1980). A droplet of pure water will never be in equilibrium with a flat surface of pure water at the same temperature because its equilibrium vapor pressure, e_c , is always higher than that for flat water, e_s . Molecules will tend to evaporate from the droplet and condense on the flat water surface until the droplet has evaporated completely.

Mixing the water with a solute perturbs the equilibrium water vapor pressure over the solution. Assuming that the solute molecules are the same size as the water molecules and that they mix without interacting (Schroeder, 2000), the change in vapor pressure scales with the mole fraction of water in solution (Seinfeld and Pandis, 2006):

$$e_{hc} = x_w e_{s,0} \exp\left(\frac{L_v}{R_w} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \exp\left(\frac{2\sigma}{R_w T \rho_w r}\right) = x_w e_c \quad (3.3)$$

where x_w is the mole fraction of water in solution and e_{hc} is the equilibrium vapor pressure over the solution. This equation applies to ideal solutions and is known as Raoult's Law. If the solute and water molecules interact, then x_w is multiplied by the activity coefficient of water, γ_w , to account for the perturbations in internal energy of the molecules due to mixing (Schroeder, 2000). At equilibrium, e_{hc} is equal to the ambient vapor pressure, e . If e is higher than e_{hc} , then water condenses on the droplet until equilibrium is established.

The saturation ratio, S , is defined as the ratio of ambient vapor pressure to the equilibrium vapor pressure of water above a flat surface of pure water:

$$S = \frac{e}{e_{s,0} \exp\left(\frac{L_v}{R_w} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right)} = \frac{e}{e_s} \quad (3.4)$$

Over a flat surface of pure water, equilibrium is reached when $S = 1$. However, the equilibrium vapor pressure over a curved surface is higher than e_s , and the equilibrium vapor pressure over a flat surface of solution is lower than e_s . The Köhler equation combines the effects of droplet curvature and dissolved solute (Seinfeld and Pandis, 2006), expressing S as a function of the solute and of n_w , with all other variables constant:

$$\ln S = \frac{4\sigma}{R_w T \rho_w} \left(\frac{6}{\pi} \left(\frac{n_s M_s}{\rho_s v} + \frac{n_w M_w}{\rho_w} \right) \right)^{-1/3} + \ln \gamma_w - \ln \left(1 + \frac{n_s}{n_w} \right) \quad (3.5)$$

where n_s is the number of moles of solute, M_s is the molar mass of solid solute, ρ_s is the density of solid solute, v is the number of ions each solute molecule dissociates into, n_w is the number of moles of water, and M_w is the molar mass of water. The maximum value of S of Equation 3.5 is the critical saturation ratio, S_c , above which a droplet containing n_s molecules of solute grows into a large droplet, limited only by the depletion of ambient water vapor.

Because vapor pressure is fundamentally the momentum flux of water molecules, the molecules evaporating from a drop per unit area per unit time, f_{out} can be expressed as:

$$f_{out} = e_{hc} \frac{N_A}{M_w c} \quad (3.6)$$

where N_A is Avogadro's number and c is the average velocity of a water molecule (Schroeder, 2000). The molecules condensing to the droplet per unit area per unit time, f_{in} , is analogously calculated from e .

Figure 3.1a shows the equilibrium droplet size as a function of f_{in} and as a function of S for two solutes. If a droplet is larger than the equilibrium size at $S < 1$, f_{out} is higher than f_{in} and the droplet will evaporate until it reaches equilibrium (point a). Likewise, if a droplet is smaller than the equilibrium size at any S , f_{in} is higher than f_{out} and the droplet will grow until it reaches equilibrium (point b). At $S > 1$, a droplet larger than the unstable equilibrium size will grow into a large droplet (point c), and a droplet smaller than the equilibrium size will evaporate until it reaches stable equilibrium size (point d). When $S > S_c$, the droplet will grow indefinitely (point e). At constant S , the droplet will never reach equilibrium, but the ambient water vapor will be depleted when the droplet becomes large.

The Köhler curve in Figure 3.1b shows the f_{out} as a function of the droplet size. The slope of the curve determines the stability of a droplet in equilibrium: a positive slope indicates that the droplet is in stable equilibrium and a negative slope indicates unstable equilibrium. Droplets in stable equilibrium remain suspended in the air and are known as haze droplets. Droplets in unstable equilibrium tend to either evaporate until they reach stable equilibrium or “activate,” growing large. At ambient S larger than S_c , all droplets activate to become cloud droplets.

The dry particles of solute that initiate the droplet's movement on the Köhler curve are known as cloud condensation nuclei (CCN). The ability of aerosol particles to serve as CCN depends only on the ambient S , D_d , and the chemical properties of the solute.

Equation 3.5 uses the molecular weight, density, and activity coefficient to show the ability of particles of pure composition to activate as CCN. The physical constants required by Equation 3.5 can be derived for a limited number of mixed composition systems. Ambient organic aerosol mixtures have unknown properties, and thus their water uptake can be parameterized by the equation:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (3.7)$$

described by Petters and Kreidenweis (2007), where κ is a hygroscopicity parameter, $a_w = x_w \gamma_w$ is the activity of water, V_s is the volume of solute, and V_w is the volume of water.

The value of S_c required for a particles of size D_d to serve as CCN uniquely defines the solute's κ -value. Together, S_c , D_d , and κ describe the relationship between the saturation ratio, the particle size, and the particle chemistry; these three variables are independent of one another. The combination of κ and the particle dry size distribution can be used to initialize a cloud formation model that treats the dynamic feedback between the generation and depletion of vapor supersaturation in the atmosphere. If κ is taken to be independent of temperature, then κ -values apply in all clouds in which liquid droplets form.

Experimentally, either D_d or S can be varied while holding the other constant. Droplet growth statistics show S_c at which particles of a certain diameter become CCN active, returning a D_d - S_c data pair that can be used with Equation 3.7 and Equation 3.5 by

iterative methods to determine the κ -value. The approximate κ -value can be found using (Petters and Kreidenweis, 2007):

$$\kappa = \frac{4A^3}{27D_d^3 \ln^2 S_c}, \quad A = \frac{4\sigma}{R_w T \rho_w} \quad (3.8)$$

Based on Equation 3.8, κ can be measured by a particle's activation as CCN in supersaturated conditions using a CCN counter (CCNC). Dry particles are size-selected by a differential mobility analyzer (DMA), and the flow is split between a condensation particle counter (CPC) and a CCNC. The CPC and CCNC count the total aerosol particles and the aerosol acting as CCN, respectively. An activation curve is fitted to the ratio of CCN to total particles to find the D_d - S_c data pair at activation, from which κ is calculated. CCN measurements are typically taken at ambient temperature. In the atmosphere, however, activation may happen over a range of temperatures. The temperature dependence of κ in general is unknown but appears to be small for inorganic compounds (Kreidenweis et al., 2009). The relationship between D_d and S_c also depends on the solubility of the particle (Petters and Kreidenweis, 2008) and the temperature dependence of solubility may play an important role in droplet activation (Kreidenweis et al., 2006). Additional temperature control in the instrument setup would be necessary to study the temperature dependence of κ .

3.2 The effect of varying reaction conditions on aerosol hygroscopicity

CCN properties of various SOA systems have been measured in order to analyze the dependence of κ on the conditions under which SOA is formed. The concentration of NO_x ,

water vapor, or precursor can all affect the mechanisms of SOA formation, and thus affect the properties of SOA. Kappa is expected to correlate with the volatility of SOA, and may also depend on the identity of the precursor, oxidant, or oxidant scavengers present. The effect of varying conditions on the κ -value of SOA systems is reviewed here.

The κ -value of condensing products could be sensitive to NO_x concentration, given that different reaction pathways occur under low and high NO_x conditions. Aerosol yield has been shown to be sensitive to the NO_x conditions, and the change in yield is dependent on the precursor's identity (Kroll and Seinfeld, 2008). By extension, the relationship between NO_x and κ -value may be dependent on precursor identity. King et al. (2010) changed the VOC: NO_x ratio in six isoprene photooxidation experiments and found no variation in the resultant κ -value, showing that NO_x concentration did not affect SOA hygroscopicity for this system. Additional chamber SOA studies conducted for other precursors with a range of NO_x conditions would be needed to establish a relationship between NO_x conditions and the CCN activity of the resultant SOA.

Water vapor present during oxidation could also affect the resultant SOA's κ -value. Although many chamber reaction studies of SOA conduct experiments using dry air, others add water vapor to the chamber as a reactant. For example, Duplissy et al. (2008) and King et al. (2010) conducted experiments at 40–50% relative humidity (48–53% and $40 \pm 2\%$, respectively) but did not test the effect of humidity on the SOA. The results of these SOA chamber experiments in the presence of water vapor are difficult to compare to the results of dry experiments because other factors differ between studies. Poulain et al. (2010) changed the relative humidity in several α -pinene ozonolysis experiments and found that increased

water vapor concentration resulted in higher κ -values. The increase in κ -value may be due to the effect of increased water vapor on the relative proportions of the several organic acids and aldehydes produced by α -pinene ozonolysis (Poulain et al., 2010; Ma et al., 2008). Typically the concentration of water vapor affects ozonolysis reactions because higher relative humidity results in a greater yield of α -hydroxy-hydroperoxides, $R(OH)R'OOH$ (Tobias and Ziemann, 2001; Kroll and Seinfeld, 2008). α -Hydroxy-hydroperoxides may be more hygroscopic than other oxidation products because they have OH and COOH functional groups, which raise their O:C ratio, and higher O:C ratios correlate with higher κ -values (Jimenez et al., 2009).

The concentration of precursor participating in the reaction may have an effect on the resultant SOA κ -value. When higher precursor concentrations are used in oxidation reactions, compounds with higher vapor pressure condense to aerosol (Robinson et al., 2007). The addition of these compounds to SOA lowers the κ -value by lowering the O:C ratio (Duplissy et al., 2008). This effect has been demonstrated in a study by Duplissy et al. (2008), wherein changes in precursor concentration ranging from 10 to 183 ppb α -pinene resulted in an appreciable decrease in growth-factor derived κ -values from 0.14 to 0.04. However, the change in κ -value was less pronounced in a study by King et al. (2009), who observed a small decrease in κ -value from 0.16 at $0.95 \mu\text{g m}^{-3}$ to 0.12 at $95 \mu\text{g m}^{-3}$ mass loading.

Further analysis of the relationship between a compound's volatility and its κ -value can be performed using a thermodenuder. The thermodenuder heats the aerosol, removing the more volatile compounds from the SOA by evaporation. King et al. (2010) show that SOA

from the photooxidation of isoprene with ammonium sulfate seed particles, when passed through a 25 °C thermodenuder, had higher κ -values than particles passed through a 100 °C. This result indicates that the less volatile components of the isoprene and ammonium sulfate SOA had higher κ -values, which is reasonable since ammonium sulfate is less volatile and more hygroscopic than organic products. However, Poulain et al. (2010) found the opposite effect – the more volatile components of SOA from the ozonolysis of α -pinene had higher κ -values. A compound's volatility and its κ -value have different dependencies on molecular size and on the number of functional groups, typically with volatility inversely proportional to molecular size and to the number of functional groups (Chattopadhyay and Ziemann, 2005; Goldstein and Galbally, 2007), and with κ inversely proportional to molecular size and proportional to the number of functional groups (Petters et al., 2009). Due to these dependencies, κ may be proportional or inversely proportional to volatility, depending on whether functional groups or carbon chain length control the volatility change. Thus, the opposite dependencies found by King et al. (2010) and Poulain et al. (2010) do not fundamentally contradict each other. Further chemical speciation would be necessary to separate the effects of molecular size and functional groups on the compounds' volatility and κ -values.

Various organic precursor gases have been oxidized in chamber experiments to form SOA and to determine κ . The most common precursors are terpenes and aromatic compounds, which represent a large fraction of biogenic and anthropogenic emissions (Lurmann et al., 1992; Geron et al., 2000). Standard reaction conditions have not been established for purpose of κ -value comparisons between studies, although SOA from many

precursors has been analyzed and has sometimes resulted in similar κ -values for one precursor or for SOA in general. The κ -value of SOA from α -pinene ozonolysis has been reported as 0.1 by three separate studies under different conditions (Prenni et al., 2007; Duplissy et al., 2008, low precursor concentration; Engelhart et al., 2008), but other studies have found lower κ -values, e.g., 0.04 (Duplissy et al., 2008, high precursor concentration).

Because changing the reaction conditions can result in different κ -values, similar reaction conditions between the experiments of one study should allow a more reliable comparison of κ -values for different precursors. Duplissy et al. (2008) report $\kappa = 0.07$ for SOA from α -pinene at 124 ppb and $\kappa = 0.10$ for SOA from 1,3,5-trimethylbenzene at 135 ppb. Engelhart et al. (2008) oxidized α -pinene alone and in a mixture with different proportions of β -pinene, limonene, and Δ^3 -carene; the resulting SOA had $\kappa = 0.10$ and $\kappa_{avg} = 0.14$, respectively. Prenni et al. (2007) found that each precursor they oxidized (α -pinene, β -pinene, Δ^3 -carene, and toluene) had a κ -value of 0.1 ± 0.04 . The κ -value of SOA seems to be somewhat insensitive to the choice of precursor. In contrast with the above studies, VanReken et al. (2005) found different κ -values for SOA from α -pinene (0.05), β -pinene (0.12), Δ^3 -carene (0.16), and limonene (0.22), using a setup optimized for measuring size distribution that necessitated an estimation of the dry diameter for κ calculation.

Oxidation continues to alter the SOA after its formation, raising the O:C ratio as the aerosol is aged (Jimenez et al., 2009; Heald et al., 2010). The increase in the O:C ratio has been shown to correlate with higher SOA κ -values (Jimenez et al., 2009), due to the higher polarity of more oxygenated compounds (Joback and Reid, 1987; Goldstein and Galbally, 2007). Duplissy et al. (2008) observed κ -values increase steadily over ~20 hrs of oxidation of

α -pinene in an environmental chamber; Engelhart et al. (2008) observed κ -values increase over ~8 hrs of oxidation of a mixture of α -pinene, β -pinene, limonene, and Δ^3 -carene. Prenni et al. (2007) observed no relationship between aerosol age and κ -value, but report that their setup was not intended to detect a change over time. Contrary to the results of Engelhart et al. (2008) and Duplissy et al. (2008), VanReken et al. (2005) observed a decrease in κ -value over time in the chamber, possibly due to the oligomerization of compounds in the SOA.

The ozonolysis of alkenes produces OH radicals, so an OH scavenger is included in many ozonolysis experiments to ensure that O₃ is the only oxidant available for reaction with the precursor. The OH scavenger is chosen such that its reaction products are volatile and do not contribute to SOA. The precursor identity and the presence or absence of an OH scavenger changes the reaction pathways and may alter the κ -value of the resulting SOA. Engelhart et al. (2008) noticed a decrease in κ -value for the first 30 minutes of an ozonolysis experiment when both O₃ and OH were allowed to react with α -pinene, as compared to the result when 1-butanol was used to scavenge OH. This may be because the reaction of α -pinene with OH can raise the fraction of pinonaldehyde with respect to carboxylic acid in the SOA (Nozière et al., 1999; Jang and Kamens, 1999), which lowers the κ -value because pinonaldehyde is less hygroscopic (Engelhart et al., 2008). In contrast with the results of Engelhart et al. (2008), Wex et al. (2009) report an increase in κ -value when both O₃ and OH reacted with α -pinene, as compared to the result with an OH scavenger. The presence or absence of an OH scavenger can change the SOA κ -value, but the changes depend on the chemistry involved in the precursor's oxidation and the conditions of the reaction.

3.3 Methods used in this study

The purpose of this study was to measure the κ -value of the constituent parts of SOA formed by oxidizing organic compounds in an environmental chamber. The distributions of underlying κ -values were examined and compared to the κ -value measured online. High-precision liquid chromatography (HPLC) was used to break the SOA into constituent parts sorted by decreasing polarity with elution time. Compounds eluting from the HPLC column were subjected to scanning flow CCN analysis in which the water vapor supersaturation that particles are passed through is controlled by continuously varying flow rate (Moore and Nenes, 2009). This method was implemented at North Carolina State University for this study. Measurements were taken with colleagues at the Air Pollution Research Center in Riverside, California between 29 June 2010 and 19 July 2010. The Air Pollution Research Center provided the environmental chamber for aerosol generation and the HPLC system for compound separation. The study has been described in a paper prepared for publication, which is included as Chapter 4 of this thesis. A summary of all experiments is appended in Appendices A through C, and Appendix D makes a note about the atomizer.

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3.5 Figures

Figure 3.1. The Köhler equation, plotted for a droplet of variable diameter in an environment of variable water vapor pressure. The dissolved solute is constant and equivalent to a dry particle of diameter D_d . **Plot a:** the equilibrium droplet size as a function of the ambient molecular flux of water to the droplet (bottom axis), or as a function of the ambient saturation ratio (top axis). Molecular flux is proportional to vapor pressure. Dissolved solute is held constant and is equivalent to $D_d = 50$ nm for both sodium chloride (NaCl) and ammonium sulfate ((NH₃)₂SO₄). Dotted lines indicate regions of unstable equilibrium. Droplets whose sizes are not in equilibrium with ambient conditions at points *a* and *d* will evaporate until reaching equilibrium; droplets at points *b* will grow until reaching equilibrium; and droplets at points *c* and *e* will grow indefinitely. In the upper righthand corner is indicated the range in saturation ratio achievable by the measurement setup used in this study. **Plot b:** the classical representation of the Köhler curve, showing the molecular flux of water molecules evaporating from a droplet as a function of the droplet diameter. The dissolved solute, (NH₃)₂SO₄, is equivalent to $D_d = 10, 50$ and 100 nm.

4. A PAPER FOR JOURNAL SUBMISSION

Hygroscopicity frequency distributions of secondary organic aerosols

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Abstract

Secondary organic compounds are an important component of ambient aerosol and potentially lower the supersaturation that is required for individual particles to serve as cloud condensation nuclei (CCN). Secondary organic aerosol (SOA) formed from the oxidation of a single precursor can be composed of many different compounds and their overall CCN efficiency has been reported for many different SOA systems. An aerosol's CCN efficiency can be described by a single hygroscopicity parameter, κ . However, this κ comprises an unknown distribution of underlying κ -values resulting from each individual compound in the SOA mixture. Here we report on a new technique for characterizing this distribution of κ . Precursor hydrocarbons were oxidized in an environmental chamber to form SOA, which was collected on filters and extracted using ethyl acetate. Extracts were then fractionated by reversed-phase high-performance liquid chromatography using gradient elution with acetonitrile and water. The eluate was atomized, the solvent was removed by evaporation, and the residual aerosol particles were analyzed as a function of retention time using scanning flow CCN analysis. Kappa-values generally decreased with column retention time. Total SOA κ -values reconstructed by integrating over the chromatogram agreed well with values measured for SOA sampled directly from the environmental chamber, suggesting that κ for SOA represents the volume-weighted average of the constituent compounds' κ -values. These κ distributions show that SOA consists of a continuum of products (with $0 < \kappa < \sim 0.4$ in this study) instead of a pseudo-binary mixture of water-soluble and water-insoluble compounds as is often assumed. We anticipate that our measured hygroscopicity distributions

will serve as validation points for mechanistic models that seek to predict the generation and evolution of organic aerosols in the atmosphere.

4.1 Introduction

Secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs) changes the distribution of particles that serve as cloud condensation nuclei (CCN) at prescribed supersaturations [e.g., *Gunthe et al.*, 2009; *Leaitch et al.*, 2010]. This leads to indirect modification of cloud and precipitation spectra, which feeds back into the Earth's radiation budget and hydrological cycle [e.g. *Andreae and Rosenfeld*, 2008]. To better characterize these effects, a large number of studies have measured the CCN efficiency of compounds identified in ambient organic aerosol [e.g., carboxylic acids and carbohydrates, see Supplementary Information in *Petters et al.*, 2009a for a list of compounds studied so far] as well as SOA generated inside environmental chambers using a diverse assortment of VOCs and oxidants [e.g. *VanReken et al.*, 2005; *Prenni et al.*, 2007; *King et al.*, 2007; *Duplissy et al.*, 2008; *Engelhart et al.*, 2008; *Asa-Awuku et al.*, 2010]. One way to parameterize the results from these studies is to report the hygroscopicity parameter κ [*Petters and Kreidenweis*, 2007], which allows comparisons of CCN efficiency for different compounds or mixtures. Remarkably, the κ -values for SOA derived from the oxidation of isoprene, monoterpenes, and toluene, compounds representative of most of the major VOC classes, fall within the narrow envelope $\kappa = 0.1 \pm 0.04$. Organic aerosol mass concentration [*King et al.*, 2009], VOC:NO_x ratio [*King et al.*, 2010], the concentration of water vapor, and the identities of OH scavengers present during

an ozonolysis reaction [Poulain *et al.*, 2010] seem to exert only minor influences on the observed κ -values.

These results are surprising, since SOA formed from these reactions is composed of many compounds with a large variety of structures [Kroll and Seinfeld, 2008]. For example, the α -pinene ozonolysis reaction yields many hundreds of products with different H:C and O:C ratios [Heaton *et al.*, 2009] and combinations of functional groups such as carbonyl, hydroxyl, carboxyl, hydroperoxy, and ester [Yu *et al.*, 2001; Docherty *et al.*, 2005]. Based on current understanding of atmospheric VOC reaction mechanisms [e.g. Atkinson and Arey, 2003], absorptive gas-particle partitioning [Pankow, 1994; Odum *et al.*, 1996; Donahue *et al.*, 2006], and the effect of molecular properties on CCN efficiency [Petters *et al.*, 2009a], the CCN experiments that systematically varied reaction conditions [Poulain *et al.*, 2010; King *et al.*, 2010] and mass concentration [King *et al.*, 2009] should have probed a wide range of molecular compositions, and thus a range of κ -values. One would expect this range to even be larger in the atmosphere; however, κ is also near 0.1 for the organic fraction of ambient aerosol [Shantz *et al.*, 2008; Wang *et al.*, 2008; Gunthe *et al.*, 2009; Shinozuka *et al.*, 2009; Dusek *et al.*, 2010; Cerully *et al.*, 2011]. This begs the question, “Why does composition appear to have such a minor effect on the κ -values of these complex SOA mixtures?”

One way to address this question is to measure the κ -values of the components of organic mixtures obtained by physical (e.g., distillation) or chemical (e.g., solvent extraction) methods of fractionation. For example, Asa-Awuku *et al.* [2010] extracted the water-soluble fraction of several SOAs using the method of Sullivan and Weber [2006] and subjected them

to CCN analysis. Based on their results, they proposed that the aerosols can be conceptualized as an effective two-component mixture with invariant values of $\kappa = 0.3$ for the water-soluble fraction and $\kappa = 0$ for the water-insoluble fraction, and that the remarkably small variations in the total SOA κ -values are attributable to small variations in the relative fraction of water-soluble compounds.

Here we report data acquired using a new method we have developed that involves separating complex SOA mixtures using reversed-phase high-performance liquid chromatography coupled with high-resolution scanning flow CCN analysis to determine κ -values of mixture components. We apply this method to filter extracts of SOA formed from many different VOC-oxidant combinations to survey κ frequency distributions resulting from a broad range of chemical reactions. Theory predicts that the volume-weighted average of the measured κ frequency distribution should reproduce the overall κ -value measured for the total SOA sampled from the environmental chamber directly into the CCN analyzer (and thus without extraction), and we show that this is indeed the case. Using the combined results from all experiments we examine the relationship between retention time and measured κ -value. For selected systems we demonstrate the correspondence of the κ frequency distribution with expectations based on differences in reaction products. Our results should aid in the development of structure-activity relationships that can predict an organic compound's κ -value based on its chemical structure. Such relationships would provide a means for predicting aerosol hygroscopicity using the aerosol composition computed from atmospheric chemical transport models.

4.2 Methods

4.2.1 Köhler Theory

Köhler Theory relates the saturation ratio over a water droplet and the droplet's diameter via

$$S = a_w \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right) \quad (4.1)$$

where S is the saturation ratio, a_w is the water activity, $\sigma_{s/a}$ is the surface tension of the solution-air interface, ρ_w is the density of water, M_w is the molecular mass of water, R is the universal gas constant, T is the temperature, and D is the droplet diameter.

We parameterize the water activity using the functional form proposed by *Petters and Kreidenweis* [2007]

$$S = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - \kappa)} \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right) \quad (4.2)$$

where D_d is the particle dry diameter and κ is the hygroscopicity parameter. The critical saturation ratio, S_c , is defined by the maximum value of S in Equation 4.2; κ can be estimated from experimentally determined S_c and D_d values by

$$\kappa = \frac{4A^3}{27D_d^3 \ln^2 S_c}, \quad A = \frac{4\sigma_{s/a}M_w}{RT\rho_w} \quad (4.3)$$

When computing κ from experimental data, $T = 298$ K and $\sigma_{s/a} = 0.072$ J m⁻² are assumed in order to yield a data set that is self-consistent between different studies.

The Zdanovskii, Stokes, and Robinson (ZSR) assumption states that the total water content equals to the sum of the water contents of the individual components. For particles that are composed of multiple components and for which the ZSR assumption holds, the κ -

value for a mixture of components is the linear addition of the volume-weighted component κ -values

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (4.4)$$

where ε_i is the volume fraction of component i , and κ_i is that component's κ -value.

4.2.2 SOA generation

The following chemicals with purities and suppliers were used: 1-octene (98%), 1-decene (94%), cis-cyclooctene (95%), 1,3-cyclohexadiene (97%), 1,5-cyclooctadiene (99+%), 1,3,5,7-cyclooctatetraene (98%), 2,3-dimethyl-2-butene (98%), n-decane (99+%), n-pentadecane (99+%), cyclooctane (99+%), cyclodecane (95%), *m*-xylene (99+%), 2-propanol (99.5%) (Sigma-Aldrich); dioctyl sebacate ($\geq 97\%$), β -caryophyllene (99%) (Fluka); cyclohexane (99.9%) (Fisher Scientific); 1,2-dimethyl cyclohexene (97%) (ChemSampCo); 3-methyl furan (98%) (Acros Organic); ocimene (99+%) (IFF Inc.); cyclohexene (99%) (Chemical Samples Co.); chlorine (99.5%) (Matheson Tri-Gas); and nitric oxide (99.5%) (Airgas). Methyl nitrite [Taylor *et al.*, 1980] and dinitrogen pentoxide [Atkinson *et al.*, 1984] were synthesized and stored under vacuum in liquid nitrogen. Ozone (2% ozone in O₂) was generated using a Welsbach T-408 ozone generator. Purchased chemicals were used without further purification.

SOA was generated from reactions performed with a suite of VOCs and oxidants that were selected to result in a wide variety of chemical compositions and κ -values. The VOC-oxidant reactions studied are summarized in Table 4.1, and include the reactions of simple linear and cyclic alkenes with ozone (O₃) in the presence of a hydroxyl (OH) radical

scavenger; linear and cyclic alkenes with nitrate (NO_3) radicals; aromatics with OH radicals in the presence of NO_x ; and alkanes with chlorine (Cl) atoms or OH radicals in the absence of NO_x . The instrument setup is shown in Figure 4.1.

SOA was generated inside a 1.7 or 5.9 m^3 Teflon (fluorinated ethylene propylene) environmental chamber operated at room temperature (~ 298 K) and pressure [Matsunaga and Ziemann, 2010]. The chamber was flushed and filled with dry ($\text{RH} < 1\%$), hydrocarbon-free (< 5 ppbv) air from an Aadco clean air generator. The VOC was added to the chamber by flushing clean air through a 500 mL glass bulb that contained a measured volume or mass of the liquid or solid VOC. The bulb was heated slightly with a heat gun when necessary to evaporate the VOC and guarantee that all constituents entered the chamber. The oxidant was either added directly to the chamber or generated in situ. O_3 was flushed into the chamber from a glass bulb. NO_3 radicals, Cl atoms, and OH radicals were generated in the chamber: NO_3 radicals by thermal dissociation of N_2O_5 , Cl atoms by photolysis of Cl_2 , and OH radicals in the presence of NO_x by photolysis of a mixture of methyl nitrite (CH_3ONO) and NO (added to suppress O_3 and NO_3 radical formation) [Atkinson *et al.*, 1981] or in the absence of NO_x by reaction of tetramethylethylene (TME) with O_3 , which produces OH radicals with a yield close to 1 [Atkinson, 1997]. Desired chamber concentrations of N_2O_5 , Cl_2 , methyl nitrite, or NO were obtained by adding a measured pressure of gas to a calibrated glass bulb on a glass vacuum rack and then flushing into the chamber with clean air. Photolysis was carried out using blacklights ($\lambda_{\text{max}} = 360$ nm) that covered two walls of the 5.9 m^3 chamber. For reactions of alkenes with NO_3 radicals or O_3 , VOC:oxidant ratios were chosen such that all C=C double bonds were reacted. For reactions with Cl atoms or OH radicals,

which occur by H-atom abstraction, the average number of abstractions was controlled by adjusting VOC:radical precursor ratios and/or the duration and intensity of blacklight irradiation.

In order to obtain particle size distributions suitable for CCN analysis it was necessary in most experiments to add to the chamber, in addition to the major VOC, a trace amount of a highly reactive VOC whose very low volatility reaction products rapidly nucleated to form high concentrations of small seed particles onto which the SOA condensed. Specifically, β -caryophyllene was added for reactions with O_3 and some of the reactions with OH radicals. In two cases, dioctyl sebacate (DOS) seed particles generated with an evaporation-condensation source [Matsunaga *et al.*, 2009] were instead added directly to the chamber (see Table 4.1). The amounts of major VOC and β -caryophyllene or DOS added were chosen to achieve <1% mass of seed relative to SOA. The volume fraction of seed material varied between particle sizes because the condensation rate is proportional to particle surface area and the size distribution evolved by coagulation. Nonetheless, the expected average contribution of the seed material to the aerosol volume and thus its κ -value is <1% and this value is smaller than the resolution of the κ measurement.

Reactions were initiated by adding the oxidant to the chamber or by turning on the blacklights to initiate oxidant formation via photolysis. Particles rapidly formed via homogeneous nucleation (except when DOS seed was present), and the size distribution evolved as reaction products condensed and coagulated. A few minutes after initiating the reaction, the sampling line was connected to a port in the chamber wall and the particle size distribution and CCN activation properties were measured. CCN measurements were

completed in ~1 hr and then particle samples were collected on Millipore filters (0.45 μm pore size, Fluoropore FHLF, 47 mm, without pretreatment) at a flow rate of 15 L min⁻¹ [Matsunaga and Ziemann, 2010].

4.2.3 Measurement of CCN efficiency of total SOA

The CCN setup was identical to that used by *Petters et al.* [2009b]. In brief, particles were sampled directly from the chamber through copper tubing and passed through two diffusion dryers and a ²¹⁰Po neutralizer before entering a differential mobility analyzer (DMA) (TSI model 3080, sheath-to-sample flow ratio 10:1.5) to select a specified mobility diameter. The flow was then split between a condensation particle counter (CPC, TSI 3010) and a CCN counter (CCNC, Droplet Measurement Technologies, sheath-to-sample flow ratio 10:1) [Roberts and Nenes, 2005] to measure total particle concentration and CCN concentration at constant water supersaturation. Particle size and CCN distributions were obtained by stepping through several dry diameters. The ratio of CCN to total particle concentration defines the CCN response curve from which the activation diameter was determined via an inversion procedure that accounts for multiply charged particles [Petters et al., 2007, 2009b]. The relationship between the temperature gradient and supersaturation in the CCNC was calibrated using dry ammonium sulfate particles [Rose et al., 2008]. The temperature gradient and particle diameter were set by the CCNC and DMA, respectively. Activation diameters from the ammonium sulfate particles were used to compute the supersaturation in the instrument using the relationship between water activity and composition from the Extended Aerosol Inorganic Model (E-AIM) [Clegg et al., 1998; Wexler and Clegg, 2002].

4.2.4 Measurement of CCN efficiency of HPLC-fractionated SOA

Generation of HPLC-fractionated SOA particles. Filter samples of SOA from the chamber experiments were extracted in ethyl acetate, which we have shown previously to efficiently extract all SOA compounds [Docherty *et al.*, 2005; Matsunaga and Ziemann, 2009]. Filters were pre-cleaned by immersing them twice in 10 mL of ethyl acetate at room temperature for >10 min and drying in a stream of N₂. After sampling, filters were extracted immediately or stored at -20 °C for up to 2 days. Filters were extracted twice in flasks containing 4 mL ethyl acetate at room temperature for >10 min following 30 s of agitation, and the extracts were combined. Extracts were analytically transferred into a vial with a conical insert, dried in a stream of N₂, and dissolved in acetonitrile to achieve 50-600 µg in a 10 µl injection. The mass of the dry extract was compared to the increase in filter mass during sampling; the extraction was >98% efficient. The extract was then fractionated using an Agilent 1100 series HPLC outfitted with a 250 × 4.6 mm Zorbax 5 µm Eclipse XDB-C18 column operating at room temperature with a guard column [Matsunaga and Ziemann, 2009]. The method employed gradient elution with a constant flow rate of 1 mL min⁻¹ using water and acetonitrile, with the acetonitrile concentration increasing linearly from 5% for 10 min to 100% over a 50 min interval. With this method, compounds elute from the column in the order of decreasing polarity. Eluate from the column was passed into a Collison atomizer, which created an aerosol that was subsequently passed through a pair of diffusion dryers, one containing activated charcoal and the other silica gel, to remove evaporated organic solvents and water, respectively. The residual aerosol particles were charge-neutralized using a ²¹⁰Po neutralizer and size classified using a DMA (TSI 3081, sheath:sample flow ratio varying

from 10:0.7 to 10:1.7). The size-classified particle flow was split between a CPC and a DMT CCNC instrument operating in scanning flow mode [Moore and Nenes, 2009].

Scanning flow cycle. The scanning flow CCN measurement method imposes a linear flow profile at a constant linear column temperature gradient ($\Delta T = 7\text{ }^{\circ}\text{C}$) to control the varying supersaturation in the CCNC column. When coupled with monodisperse aerosol, the method is equivalent to traditional supersaturation scans but operates at much higher time resolution. Total flow was controlled by continuously varying the direct current voltage supplied to an externally installed blower (flow rate 0.2 to 1.2 L min⁻¹). Each 2 min flow scan was separated by a 30 s interval of constant flow rate to allow the system to flush. The duty cycle, shown in Figure 4.2, lasted 5 min, consisting of an upscan during which flow was increased and downscan during which flow was decreased. Raw data were recorded at 1 Hz and each upscan and downscan was processed using the procedure described below.

Time series processing. Due to the continuous variation in flow rate, the ratio of CPC and CCNC residence times was not constant; therefore, the raw CPC and CCNC time series were misaligned. The delay between the two detectors was measured by placing a HEPA filter upstream and recording the flush time for each instrument. Repeating this procedure for different flow rates resulted in an empirical relationship between the delay and flow rate that is well described by $\Delta t = A/Q + B$, where Δt is the delay, Q is the total flow rate in the CCNC, and A and B are constants fitted to the data. To align the data, the CPC time series was shifted by Δt according to the instantaneous flow rate. The CPC and CCNC data reported in Figure 4.2 show an example after the alignment procedure and demonstrate

excellent agreement, as is seen when all condensation nuclei (CN) activated as CCN at high flow rates.

After alignment, the 1 Hz data were averaged into 4 s bins to reduce noise stemming from low counting statistics. The CCN response curve shown in the right panel of Figure 4.2 shows the ratio between the CCNC and CPC time series as a function of flow rate. A sigmoid activation curve [Sullivan *et al.*, 2009] was fitted to the response curve for each upscan and downscan:

$$y = \frac{A_{min} - A_{max}}{1 + \exp(-(Q - Q_{50})/dx)} + A_{max} \quad (4.5)$$

where y is the fitted activated fraction, A_{min} is the lower limit of activation, A_{max} is the upper limit of activation, Q is the flow, Q_{50} is the flow at 50% activation, and dx is the rate of change in activated fraction with respect to the increasing flow rate.

Flow-to-supersaturation calibration. The relationship between Q_{50} and supersaturation was determined by calibration with atomized ammonium sulfate particles [Rose *et al.*, 2008]. The supersaturation at activation was modeled for each dry diameter using E-AIM [Clegg *et al.*, 1998; Wexler and Clegg, 2002] and correlated with the experimentally determined Q_{50} value for those diameters. Figure 4.3 shows an example of the relationship between modeled supersaturation and experimental Q_{50} for 10 dry diameters. A nearly linear calibration curve of the form $s_c = C Q_{50}^E$ was applied to fit the data, where C and E are the fitted constants. Typically, a calibration curve of this type was obtained once per day. Calibrated supersaturation for the upscan and downscan are slightly different, which Moore and Nenes [2009] attributed to wall thermal effects and droplet inertial effects. For

particles of unknown composition, the experimentally determined Q_{50} from size-selected aerosol was used with the calibration to assign the critical supersaturation. The resulting dry diameter and critical supersaturation were then used to compute the κ -value using Equation 4.3. With this method, κ -values could be determined approximately every 2.5 min.

Envelope of resolvable κ -values. The dynamic range of the supersaturation differs slightly for each scan due to small changes in flow rate, but is usually between 0.3% and 0.7%, as shown in Figure 4.3. Combined with the selected dry diameter, this corresponds to an envelope of κ -values that can be resolved for any particular flow scan. Because κ -values are expected to decrease with increasing retention time due to elution of less polar products, we programmed a step-wise increase of dry diameter with each scan, thereby moving the envelope to smaller κ -values. Typically 12 diameters were measured between 50 and 200 nm, corresponding to a κ -envelope of $0.004 < \kappa < 1.22$. An activation curve was fitted to each scan. Any κ -values falling above this envelope of measurable κ -values were discarded; often these values were not resolved because low particle number concentration resulted in poor fits of these activation curves to the data. On average, each chromatogram had 24 κ -values, of which one value outside the envelope was discarded. Kappa-values falling below the envelope were raised to the envelope's lower bound, providing an upper estimate of the κ -value for these compounds.

Reconstructing the κ -value of total SOA from component κ -values. One useful test of the validity of our approach for measuring component κ -values is to reconstruct the κ -value of the total SOA using Equation 4.3, for comparison with the value measured by directly sampling SOA from the chamber into the CCN counter. However, this reconstruction

requires knowledge of the volume fraction of each fractionated component in the sample. To determine these volume fractions, a number of assumptions were made, which are discussed below.

The first assumption is that for a given line pressure and solvent mixture, the atomizer produces a constant number concentration of droplets. In our experiments, the number concentration of droplets is not constant throughout a chromatogram, but increases with retention time because of the gradual increase in the acetonitrile:water ratio. This lowers the surface tension of the solvent mixture, leading to increased droplet breakup. This is demonstrated in Figure 4.4, which shows the size distribution for pentadecane + Cl SOA. This experiment was chosen to characterize the atomizer output because a continuum of products eluted from the HPLC column without gaps. The number concentration obtained from integration over the size distribution increased from $\sim 6 \times 10^4 \text{ cm}^{-3}$ at 2 – 13 min to $\sim 16 \times 10^4 \text{ cm}^{-3}$ at 35 – 46 min retention time. The atomizer would have produced a constant number concentration if it had not been affected by the increasing acetonitrile fraction, which caused an estimated threefold increase in number concentration in the 60 min scan. We corrected for this increase by scaling the measured number concentration at time $t + \Delta t$ using a linear gradient, making it equal to number concentrations measured at time t . This number scaling was performed for all experiments, providing a quantity N_{scaled} for each retention time.

The second assumption is that the shape of the atomized droplet size distribution is constant, implying that the dried aerosol distribution shifts to larger diameters with increasing droplet solute concentration. The number density of particles at diameter $D + \Delta D$

is lower than at diameter D provided that the selected diameter is larger than that of the mode diameter. Mass concentrations of solute in the filter sample were generally similar between experiments, and particles with $50 < D_d < 200$ nm were used for all HPLC experiments. Given the observed mode diameters in Figure 4.4, we assume that our diameters were sampled along the descending branch of the size distribution. A curve of the form $N = F D_d^{-G}$ approximates the atomized particle size at the upper tail of a lognormal distribution, where N is the number concentration, D_d is dry diameter, and F and G are constants. We compute the effective number concentration $N_{D,ref}$ we would expect at a selected reference diameter using

$$N_{D,ref} = N_{scaled} \left(\frac{D_{ref}}{D_d} \right)^{-G} \quad (4.6)$$

where $G = 2 \pm 2$ captures the full range of slopes. $G = 0$ corresponds to a uniform size distribution and $G = 4$ captures the observed upper end of the slope produced by the atomizer.

The third assumption is that the mode diameter of the dried aerosol size distribution is smaller than the diameters we used in our experiments, which allows us to use Equation 4.6 as an estimate of the number concentration at the reference diameter. The quantity $N_{D,ref}$ serves as proxy for the amount of solute in the eluate. This is because higher solute concentrations correspond to a shift towards larger mode diameters [*Liu and Lee, 1975*], thereby raising the number concentration of particles larger than the mode diameter. The increase in number concentration with higher solute concentration is nearly linear if the fixed reference diameter is much larger than the mode diameter (see Appendix D). Thus, the total

volume and corresponding volume fractions are obtained by numerical integration of the chromatogram. Formally the volume fraction of the t^{th} scan is given by:

$$\epsilon_i = \frac{\int_{scan} N_{D,ref} dt}{\int_{chromatogram} N_{D,ref} dt} \quad (4.7)$$

An example chromatogram including the raw time series and the processed κ values is shown in Figure 4.5 for SOA generated from the reaction of 1,5-cyclooctadiene + NO₃ radicals. We note that in each chromatogram there is an initial peak occurring at $t \sim 3$ min. This peak contains all compounds which are not retained by the C18 column. The peak was generally narrow and the compounds were highly hygroscopic which prevented us from capturing it consistently in our setup. We therefore excluded the first peak from the analysis of all the chromatograms.

The individual κ_i and ϵ_i were aggregated into histograms shown in Figure 4.6. These were constructed in log- κ space using geometrically spaced κ bins to achieve equidistant histogram bars. Bar heights were determined by summing the ϵ_i associated with κ_i falling within the bin bounds. The choice of bin width has no effect on the total SOA κ -value, which was computed from the κ_i and ϵ_i for each scan cycle using the mixing rule described by Equation 4.4. This volume-weighted average value is indicated on each histogram.

Uncertainties and reproducibility of individual κ measurements. The main uncertainties of this procedure stem from the increase of particle number concentration with retention time due to droplet breakup and the slope of the descending branch of the size distribution. Repeating the analysis with no scaling parameter results in a $\sim 6\%$ shift in the reconstructed κ -value. Changing the slope parameter G by ± 2 leads to an average difference

in reconstructed κ -value of $\pm 9\%$ depending on the distribution of products. Including the chromatogram's initial peak resulted in a $\sim 20\%$ increase in the reconstructed κ -value. Faster scans could be used to better capture this peak. We tested the reproducibility of the method by splitting the filter extract into two samples that were analyzed separately. Figure 4.5 shows the HPLC eluate and κ -values for the repeated injection of a 1,5-cyclooctadiene + NO_3 filter extract, and Figure 4.6 shows κ distributions of several repeat injections. The chromatograms and resultant reconstructed κ -values generally compare well ($R^2 = 0.98, n = 4$).

4.3 Results and discussion

The chromatogram shown in Figure 4.5 for SOA generated from the reaction of 1,5-cyclooctadiene + NO_3 radicals contains some peaks as narrow as ~ 60 to 90 s, typical of single compounds, but is dominated by broader peaks indicative of a highly complex mixture. Kappa-values are reported as a function of retention time and graphed at the estimated time that Q_{50} was observed. The values are spaced unevenly over time because activation may occur at any point during the upscan or downscan. One noteworthy observation from the chromatogram is that constituent compounds making up the SOA samples elute from the HPLC with a continuum of κ -values that decreased almost monotonically with retention time for a single scan. Figure 4.7 pools the relationship between κ -values and retention time for all systems measured using the HPLC-CCN method, showing that there is ~ 1 order of magnitude spread in the κ -values of compounds eluting from the HPLC at any given retention time. The spread demonstrates that κ is not a unique function of

retention time. However, the κ -value of the HPLC eluate generally decreased with retention time, as expected, since in reversed-phase chromatography compounds elute in order of decreasing polarity and less polar compounds are expected to be less hygroscopic.

Figure 4.8 summarizes the hygroscopicity distributions for several systems, grouped by the reconstructed SOA κ -value obtained via the volume-weighted integration of the chromatogram. The data show that SOAs with similar reconstructed κ -values can have substantially different underlying κ distributions, which reflect differences in the hygroscopicities of the constituent compounds. For example, whereas the reconstructed κ -values for SOA formed from the reactions of 1,3,5,7-cyclooctatetraene + NO₃ and 3-methyl furan + OH in the presence of NO_x (columns 3 and 4, row 1) were similar, at $\kappa = 0.05$ and $\kappa = 0.06$, respectively, the first SOA had a broad distribution of values that ranged from about 0.02 to 0.20 while the second SOA had a narrow distribution centered at 0.06. Similarly, SOA formed from the reactions of cyclohexene + O₃ and cyclooctane + OH without NO_x had the same reconstructed κ -value of 0.22, but whereas the first SOA had a narrow distribution of values centered at 0.20 the second SOA had a much broader distribution (columns 3 and 4, row 3). Thus, while the hygroscopicity of individual products may vary substantially, the volume-weighted average is less sensitive to these variations, as shown by the tendency for κ -values of SOA formed from different VOC reactions to be similar (e.g. from α -pinene ozonolysis [Prenni *et al.*, 2007] and photooxidation of isoprene [King *et al.*, 2007]).

In an attempt to substantiate this conclusion, in Figure 4.9 we compare the reconstructed SOA κ -values (κ_{HPLC}) to the total SOA κ -values measured by online analysis

of SOA sampled directly from the chamber (κ_{online}). The values correlate reasonably well, with a trend in the data given by $\kappa_{HPLC} = 1.19 \times \kappa_{online}$ ($R^2 = 0.66$, $n = 24$). Although there appears to be a slight high bias in the HPLC-derived values, we consider the agreement to be good, especially given the assumptions that were necessary to obtain the volume fractions of eluting compounds in the mixture. The high bias in the HPLC-derived values occurs despite the removal of the first diameter in each scan, whose κ -value was typically very high. Although the HPLC-CCN measurements had a higher time resolution than the online CCN measurements, sharp peaks in the chromatogram sometimes eluted before a flow scan was completed. This forced the measured κ -values into bins of similar retention time. Specifically, if CCN activation occurs just before a peak in the chromatogram, the κ -value attributed to the peak will reflect the κ -value at activation, measured close to but not concurrently with the κ -value at the time of the peak. The scanning flow CCN duty cycle should be shortened in future applications of this technique to avoid this issue. Future studies with reduced measurement uncertainty could also explore the possibility of aerosol constituents mixing in a manner inconsistent with the ZSR assumption.

We believe that the SOA κ distributions shown here have the potential to provide quantitative links between SOA hygroscopicity and the chemical reaction mechanisms involved in SOA formation. Because the wealth of data presented here is beyond the scope of complete analysis at this time, we focus on two particular systems to demonstrate this potential.

Two experiments were performed with 1-decene + O₃ in which the reaction conditions were identical except for the amount of H₂O present in the chamber. Figure 4.10

(column 1) shows the κ frequency distributions resulting from these experiments. Briefly, the chemistry of the reaction [Tobias and Ziemann, 2001] can be summarized as follows: the reaction between 1-decene and O₃ results in the formation of formaldehyde and nonanal, C₁ and C₉ stabilized Criegee intermediates (SCI), and some minor C₁ and C₉ carboxylic acids. Subsequently, the C₁-SCI reacts further to form formic acid and other small products, but reactions of C₁-SCI do not form aerosol. The C₉-SCI reacts with H₂O, formaldehyde, nonanal, and formic acid to produce α -hydroxy-nonyl-hydroperoxide, a C₁₀ and a C₁₈ secondary ozonide (SOZ), and α -alcyloxy-nonyl-hydroperoxide, respectively. The C₁₀ SOZ is volatile and not expected to be in the condensed phase. The relative quantity of the other products depends on the availability of H₂O molecules. At low relative humidity, the dominant product is the C₁₈ SOZ, and as RH is increased, the product distribution shifts towards α -hydroxy-nonyl-hydroperoxide. The C₁₈ SOZ is expected to have a lower κ -value than the α -hydroxy-nonyl-hydroperoxide due to its large molar volume and lower O:C ratio (κ scales inversely with molar volume [Petters *et al.*, 2009a] and correlates with the O:C ratio [Jimenez *et al.*, 2009, Chang *et al.*, 2010, Duplissy *et al.*, 2011]). The observed κ distributions are consistent with this chemical mechanism, revealing a cluster of low- κ products when the reaction RH is low (20%) and an increased fraction of high- κ products when the reaction proceeds at high RH (82%). However, even at high RH some low- κ compounds remain visible in the spectra. These may be due to the formation of peroxyhemiacetals from the reaction of the α -hydroxy-nonyl-hydroperoxide with gas phase aldehydes occurring on the surface of the particle [Tobias and Ziemann, 2001]. The

peroxyhemiacetal is expected to have a lower κ -value because of its larger molar volume and lower O:C ratio, similar to the C₁₈ SOZ.

Another set of experiments was performed by reacting *n*-decane and *n*-pentadecane with Cl atoms. Chlorine atoms initiate reaction by abstracting H atoms from the carbon chain, similarly to H-atom abstraction by OH radicals. The degree of oxidation can be controlled by the amount of Cl₂ added to the chamber and the duration of blacklight exposure. In our experiment the *n*-decane + Cl₂ mixture was irradiated twice, with a separate filter sample collected after each irradiation. *n*-Pentadecane experiments were performed at various Cl:VOC ratios. Because the aerosol collected after the second irradiation was more oxidized, we expect its κ -value to be higher. The histograms in Figure 4.10 (column 2) and Figure 4.6 confirm this prediction, showing that the κ frequency distribution is generally shifted towards higher κ -values when more oxidant was present. The less hygroscopic products ($\kappa < 0.10$) become more hygroscopic while the products at the higher end of the distribution ($\kappa > 0.10$) appear unchanged. One possible explanation is a SOA formation mechanism similar to one suggested by *Robinson et al.* [2007], in which the SOA becomes more highly oxidized over time due to coupling between gas-phase oxidation and gas-particle partitioning. In this scenario, semi-volatile products present in the gas phase undergo further reactions to form more highly oxidized products that condense due to their lower volatility. The semi-volatile products lost from the gas phase by reaction are subsequently replaced by evaporation of less oxidized compounds from the particles, maintaining gas-particle partitioning equilibrium. The net result is that particles become more oxidized as the less oxidized products are replaced by more oxidized products. In our examples, the low- κ

products are expected to be more volatile than the high- κ products, and are thus replaced by these high- κ products in the particles as oxidation proceeds.

Another application of the HPLC-CCN method is to measure κ -values for compounds that are formed in chamber reactions but are otherwise inaccessible for CCN studies because they are not commercially available. This can be done, for example, by performing chamber experiments with VOC-oxidant systems that yield a small number of SOA products that can be separated by HPLC. The relationship between hygroscopicity and polarity shown in Figure 4.7 suggests that a compound's κ -value can be predicted by analysis of molecular functional groups. Further tests can be designed to probe the relationship between functional groups and κ -value by coupling the HPLC output to a chemical composition measurement while simultaneously measuring the κ -value.

Our hygroscopicity frequency distributions extend the results of *Asa-Awuku et al.* [2010], adding finer κ resolution. In their study, the CCN properties were determined from filter extracts using pure water. The water-soluble SOA was found to have an average κ -value of ~ 0.3 , and the remaining sample was assumed to have $\kappa = 0$. Applying the mixing rule, the overall κ -value was thus found to be the volume fraction of water-soluble organic carbon multiplied by 0.3. In this study we extracted SOA using ethyl acetate, a moderately polar solvent, and fractionated the extract by HPLC using acetonitrile-water mixtures. Because of the large range in component polarities indicated by the chromatograms, we expect that filter extraction with water, a highly polar solvent, would be a less efficient than with ethyl acetate. The bulk value of $\kappa = 0.3$ for water-soluble SOA found by *Asa-Awuku et al.* [2010] is likely the average of a broader range of constituent κ -values. Although our data

sometimes shows the presence of compounds with $\kappa < 0.004$, i.e. compounds that do not activate at the diameter and supersaturation combination achieved in our setup, their fraction is generally small. As is shown in Figure 4.7, some of the κ -values measured here were higher than 0.3, suggesting the presence of low molecular weight organic compounds [Petters *et al.*, 2009a]. We therefore believe that a binary distinction between water-soluble and water-insoluble ($\kappa = 0$) organic compounds does not capture the full complexity of the hygroscopicity distribution of SOA components. Many of the hygroscopicity distributions, however, are either bimodal, do not contain products with $\kappa < 0.05$, or both (cf. Figure 4.8), and thus describing organic aerosol mixtures as the combination of a hygroscopic and non-hygroscopic fraction might be suitably accurate for many applications.

4.4 Summary and conclusions

We present a new method, HPLC-CCN analysis, which couples high-performance liquid chromatography with scanning flow CCN analysis to characterize the distribution of the hygroscopicity parameter for polarity-separated constituents of complex SOA. The observed distributions reveal that the investigated SOA comprises a diverse array of products with hygroscopicities in the range $\sim 0 < \kappa < \sim 0.4$, with some product κ -values below the measurement envelope. Some SOA systems are composed of a few products with distinct κ -values while others exhibit a broad spectrum of component κ -values. For two selected systems we show that the distribution of SOA κ -values is consistent with our mechanistic understanding of SOA formation. For example, we demonstrate that our method resolves changes in the hygroscopicity distribution of SOA formed from the 1-decene + O₃ reaction –

changes consistent with our expectation of the product distribution for reactions run at different relative humidities.

Our results show that the distributions of constituent κ -values vary widely over a range of SOA systems. This is consistent with the range of chemical mechanisms and products that govern the formation of SOA from the different VOC and oxidant combinations. Most distributions are broad and consist of a continuum of κ -values rather than a pseudo-binary mixture of water-soluble and water-insoluble ($\kappa = 0$) compounds. However, the CCN activity of the total SOA varies less, due to the averaging effect of the mixture. We demonstrate that total SOA κ -values can be reconstructed from those of the constituents resolved by the HPLC separation. For the 24 systems studied here, the reconstructed κ -values agreed well with the total SOA κ -values measured by direct sampling and analysis of chamber SOA ($R^2 = 0.66$, $n = 24$). Because SOA comprises many compounds with a broad spectrum of κ -values, and because the κ of the total SOA is a volume-weighted average of these values, it is reasonable that SOAs formed from the reactions of hundreds of VOCs with OH radicals, O₃, and NO₃ radicals have relatively smaller variability in their net κ -value despite the different sources and compositions.

The HPLC method separates compounds according to the polarity of the molecules, with less polar products eluting at later times. Not surprisingly, we found that κ -values decreased with increasing retention time and thus with decreasing polarity. However, the retention time did not unambiguously determine the κ -value, showing ~ 1 order of magnitude spread for any given retention time. Nevertheless, the relationship between a compound's κ -value and its polarity suggests that a relationship may exist between κ -value, functional

group composition, and carbon number, the latter of which determine the compound's polarity.

There are several limitations to the HPLC-CCN technique presented here. Due to the low time resolution, some narrow peaks in the chromatogram could have been mis-classified by the CCN analysis, resulting in mismatch between the measured κ -value and its assigned volume fraction. Future studies may overcome this limitation by increasing the scan rate. Several assumptions were necessary to characterize the changing particle size distribution and relate the instantaneous particle concentration to the solute mass in the eluate (Section 4). We estimate that these assumptions lead to $\sim \pm 10\%$ uncertainty in the reconstructed κ -values.

The method described here might also be useful in future studies for constraining proposed chemical mechanisms of SOA formation. For simple systems with a few reaction products, the HPLC separation might yield individual product peaks for which κ can be determined. If products formed by the reaction are modeled and product κ -values can be computed, the chemical mechanisms will yield a hygroscopicity distribution that can be directly compared to observations. The resultant κ distributions are further useful in exploring mechanisms that relate changes in κ to chemical reactions such as chemical aging, as we demonstrated by contrasting different oxidation stages of SOA generated from the oxidation of *n*-decane and *n*-pentadecane. Future applications of this method could be used in this manner to effectively combine modeling and observations to improve our mechanistic understanding of the formation and evolution of organic aerosol.

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4.6 References

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4.7 Figures

Figure 4.1. Schematic of the instrument setup.

Figure 4.2. Left plot: example duty cycle illustrating the flow rate (grey line), CCN (solid black line) and CN (dashed line) time series. Right plot: Inferred CCN activation curve for the upscan (black circles) and downscan (red circles). Each circle represents a 4 s average. Lines represent a fit to the data from which the flow at 50% activation is inferred.

Figure 4.3. Relationship between CCNC flow rate at 50% activated fraction and calculated supersaturation percent for size selected ammonium sulfate particles

Figure 4.4. Size distribution of particles from the HPLC CCN measurement system for SOA from an *n*-pentadecane + Cl experiment, as measured by the online CCN measurement setup. Times reported are the start times for the 11 min scans. The stepped lines show the measured size distribution over the scan, and the dotted lines show a fit to the data. The integrated total count over the fit, N_{tot} , the mode diameter, D , and the standard deviation, σ , are noted in a table below the distributions.

Figure 4.5. CN (black lines) and CCN (grey lines) concentrations vs. HPLC retention time, for the SOA from 1,5-cyclooctadiene + NO₃ A (top) and B (middle) using the same filter extract. Bottom timeseries: κ -values (symbols) and envelope of measurable κ -values (grey lines) vs. HPLC retention time for 1,5-cyclooctadiene + NO₃ A (circles) and B (triangles). The selected dry diameter is indicated below the symbols. Scan A was terminated prematurely due to erroneous software settings.

Figure 4.6. Kappa frequency distributions of pairs of repeated HPLC experiments using the same filter extract. Experiment A in the pair is in the first row, and experiment B is in the second row. The oxidant:precursor ratio for each pentadecane + Cl chamber experiment is indicated on the plot as Cl : C₁₅. The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value.

Figure 4.7. The HPLC eluate hygroscopicities for all experiments as a function of their retention time.

Figure 4.8. Kappa frequency distributions of selected SOA systems. The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value.

Figure 4.9. Scatter plot of reconstructed HPLC eluate κ -values versus κ -values measured for SOA sampled directly from the chamber. The 1:1 line is printed in grey behind the data. Numbers on the graph correspond to the experiment number given in Table 4.1. Horizontal bars indicate the sensitivity of the HPLC κ -value to the choice of exponent G in the size correction. Vertical bars indicate the uncertainty in the online κ -value determined from the reproducibility of the calibration.

Figure 4.10. Kappa frequency distributions of SOA from the 1-decene + O₃ and *n*-decane + Cl chamber experiments. The overall κ -value, as reconstructed by Equation 4.4, is indicated with a small vertical line and printed value.

4.8 Tables

Table 4.1. Summary of oxidation reactions performed. The number in column 1 is an identifier for experiments shown in Figure 4.8. V_{chamber} denotes the volume of the chamber used for the experiment.

#	Label: VOC + Oxidant	VOC [ppmv]	Oxidant or precursors [ppmv]	V_{chamber} [m ³]	K_{chamber} [-]	K_{HPLC} [-]
1	1-decene + O ₃ , RH 20% *	1.2	O ₃ 7.0	1.7	0.04	0.02
2	ocimene + NO ₃	0.7	N ₂ O ₅ 2.0	1.7	0.04	0.04
3	1,3-cyclohexadiene + NO ₃	0.3	N ₂ O ₅ 0.6	1.7	0.03	0.05
4	1,5-cyclooctadiene + NO ₃ A	0.3	N ₂ O ₅ 0.6	1.7	0.07	0.05
5	1,3,5,7-cyclooctatetraene + NO ₃	0.3	N ₂ O ₅ 1.2	1.7	0.03	0.05
6	1,5-cyclooctadiene + NO ₃ B	0.3	N ₂ O ₅ 0.6	1.7	0.07	0.06
7	3-methyl furan + OH with NO _x **	10.0	CH ₃ ONO / NO 10 / 10	5.9	0.07	0.06
8	1-decene + O ₃ , RH 82%	1.2	O ₃ 7.0	1.7	0.09	0.08
9	<i>n</i> -pentadecane + Cl (9 July A)	0.5	Cl ₂ 2.0	5.9	0.06	0.08
10	<i>n</i> -pentadecane + Cl (9 July B)	0.5	Cl ₂ 2.0	5.9	0.06	0.08
11	<i>n</i> -decane + Cl, 1 st irr.	0.5	Cl ₂ 8.0	5.9	0.08	0.09
12	<i>n</i> -pentadecane + Cl (13 July)	0.1	Cl ₂ 0.2	5.9	0.09	0.09
13	<i>n</i> -pentadecane + Cl (16 July B)	0.5	Cl ₂ 0.5	5.9	0.05	0.09
14	cyclodecane + OH with NO _x	0.3	CH ₃ ONO / NO 6.5 / 5.5	5.9	0.11	0.10
15	<i>n</i> -pentadecane + Cl (16 July A)	0.5	Cl ₂ 0.5	5.9	0.05	0.10
16	1-octene + O ₃ + 2-propanol	0.4	O ₃ 7.0	1.7	0.11	0.12
17	<i>n</i> -pentadecane + Cl (8 July B)	0.1	Cl ₂ 2.0	5.9	0.15	0.15
18	<i>n</i> -pentadecane + Cl (8 July A)	0.1	Cl ₂ 2.0	5.9	0.15	0.15
19	<i>m</i> -xylene + OH with NO _x **	4.0	CH ₃ ONO / NO 4.0 / 4.0	5.9	0.07	0.16
20	1,2-dimethyl cyclohexene + O ₃	0.5	O ₃ 7.0	1.7	0.15	0.17
21	<i>n</i> -decane + Cl, 2 nd irr.	0.5	Cl ₂ 8.0	5.9	0.16	0.17
22	cyclooctene + O ₃	1.1	O ₃ 7.0	1.7	0.12	0.20
23	cyclohexene + O ₃	1.0	O ₃ 7.0	1.7	0.17	0.22
24	cyclooctane + OH w/o NO _x	5.6	TME / O ₃ *** 7.0 / 1.4	1.7	0.13	0.22

* All ozonolysis reactions included 1000:1 (ppm:ppm) excess of cyclohexane to scavenge OH radicals formed during the reaction, and β -caryophyllene as a precursor to seed aerosol.

** Experiments 7 and 19 used dioctyl sebecate (DOS) seed aerosol.

*** TME = trimethyl ethylene (2,3-dimethyl-2-butene); experiment 24 used β -caryophyllene as a precursor to seed aerosol.

5. SUMMARY

SOA was generated by oxidizing organic precursor gases in a Teflon environmental chamber. Six linear and cyclic alkenes were oxidized by dark ozonolysis with an OH scavenger and β -caryophyllene as a precursor to seed aerosol; three cyclic alkenes and one monoterpene were oxidized without irradiation by NO_3 , formed by the thermal dissociation of N_2O_5 , with an oxidant to organic double bond ratio of ~ 1 ; four cyclic alkanes and aromatic compounds were oxidized by OH, formed by either irradiation of CH_3ONO with an O_3 scavenger or by dark ozonolysis, and with either no seed aerosol, DOS seed, or β -caryophyllene precursor to form seed; and two linear alkanes were oxidized by Cl atoms formed by the irradiation of Cl_2 .

The hygroscopicity of SOA was summarized by CCN activation statistics during the chamber experiments and the hygroscopicity parameter, κ , was computed. Filter samples were taken after ~ 1 hr when reactions had concluded and extracted using ethyl acetate. These extracts were fractionated using reverse-phase high-precision liquid chromatography with a linear gradient of water-to-acetonitrile eluent, such that the solubility of the eluting compounds in water decreased with retention time. The hygroscopicity of the eluting compounds was measured using a fast flow-scanning instrument configuration to increase the CCN activation time resolution to 0.4 min^{-1} . The κ -value of the total SOA sample was reconstructed from the fractionated SOA κ -values by estimating the volume fraction associated with each κ measurement. The volume fraction was obtained by numerical

integration of the chromatogram; adjustments were necessary to correct for the changing water content in the eluent and for the changing particle diameters selected for analysis.

The distributions of κ -values underlying the SOA samples showed a wide range of shapes. The κ -values measured online for whole SOA samples had a narrower range, suggesting that κ -value of the whole sample is not as sensitive to reaction chemistry as the κ -value of individual SOA constituents because it is an average of constituents.

The increase in chamber RH for the second 1-decene + O₃ reaction shifted the κ distribution to higher values; the second irradiation of *n*-decane + Cl also shifted the κ distribution higher. These examples show that a change in the chamber reaction may affect the resulting κ distribution, and that the method presented here might be useful in further studies of reaction mechanisms. For example, the distribution of reaction products from α -pinene + O₃, modeled by a chemical mechanism such as the Master Chemical Mechanism (MCM) could be compared to the underlying κ distribution in the resultant SOA to associate a κ -value with each reaction product. The results from various κ distributions could be extended to explicitly treat the interaction of VOC oxidation products with water vapor, given the reaction precursors and conditions.

In future studies of underlying κ distributions using the method presented here, a faster flow scan would be helpful to resolve some of the narrow peaks in the chromatogram. The results may also be improved by using a scanning mobility particle sizer to survey the size distribution of eluting particles with higher time resolution than the method used here. A

more precise size distribution would have precluded the approximations necessary in this study to assign a volume fraction to each constituent κ -value.

5.1 References

Saunders, S. M., M. E. Jenkin, R. G. Derwent, and M. J. Pilling (2003), Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3(1), 161–180, doi: 10.5194/acp-3-161-2003.

APPENDICES

APPENDIX A

Tabulated results

Table A.1a. 1-Decene + O₃: Detailed CN count for each particle dry diameter measured. CN at D_{ref} is calculated using Equation 4.6 with an exponential slope parameter $G = -2$. The number fraction is calculated including CN counted between flow scans, and the adjusted fraction excludes the first scan. The average κ calculation is shown in the corresponding table below (part b).

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	70	265	266	141	141	0.0074		0.3469
2	75	299	300	22	26	0.0013	0.0013	0.2998
3	81	299	300	8	11	0.0006	0.0006	0.1904
4	88	299	300	6	10	0.0005	0.0005	0.1116
5	95	299	300	6	12	0.0006	0.0006	0.1351
6	103	299	300	6	13	0.0007	0.0007	
7	111	299	300	3	8	0.0004	0.0004	0.0940
8	120	299	300	2	6	0.0003	0.0003	0.0696
9	131	299	300	12	41	0.0021	0.0021	0.0431
10	142	299	300	24	98	0.0051	0.0051	0.0576
11	154	299	300	21	104	0.0054	0.0054	0.0349
12	168	299	300	264	1521	0.0796	0.0802	0.0364
13	183	299	300	2488	17001	0.8898	0.8966	0.0151
14	200	299	300	14	115	0.0060	0.0060	0.0101
Volume-weighted average κ								0.0179

Scan #	D_d [nm]	Upscan					Downscan					Average κ
		S_c	κ_{orig}	envelope		κ_{final}	S_c	κ_{orig}	envelope		κ_{final}	
1	70	0.38	0.2777	0.0754	0.7037	0.2777	0.31	0.4161	0.0711	0.5370	0.4161	0.3469
2	75	0.26	0.5000	0.0618	0.5631	0.5000	0.57	0.0995	0.0581	0.4504	0.0995	0.2998
3	81	0.32	0.2454	0.0491	0.4531	0.2454	0.44	0.1353	0.0463	0.3427	0.1353	0.1904
4	88	0.43	0.1116	0.0383	0.3482	0.1116	0.26	0.3080	0.0361	0.2636		0.1116
5	95	0.29	0.1892	0.0304	0.2728	0.1892	0.45	0.0811	0.0287	0.2210	0.0811	0.1351
6	103	0.23	0.2450	0.0242	0.2214		0.26	0.1924	0.0249	0.1754		
7	111	0.33	0.0929	0.0196	0.1813	0.0929	0.33	0.0951	0.0183	0.1392	0.0951	0.0940
8	120	0.25	0.1248	0.0152	0.1414	0.1248	0.76	0.0140	0.0144	0.1082	< 0.0144	0.0696
9	131	0.31	0.0625	0.0120	0.1090	0.0625	0.51	0.0238	0.0113	0.0850	0.0238	0.0431
10	142	0.32	0.0484	0.0095	0.0860	0.0484	0.27	0.0669	0.0090	0.0673	0.0669	0.0576
11	154	0.31	0.0390	0.0075	0.0670	0.0390	0.35	0.0307	0.0069	0.0521	0.0307	0.0349
12	168	0.28	0.0364	0.0056	0.0509	0.0364	0.25	0.0447	0.0053	0.0403		0.0364
13	183	0.30	0.0258	0.0043	0.0384	0.0258	0.71	0.0045	0.0041	0.0305	0.0045	0.0151
14	200	0.38	0.0119	0.0033	0.0303	0.0119	0.46	0.0083	0.0031	0.0240	0.0083	0.0101

Table A.1b. 1-Decene + O₃: Detailed κ measurements for each upscan and downscan, for each dry particle diameter. Each upscan and downscan produces a D_d - S_c data pair from which κ_{orig} is calculated. The critical supersaturation, s_c , is defined as $(S_c - 1) \times 100$. The final κ -value (κ_{final}) is adjusted based on the envelope of measurable κ -values. Values above the κ envelope are discarded, and values below the envelope are set to the envelope lower bound.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	5894	5894	0.0071		0.5394
2	63	299	300	368	406	0.0005	0.0005	0.4150
3	67	299	300	145	181	0.0002	0.0002	0.4110
4	71	299	300	699	979	0.0012	0.0012	0.2716
5	75	299	300	1073	1677	0.0020	0.0020	0.2177
6	79	299	300	4213	7304	0.0088	0.0089	0.1627
7	83	299	300	6388	12225	0.0147	0.0148	0.1397
8	88	299	300	16358	35188	0.0422	0.0425	0.1221
9	93	299	300	50881	122242	0.1466	0.1476	0.0761
10	99	299	300	63186	172024	0.2062	0.2076	0.0347
11	104	299	300	87012	261423	0.3134	0.3156	0.0224
12	111	299	300	57919	198229	0.2377	0.2394	0.0226
13	117	299	300	4289	16309	0.0196	0.0197	0.0203
Volume-weighted average κ								0.0411

Table A.2a. Ocimene + NO₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.31	0.6670	0.1207	1.3943	0.6670	0.39	0.4119	0.1077	0.8041	0.4119	0.5394
2	63	0.37	0.3992	0.1036	1.1834	0.3992	0.36	0.4308	0.0935	0.6952	0.4308	0.4150
3	67	0.38	0.3179	0.0891	0.9873	0.3179	0.30	0.5041	0.0769	0.5710	0.5041	0.4110
4	71	0.36	0.2949	0.0716	0.8430	0.2949	0.39	0.2483	0.0641	0.4749	0.2483	0.2716
5	75	0.37	0.2352	0.0603	0.7816	0.2352	0.40	0.2002	0.0543	0.4083	0.2002	0.2177
6	79	0.40	0.1733	0.0520	0.6492	0.1733	0.43	0.1520	0.0465	0.3470	0.1520	0.1627
7	83	0.41	0.1428	0.0446	0.5295	0.1428	0.42	0.1365	0.0404	0.2969	0.1365	0.1397
8	88	0.41	0.1187	0.0373	0.4144	0.1187	0.40	0.1254	0.0337	0.2518	0.1254	0.1221
9	93	0.40	0.1077	0.0315	0.3580	0.1077	0.62	0.0446	0.0287	0.2126	0.0446	0.0761
10	99	0.56	0.0449	0.0264	0.2936	0.0449	0.76	0.0245	0.0236	0.1756	0.0245	0.0347
11	104	0.75	0.0219	0.0229	0.2586	< 0.0229	0.75	0.0220	0.0209	0.1646	0.0220	0.0224
12	111	0.68	0.0217	0.0234	0.2169	< 0.0234	0.68	0.0217	0.0216	0.1310	0.0217	0.0226
13	117	0.60	0.0236	0.0188	0.2026	0.0236	0.71	0.0170	0.0168	0.1150	0.0170	0.0203

Table A.2b. Ocimene + NO₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	2468	2468	0.0407		0.4889
2	63	299	300	249	274	0.0045	0.0047	0.4250
3	67	299	300	104	130	0.0021	0.0022	0.3938
4	71	299	300	180	252	0.0042	0.0044	0.1635
5	75	299	300	290	452	0.0075	0.0078	0.2223
6	79	299	300	490	849	0.0140	0.0146	0.1794
7	83	299	300	719	1375	0.0227	0.0237	0.1522
8	88	299	300	1883	4051	0.0668	0.0696	0.0946
9	93	299	300	18347	44079	0.7265	0.7572	0.0301
10	99	299	300	2350	6399	0.1055	0.1100	0.0443
11	104	299	300	113	341	0.0056	0.0058	0.0752
Volume-weighted average κ								0.0462

Table A.3a. 1,3-Cyclohexadiene + NO₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.35	0.5233	0.0911	0.6573	0.5233	0.37	0.4544	0.0832	0.5270	0.4544	0.4889
2	63	0.37	0.4103	0.0782	0.5463	0.4103	0.35	0.4396	0.0722	0.4551	0.4396	0.4250
3	67	0.32	0.4433	0.0656	0.4493	0.4433	0.36	0.3443	0.0597	0.3782	0.3443	0.3938
4	71	0.53	0.1357	0.0547	0.3699	0.1357	0.45	0.1914	0.0503	0.3161	0.1914	0.1635
5	75	0.35	0.2623	0.0462	0.3211	0.2623	0.42	0.1822	0.0431	0.2653	0.1822	0.2223
6	79	0.38	0.1963	0.0398	0.2736	0.1963	0.41	0.1626	0.0368	0.2310	0.1626	0.1794
7	83	0.39	0.1559	0.0341	0.2355	0.1559	0.40	0.1484	0.0317	0.1982	0.1484	0.1522
8	88	0.41	0.1185	0.0285	0.1969	0.1185	0.54	0.0707	0.0265	0.1650	0.0707	0.0946
9	93	0.75	0.0306	0.0242	0.1676	0.0306	0.76	0.0295	0.0226	0.1416	0.0295	0.0301
10	99	0.58	0.0423	0.0202	0.1401	0.0423	0.55	0.0463	0.0186	0.1129	0.0463	0.0443
11	104	0.46	0.0576	0.0172	0.1201	0.0576	0.36	0.0929	0.0160	0.0991	0.0929	0.0752

Table A.3b. 1,3-Cyclohexadiene + NO₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	3008	3008	0.0109		0.3341
2	63	299	300	481	530	0.0019	0.0019	0.3345
3	67	299	300	402	502	0.0018	0.0018	0.2616
4	71	299	300	2735	3830	0.0139	0.0141	0.2190
5	75	299	300	1844	2881	0.0104	0.0105	0.1777
6	79	299	300	5755	9977	0.0361	0.0365	0.1389
7	83	299	300	13980	26752	0.0968	0.0979	0.1043
8	88	299	300	18756	40345	0.1460	0.1476	0.0751
9	93	299	300	40110	96364	0.3486	0.3524	0.0286
10	99	299	300	29693	80839	0.2925	0.2957	0.0195
11	104	2	2	-153	-460	-0.0017	-0.0017	
12	200	299	302	1064	11825	0.0428	0.0433	0.0092
Volume-weighted average κ								0.0486

Table A.4a. 1,5-Cyclooctadiene + NO₃ A: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.43	0.3413	0.0904	0.6182	0.3413	0.44	0.3270	0.0831	0.5243	0.3270	0.3341
2	63	0.40	0.3449	0.0799	0.5473	0.3449	0.41	0.3241	0.0716	0.4481	0.3241	0.3345
3	67	0.44	0.2363	0.0652	0.4541	0.2363	0.40	0.2869	0.0597	0.3664	0.2869	0.2616
4	71	0.40	0.2393	0.0544	0.3796	0.2393	0.44	0.1988	0.0502	0.3153	0.1988	0.2190
5	75	0.43	0.1805	0.0459	0.3183	0.1805	0.43	0.1748	0.0425	0.2627	0.1748	0.1777
6	79	0.45	0.1386	0.0398	0.2744	0.1386	0.45	0.1392	0.0364	0.2171	0.1392	0.1389
7	83	0.45	0.1184	0.0341	0.2382	0.1184	0.52	0.0902	0.0315	0.1937	0.0902	0.1043
8	88	0.49	0.0860	0.0286	0.1981	0.0860	0.56	0.0642	0.0265	0.1645	0.0642	0.0751
9	93	0.71	0.0345	0.0244	0.1676	0.0345	0.87	0.0227	0.0224	0.1392	0.0227	0.0286
10	99	0.87	0.0190	0.0202	0.1388	< 0.0202	0.87	0.0187	0.0185	0.1156	0.0187	0.0195
11	104											
12	200	0.35	0.0139	0.0024	0.0169	0.0139	0.62	0.0045	0.0022	0.0141	0.0045	0.0092

Table A.4b. 1,5-Cyclooctadiene + NO₃ A: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	10494	10494	0.0293		0.2464
2	63	299	300	2607	2875	0.0080	0.0082	0.2465
3	67	299	300	1086	1354	0.0038	0.0039	0.2495
4	71	299	300	2643	3702	0.0103	0.0106	0.1871
5	75	299	300	6658	10403	0.0290	0.0299	0.1389
6	79	299	300	12357	21422	0.0598	0.0616	0.1147
7	83	299	300	22625	43295	0.1209	0.1246	0.0784
8	88	299	300	46941	100976	0.2819	0.2904	0.0475
9	93	299	300	45234	108675	0.3034	0.3126	0.0249
10	99	299	300	19220	52327	0.1461	0.1505	0.0207
11	104	1	1	-85	-254	-0.0007	-0.0007	
12	120	299	301	729	2916	0.0081	0.0083	0.0268
Volume-weighted average κ								0.0509

Table A.5a. 1,3,5,7-Cyclooctatetraene + NO₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.51	0.2481	0.0921	0.6200	0.2481	0.51	0.2447	0.0840	0.5290	0.2447	0.2464
2	63	0.47	0.2484	0.0794	0.5426	0.2484	0.47	0.2445	0.0725	0.4449	0.2445	0.2465
3	67	0.43	0.2456	0.0659	0.4479	0.2456	0.43	0.2534	0.0606	0.3740	0.2534	0.2495
4	71	0.44	0.1961	0.0563	0.3760	0.1961	0.46	0.1782	0.0513	0.3440	0.1782	0.1871
5	75	0.46	0.1545	0.0475	0.3409	0.1545	0.51	0.1233	0.0442	0.3177	0.1233	0.1389
6	79	0.45	0.1373	0.0410	0.3128	0.1373	0.55	0.0921	0.0382	0.2636	0.0921	0.1147
7	83	0.54	0.0814	0.0359	0.2913	0.0814	0.57	0.0754	0.0332	0.2228	0.0754	0.0784
8	88	0.55	0.0665	0.0303	0.2207	0.0665	0.84	0.0286	0.0279	0.1804	0.0286	0.0475
9	93	0.84	0.0243	0.0256	0.1845	< 0.0256	0.84	0.0242	0.0237	0.1515	0.0242	0.0249
10	99	0.84	0.0202	0.0213	0.1486	< 0.0213	0.84	0.0201	0.0196	0.1219	0.0201	0.0207
11	104											
12	120	0.59	0.0231	0.0120	0.0809	0.0231	0.51	0.0306	0.0108	0.0632	0.0306	0.0268

Table A.5b. 1,3,5,7-Cyclooctatetraene + NO₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	269	5662	5662	0.0162		0.3534
2	63	299	300	844	931	0.0027	0.0027	0.3311
3	67	299	300	757	943	0.0027	0.0027	0.2920
4	71	299	300	6652	9315	0.0266	0.0270	0.2179
5	75	299	300	3365	5258	0.0150	0.0152	0.1722
6	79	299	300	11419	19796	0.0566	0.0575	0.1343
7	83	299	300	24829	47513	0.1359	0.1382	0.0956
8	88	299	300	23672	50922	0.1456	0.1480	0.0747
9	93	299	300	49309	118465	0.3388	0.3444	0.0277
10	99	299	300	29306	79785	0.2282	0.2320	0.0195
11	104	299	300	3674	11038	0.0316	0.0321	0.0223
Volume-weighted average κ								0.0570

Table A.6a. 1,5-Cyclooctadiene + NO₃ B: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.31	0.6523	0.0928	0.6116		0.42	0.3534	0.0819	0.4681	0.3534	0.3534
2	63	0.39	0.3586	0.0809	0.5269	0.3586	0.43	0.3036	0.0705	0.4062	0.3036	0.3311
3	67	0.41	0.2741	0.0665	0.4356	0.2741	0.38	0.3100	0.0588	0.3343	0.3100	0.2920
4	71	0.41	0.2329	0.0565	0.3642	0.2329	0.44	0.2028	0.0495	0.2836	0.2028	0.2179
5	75	0.43	0.1762	0.0474	0.3076	0.1762	0.44	0.1682	0.0423	0.2376	0.1682	0.1722
6	79	0.45	0.1408	0.0409	0.2659	0.1408	0.47	0.1278	0.0360	0.2007	0.1278	0.1343
7	83	0.44	0.1220	0.0351	0.2277	0.1220	0.59	0.0693	0.0312	0.1782	0.0693	0.0956
8	88	0.48	0.0893	0.0296	0.1912	0.0893	0.58	0.0600	0.0261	0.1473	0.0600	0.0747
9	93	0.72	0.0332	0.0249	0.1632	0.0332	0.89	0.0218	0.0221	0.1211	< 0.0221	0.0277
10	99	0.85	0.0197	0.0207	0.1348	< 0.0207	0.89	0.0181	0.0183	0.1049	< 0.0183	0.0195
11	104	0.79	0.0199	0.0178	0.1171	0.0199	0.70	0.0247	0.0158	0.0858	0.0247	0.0223

Table A.6b. 1,5-Cyclooctadiene + NO₃ B: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	12496	12496	0.0701		0.4511
2	63	299	300	1558	1718	0.0096	0.0103	0.3190
3	67	299	300	288	359	0.0020	0.0022	0.4077
4	71	299	300	340	476	0.0027	0.0029	0.3246
5	75	299	300	841	1314	0.0074	0.0080	0.2122
6	79	299	300	1799	3119	0.0175	0.0188	0.1648
7	83	299	300	79568	152262	0.8547	0.9191	0.0547
8	88	299	300	2788	5996	0.0337	0.0362	0.1194
9	93	299	300	173	415	0.0023	0.0025	0.1543
Volume-weighted average κ								0.0648

Table A.7a. Methyl furan + OH with NO_x: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.32	0.6278	0.1186	1.5018	0.6278	0.48	0.2743	0.1064	0.8088	0.2743	0.4511
2	63	0.43	0.2949	0.1019	1.1534	0.2949	0.40	0.3431	0.0930	0.6734	0.3431	0.3190
3	67	0.37	0.3387	0.0846	1.0651	0.3387	0.31	0.4767	0.0778	0.5560	0.4767	0.4077
4	71	0.32	0.3758	0.0724	0.8017	0.3758	0.38	0.2734	0.0644	0.4689	0.2734	0.3246
5	75	0.39	0.2116	0.0605	0.7064	0.2116	0.39	0.2128	0.0552	0.3879	0.2128	0.2122
6	79	0.43	0.1497	0.0520	0.5588	0.1497	0.39	0.1799	0.0474	0.3402	0.1799	0.1648
7	83	0.60	0.0669	0.0463	0.4754	0.0669	0.75	0.0424	0.0410	0.2906	0.0424	0.0547
8	88	0.47	0.0898	0.0363	0.3918	0.0898	0.37	0.1490	0.0332	0.2468	0.1490	0.1194
9	93	0.33	0.1543	0.0306	0.3294	0.1543	0.28	0.2156	0.0279	0.2107		0.1543

Table A.7b. Methyl furan + OH with NO_x: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	727	727	0.0108		0.6148
2	63	299	300	61	67	0.0010	0.0010	0.5411
3	67	299	300	25	32	0.0005	0.0005	0.2005
4	70	299	300	40	54	0.0008	0.0008	0.3412
5	74	299	300	47	72	0.0011	0.0011	0.3864
6	78	299	300	41	69	0.0010	0.0010	0.3012
7	82	299	300	73	136	0.0020	0.0020	0.2263
8	87	299	300	73	154	0.0023	0.0023	0.1502
9	91	299	300	410	942	0.0140	0.0142	0.1471
10	96	299	300	1030	2636	0.0392	0.0396	0.1435
11	102	299	300	2398	6929	0.1031	0.1042	0.1265
12	108	299	300	8166	26459	0.3938	0.3981	0.1067
13	114	299	300	7797	28146	0.4189	0.4235	0.0295
14	120	299	300	192	768	0.0114	0.0115	0.0175
Volume-weighted average κ								0.0786

Table A.8a. 1-Decene + O₃, RH 82%: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.31	0.6694	0.1489	1.1620	0.6694	0.34	0.5602	0.1322	0.9339	0.5602	0.6148
2	63	0.31	0.5741	0.1213	1.0316	0.5741	0.33	0.5081	0.1152	0.8138	0.5081	0.5411
3	67	0.57	0.1434	0.1059	0.8627	0.1434	0.42	0.2576	0.0974	0.6618	0.2576	0.2005
4	70	0.30	0.4488	0.0905	0.7419	0.4488	0.41	0.2337	0.0858	0.6164	0.2337	0.3412
5	74	0.32	0.3392	0.0762	0.6535	0.3392	0.28	0.4335	0.0720	0.4991	0.4335	0.3864
6	78	0.31	0.2943	0.0652	0.5441	0.2943	0.31	0.3080	0.0621	0.4313	0.3080	0.3012
7	82	0.33	0.2263	0.0561	0.4815	0.2263	0.25	0.3847	0.0530	0.3622		0.2263
8	87	0.37	0.1502	0.0473	0.3907	0.1502	0.26	0.3153	0.0444	0.3120		0.1502
9	91	0.22	0.3837	0.0409	0.3510		0.35	0.1471	0.0388	0.2742	0.1471	0.1471
10	96	0.32	0.1555	0.0351	0.2961	0.1555	0.34	0.1314	0.0330	0.2320	0.1314	0.1435
11	102	0.31	0.1308	0.0295	0.2425	0.1308	0.33	0.1221	0.0275	0.1894	0.1221	0.1265
12	108	0.29	0.1296	0.0243	0.2018	0.1296	0.36	0.0838	0.0232	0.1610	0.0838	0.1067
13	114	0.52	0.0351	0.0209	0.1715	0.0351	0.62	0.0240	0.0199	0.1384	0.0240	0.0295
14	120	0.73	0.0149	0.0181	0.1538	< 0.0181	0.69	0.0166	0.0170	0.1161	< 0.0170	0.0175

Table A.8b. 1-Decene + O₃, RH 82%: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	70	265	266	3982	3982	0.0127		0.3427
2	73	299	300	237	258	0.0008	0.0008	0.3558
3	77	299	300	77	93	0.0003	0.0003	0.3118
4	81	299	300	257	343	0.0011	0.0011	0.2659
5	85	299	300	1542	2274	0.0073	0.0074	0.2340
6	89	299	300	4667	7545	0.0241	0.0244	0.1716
7	94	299	300	13779	24847	0.0795	0.0805	0.1625
8	99	299	300	17481	34965	0.1119	0.1134	0.1442
9	104	299	300	17146	37848	0.1211	0.1227	0.1073
10	109	299	300	17905	43415	0.1390	0.1408	0.0956
11	115	299	300	19977	53918	0.1726	0.1749	0.0554
12	121	299	300	22256	66500	0.2128	0.2156	0.0327
13	128	299	300	9542	31906	0.1021	0.1034	0.0168
14	135	299	300	1118	4159	0.0133	0.0135	0.0133
15	142	299	300	77	318	0.0010	0.0010	0.0168
16	150	299	300	13	59	0.0002	0.0002	0.0208
Volume-weighted average κ								0.0813

Table A.9a. *n*-Pentadecane + Cl (9 July A): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	70	0.35	0.3371	0.0848	0.7730	0.3371	0.34	0.3482	0.0794	0.5773	0.3482	0.3427
2	73	0.29	0.4238	0.0745	0.6563	0.4238	0.35	0.2879	0.0689	0.4984	0.2879	0.3558
3	77	0.22	0.6006	0.0633	0.5603		0.31	0.3118	0.0587	0.4336	0.3118	0.3118
4	81	0.22	0.5115	0.0547	0.4972		0.31	0.2659	0.0511	0.3670	0.2659	0.2659
5	85	0.32	0.2199	0.0481	0.4377	0.2199	0.30	0.2480	0.0438	0.3561	0.2480	0.2340
6	89	0.34	0.1725	0.0424	0.4216	0.1725	0.34	0.1707	0.0395	0.3072	0.1707	0.1716
7	94	0.32	0.1606	0.0366	0.3616	0.1606	0.32	0.1644	0.0343	0.2668	0.1644	0.1625
8	99	0.31	0.1479	0.0318	0.3270	0.1479	0.32	0.1404	0.0292	0.2256	0.1404	0.1442
9	104	0.32	0.1215	0.0272	0.2690	0.1215	0.36	0.0930	0.0248	0.1877	0.0930	0.1073
10	109	0.35	0.0872	0.0235	0.2276	0.0872	0.32	0.1039	0.0218	0.1612	0.1039	0.0956
11	115	0.38	0.0622	0.0234	0.1940	0.0622	0.43	0.0486	0.0189	0.1724	0.0486	0.0554
12	121	0.46	0.0374	0.0176	0.2145	0.0374	0.53	0.0280	0.0164	0.1298	0.0280	0.0327
13	128	0.58	0.0197	0.0152	0.1455	0.0197	0.69	0.0137	0.0139	0.1010	< 0.0139	0.0168
14	135	0.71	0.0112	0.0128	0.1180	< 0.0128	0.64	0.0137	0.0119	0.0893	0.0137	0.0133
15	142	0.47	0.0218	0.0111	0.1020	0.0218	0.64	0.0119	0.0102	0.0770	0.0119	0.0168
16	150	0.35	0.0328	0.0095	0.0848	0.0328	0.68	0.0088	0.0087	0.0623	0.0088	0.0208

Table A.9b. *n*-Pentadecane + Cl (9 July A): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	7622	7622	0.0056		0.4923
2	64	299	300	1206	1372	0.0010	0.0010	0.3829
3	68	299	300	227	291	0.0002	0.0002	0.4197
4	72	299	300	897	1292	0.0010	0.0010	0.2858
5	77	299	300	5153	8487	0.0063	0.0063	0.1952
6	82	299	300	24300	45387	0.0336	0.0338	0.1628
7	87	299	300	57716	121348	0.0899	0.0904	0.1585
8	93	299	300	74791	179685	0.1332	0.1340	0.1482
9	100	299	300	69745	193736	0.1436	0.1444	0.1032
10	106	299	300	63150	197099	0.1461	0.1469	0.0721
11	114	299	300	56605	204345	0.1514	0.1523	0.0517
12	121	299	300	55529	225833	0.1674	0.1683	0.0326
13	130	299	300	28720	134827	0.0999	0.1005	0.0167
14	139	299	300	4549	24416	0.0181	0.0182	0.0108
15	149	299	300	476	2938	0.0022	0.0022	0.0115
16	160	299	300	88	625	0.0005	0.0005	0.0098
Volume-weighted average κ								0.0825

Table A.10a. *n*-Pentadecane + Cl (9 July B): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.32	0.6088	0.1434	1.2989	0.6088	0.41	0.3759	0.1331	0.9101	0.3759	0.4923
2	64	0.38	0.3648	0.1171	1.0115	0.3648	0.36	0.4011	0.1076	0.7308	0.4011	0.3829
3	68	0.31	0.4584	0.0937	0.8298	0.4584	0.34	0.3809	0.0869	0.6124	0.3809	0.4197
4	72	0.33	0.3289	0.0782	0.6942	0.3289	0.39	0.2427	0.0717	0.5116	0.2427	0.2858
5	77	0.37	0.2170	0.0631	0.5688	0.2170	0.42	0.1733	0.0587	0.4184	0.1733	0.1952
6	82	0.39	0.1652	0.0524	0.4757	0.1652	0.39	0.1603	0.0487	0.3545	0.1603	0.1628
7	87	0.37	0.1553	0.0450	0.4015	0.1553	0.36	0.1616	0.0433	0.3359	0.1616	0.1585
8	93	0.34	0.1500	0.0382	0.3576	0.1500	0.34	0.1464	0.0352	0.2525	0.1464	0.1482
9	100	0.34	0.1182	0.0308	0.2815	0.1182	0.40	0.0883	0.0282	0.2001	0.0883	0.1032
10	106	0.38	0.0799	0.0259	0.2273	0.0799	0.42	0.0644	0.0239	0.1636	0.0644	0.0721
11	114	0.40	0.0583	0.0201	0.1796	0.0583	0.45	0.0451	0.0186	0.1308	0.0451	0.0517
12	121	0.46	0.0369	0.0165	0.1483	0.0369	0.52	0.0283	0.0153	0.1104	0.0283	0.0326
13	130	0.56	0.0202	0.0134	0.1203	0.0202	0.69	0.0132	0.0125	0.0884	0.0132	0.0167
14	139	0.73	0.0097	0.0113	0.0992	< 0.0113	0.71	0.0101	0.0103	0.0732	< 0.0103	0.0108
15	149	0.63	0.0106	0.0090	0.0805	0.0106	0.58	0.0123	0.0084	0.0585	0.0123	0.0115
16	160	0.55	0.0112	0.0074	0.0666	0.0112	0.63	0.0085	0.0068	0.0487	0.0085	0.0098

Table A.10b. *n*-Pentadecane + Cl (9 July B): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	50	265	266	10237	10237	0.0092		0.5040
2	53	299	300	1334	1499	0.0014	0.0014	0.4171
3	57	299	300	645	839	0.0008	0.0008	0.4094
4	61	299	300	4078	6070	0.0055	0.0056	0.2798
5	65	299	300	7283	12308	0.0111	0.0112	0.2125
6	69	299	300	5811	11067	0.0100	0.0101	0.1948
7	74	299	300	13164	28834	0.0260	0.0262	0.1821
8	79	299	300	27626	68965	0.0621	0.0627	0.1776
9	85	299	300	46650	134818	0.1214	0.1225	0.1488
10	91	299	300	62459	206889	0.1864	0.1881	0.1000
11	97	299	300	68835	259068	0.2334	0.2355	0.0669
12	104	299	300	64088	277271	0.2498	0.2521	0.0394
13	112	299	300	16863	84612	0.0762	0.0769	0.0225
14	120	299	300	1319	7596	0.0068	0.0069	0.0133
Volume-weighted average κ								0.0872

Table A.11a. *n*-Decane + Cl, 1st irradiation: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	50	0.40	0.6902	0.1907	1.7878	0.6902	0.59	0.3177	0.1770	1.3677	0.3177	0.5040
2	53	0.47	0.4178	0.1587	1.4933	0.4178	0.47	0.4164	0.1494	1.1425	0.4164	0.4171
3	57	0.42	0.4274	0.1291	1.2305	0.4274	0.44	0.3914	0.1200	0.9185	0.3914	0.4094
4	61	0.43	0.3297	0.1039	0.9872	0.3297	0.51	0.2299	0.0976	0.7451	0.2299	0.2798
5	65	0.47	0.2235	0.0858	0.8267	0.2235	0.50	0.2015	0.0807	0.6270	0.2015	0.2125
6	69	0.45	0.2033	0.0723	0.6819	0.2033	0.47	0.1863	0.0679	0.4968	0.1863	0.1948
7	74	0.42	0.1894	0.0583	0.5564	0.1894	0.44	0.1748	0.0547	0.4154	0.1748	0.1821
8	79	0.40	0.1743	0.0478	0.4575	0.1743	0.39	0.1808	0.0450	0.3392	0.1808	0.1776
9	85	0.37	0.1622	0.0385	0.3608	0.1622	0.41	0.1354	0.0361	0.2748	0.1354	0.1488
10	91	0.39	0.1192	0.0314	0.2979	0.1192	0.48	0.0807	0.0295	0.2210	0.0807	0.1000
11	97	0.44	0.0777	0.0262	0.2472	0.0777	0.52	0.0561	0.0245	0.1826	0.0561	0.0669
12	104	0.53	0.0440	0.0209	0.1950	0.0440	0.59	0.0348	0.0199	0.1518	0.0348	0.0394
13	112	0.58	0.0291	0.0172	0.1597	0.0291	0.80	0.0155	0.0159	0.1167	< 0.0159	0.0225
14	120	0.81	0.0121	0.0137	0.1332	< 0.0137	0.80	0.0126	0.0129	0.0988	< 0.0129	0.0133

Table A.11b. *n*-Decane + Cl, 1st irradiation: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	80	265	266	74	74	0.0006		
2	83	299	300	53	57	0.0005	0.0005	0.1280
3	86	299	300	154	178	0.0015	0.0015	
4	89	8	9	4	6	0.0000	0.0000	
5	150	79	90	53	187	0.0016	0.0016	
6	90	298	301	517	655	0.0057	0.0057	0.1989
7	94	299	300	1812	2501	0.0217	0.0217	0.1702
8	97	299	300	5312	7810	0.0677	0.0677	0.1634
9	101	299	300	6760	10774	0.0935	0.0936	0.1425
10	105	299	300	8056	13877	0.1204	0.1205	0.1286
11	110	299	300	9611	18171	0.1576	0.1577	0.1062
12	114	299	300	11026	22389	0.1942	0.1943	0.0784
13	119	299	300	13733	30387	0.2636	0.2638	0.0395
14	124	299	300	2901	6970	0.0605	0.0605	0.0165
15	129	299	300	427	1109	0.0096	0.0096	0.0220
16	134	299	300	53	149	0.0013	0.0013	0.0295
Volume-weighted average κ								0.0887

Table A.12a. *n*-Pentadecane + Cl (13 July): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	80	0.27	0.3761	0.0455	0.3410		0.29	0.3097	0.0428	0.2743		0.1280
2	83	0.26	0.3447	0.0404	0.3082		0.43	0.1280	0.0383	0.2489	0.1280	
3	86	0.27	0.3046	0.0364	0.2707		0.29	0.2506	0.0341	0.2141		
4	89											
5	150											
6	90	0.31	0.1989	0.0321	0.2436	0.1989	0.31	0.1989	0.0300	0.1891	0.1989	0.1989
7	94	0.31	0.1702	0.0279	0.2087	0.1702	0.32	0.1663	0.0265	0.1662		0.1702
8	97	0.30	0.1634	0.0256	0.1895	0.1634	0.29	0.1737	0.0241	0.1519		0.1634
9	101	0.31	0.1425	0.0225	0.1685	0.1425	0.29	0.1539	0.0213	0.1338		0.1425
10	105	0.30	0.1286	0.0201	0.1493	0.1286	0.29	0.1371	0.0189	0.1197		0.1286
11	110	0.31	0.1103	0.0177	0.1303	0.1103	0.32	0.1021	0.0165	0.1040	0.1021	0.1062
12	114	0.32	0.0927	0.0159	0.1160	0.0927	0.38	0.0641	0.0149	0.0920	0.0641	0.0784
13	119	0.39	0.0525	0.0140	0.1032	0.0525	0.56	0.0265	0.0137	0.0945	0.0265	0.0395
14	124	0.59	0.0211	0.0128	0.1011	0.0211	0.80	0.0114	0.0118	0.0720	< 0.0118	0.0165
15	129	0.44	0.0332	0.0107	0.0788	0.0332	0.77	0.0107	0.0101	0.0634	0.0107	0.0220
16	134	0.34	0.0492	0.0095	0.0699	0.0492	0.76	0.0099	0.0091	0.0562	0.0099	0.0295

Table A.12b. *n*-Pentadecane + Cl (13 July): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	1713	1713	0.0071		0.5570
2	63	299	300	183	202	0.0008	0.0008	0.4068
3	65	299	300	60	70	0.0003	0.0003	0.5223
4	68	299	300	58	75	0.0003	0.0003	0.5068
5	71	299	300	72	100	0.0004	0.0004	0.5183
6	74	299	300	180	274	0.0011	0.0011	0.3272
7	78	299	300	954	1612	0.0067	0.0067	0.2468
8	81	299	300	2341	4266	0.0176	0.0177	0.1931
9	85	299	300	6112	12266	0.0506	0.0510	0.1619
10	89	299	300	34971	76946	0.3177	0.3200	0.1211
11	93	299	300	20025	48111	0.1986	0.2000	0.1108
12	97	299	300	13393	35005	0.1445	0.1455	0.0877
13	101	299	300	11297	32011	0.1322	0.1331	0.0256
14	106	299	300	6454	20144	0.0832	0.0838	0.0210
15	111	299	300	1827	6252	0.0258	0.0260	0.0182
16	116	299	300	846	3162	0.0131	0.0132	0.0158
Volume-weighted average κ								0.0941

Table A.13a. *n*-Pentadecane + Cl (16 July B): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.30	0.7155	0.1189	1.7532	0.7155	0.40	0.3986	0.1075	0.8145	0.3986	0.5570
2	63	0.38	0.3840	0.1050	1.3290	0.3840	0.36	0.4295	0.0931	0.6966	0.4295	0.4068
3	65	0.32	0.4832	0.0933	1.1374	0.4832	0.30	0.5613	0.0851	0.6471	0.5613	0.5223
4	68	0.29	0.5068	0.0839	1.0574	0.5068	0.27	0.5930	0.0743	0.5393		0.5068
5	71	0.25	0.6055	0.0714	0.8164	0.6055	0.30	0.4312	0.0648	0.4572	0.4312	0.5183
6	74	0.31	0.3491	0.0628	0.6668	0.3491	0.33	0.3054	0.0572	0.4132	0.3054	0.3272
7	78	0.32	0.2758	0.0539	0.6114	0.2758	0.37	0.2178	0.0487	0.3503	0.2178	0.2468
8	81	0.36	0.1955	0.0477	0.5372	0.1955	0.37	0.1906	0.0440	0.3018	0.1906	0.1931
9	85	0.37	0.1633	0.0414	0.4539	0.1633	0.37	0.1604	0.0379	0.2728	0.1604	0.1619
10	89	0.39	0.1281	0.0363	0.4026	0.1281	0.41	0.1140	0.0329	0.2421	0.1140	0.1211
11	93	0.42	0.0985	0.0322	0.3533	0.0985	0.37	0.1231	0.0289	0.2100	0.1231	0.1108
12	97	0.37	0.1081	0.0284	0.3095	0.1081	0.47	0.0673	0.0255	0.1850	0.0673	0.0877
13	101	0.70	0.0278	0.0248	0.2775	0.0278	0.76	0.0234	0.0226	0.1665	0.0234	0.0256
14	106	0.75	0.0204	0.0218	0.2397	< 0.0218	0.76	0.0202	0.0196	0.1432	0.0202	0.0210
15	111	0.75	0.0178	0.0186	0.2078	< 0.0186	0.76	0.0177	0.0170	0.1181	0.0177	0.0182
16	116	0.75	0.0156	0.0163	0.1795	< 0.0163	0.76	0.0154	0.0149	0.1079	0.0154	0.0158

Table A.13b. *n*-Pentadecane + Cl (16 July B): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	5922	5922	0.0301		0.3285
2	63	299	300	551	608	0.0031	0.0032	0.3607
3	67	299	300	315	393	0.0020	0.0021	0.3613
4	71	299	300	1338	1874	0.0095	0.0098	0.2465
5	75	299	300	6287	9824	0.0499	0.0514	0.1749
6	79	299	300	14632	25366	0.1287	0.1327	0.1404
7	83	299	300	5645	10802	0.0548	0.0565	0.1521
8	88	299	300	11643	25045	0.1271	0.1310	0.1252
9	93	299	300	9717	23344	0.1185	0.1222	0.0962
10	99	299	300	10289	28012	0.1422	0.1466	0.0737
11	104	299	300	10252	30802	0.1563	0.1612	0.0578
12	111	299	300	8467	28978	0.1471	0.1517	0.0408
13	117	299	300	1535	5838	0.0296	0.0305	0.0182
14	124	299	300	50	212	0.0011	0.0011	0.0186
Volume-weighted average κ								0.0956

Table A.14a. Cyclodecane + OH with NO_x: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.37	0.4560	0.1171	1.3625	0.4560	0.56	0.2010	0.1066	0.7892	0.2010	0.3285
2	63	0.40	0.3409	0.1017	1.2059	0.3409	0.38	0.3805	0.0933	0.7032	0.3805	0.3607
3	67	0.36	0.3589	0.1011	1.0239	0.3589	0.35	0.3637	0.0961	0.6319	0.3637	0.3613
4	71	0.37	0.2749	0.0817	0.8687	0.2749	0.42	0.2181	0.0736	0.5095	0.2181	0.2465
5	75	0.40	0.2051	0.0649	0.7507	0.2051	0.48	0.1448	0.0577	0.4205	0.1448	0.1749
6	79	0.44	0.1412	0.0537	0.6161	0.1412	0.45	0.1396	0.0485	0.3579	0.1396	0.1404
7	83	0.40	0.1470	0.0479	0.5530	0.1470	0.39	0.1572	0.0444	0.3242	0.1572	0.1521
8	88	0.38	0.1426	0.0428	0.4541	0.1426	0.43	0.1077	0.0386	0.2712	0.1077	0.1252
9	93	0.41	0.1030	0.0328	0.3964	0.1030	0.44	0.0894	0.0295	0.2160	0.0894	0.0962
10	99	0.42	0.0799	0.0258	0.3022	0.0799	0.46	0.0675	0.0239	0.1769	0.0675	0.0737
11	104	0.44	0.0637	0.0228	0.2661	0.0637	0.49	0.0519	0.0206	0.1554	0.0519	0.0578
12	111	0.47	0.0461	0.0186	0.2137	0.0461	0.53	0.0356	0.0172	0.1321	0.0356	0.0408
13	117	0.65	0.0205	0.0175	0.1926	0.0205	0.74	0.0159	0.0155	0.1127	0.0159	0.0182
14	124	0.63	0.0185	0.0136	0.1528	0.0185	0.62	0.0188	0.0123	0.0920	0.0188	0.0186

Table A.14b. Cyclodecane + OH with NO_x: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	1510	1510	0.1010		0.4100
2	64	299	300	114	130	0.0087	0.0097	0.3164
3	68	299	300	15	19	0.0013	0.0014	0.1233
4	73	299	300	55	81	0.0054	0.0060	0.1625
5	78	299	300	26	44	0.0030	0.0033	0.1579
6	84	299	300	27	53	0.0036	0.0040	0.1374
7	89	299	300	69	152	0.0101	0.0112	0.1202
8	96	299	300	139	356	0.0238	0.0265	0.1850
9	103	299	300	320	943	0.0631	0.0702	0.1415
10	110	299	300	1924	6465	0.4326	0.4811	0.1110
11	118	299	300	764	2955	0.1977	0.2199	0.0893
12	127	299	300	243	1087	0.0727	0.0809	0.0707
13	136	299	300	168	863	0.0578	0.0643	0.0362
14	147	299	300	32	190	0.0127	0.0141	0.0185
15	158	299	300	9	59	0.0040	0.0044	0.0272
16	170	299	300	5	39	0.0026	0.0029	0.0173
Volume-weighted average κ								0.1030

Table A.15a. *n*-Pentadecane + Cl (16 July A): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.42	0.3606	0.1191	1.3562	0.3606	0.37	0.4595	0.1072	0.7670	0.4595	0.4100
2	64	0.34	0.4509	0.0971	1.0707	0.4509	0.54	0.1819	0.0881	0.6176	0.1819	0.3164
3	68	0.61	0.1182	0.0818	0.9321	0.1182	0.58	0.1285	0.0736	0.5265	0.1285	0.1233
4	73	0.53	0.1268	0.0653	0.7297	0.1268	0.42	0.1981	0.0592	0.4161	0.1981	0.1625
5	78	0.49	0.1228	0.0536	0.5993	0.1228	0.39	0.1929	0.0487	0.3530	0.1929	0.1579
6	84	0.39	0.1506	0.0432	0.4703	0.1506	0.43	0.1242	0.0392	0.2749	0.1242	0.1374
7	89	0.40	0.1202	0.0366	0.3998	0.1202	0.27	0.2594	0.0329	0.2292		0.1202
8	96	0.28	0.2013	0.0289	0.3188	0.2013	0.30	0.1687	0.0260	0.1873	0.1687	0.1850
9	103	0.30	0.1415	0.0233	0.2659	0.1415	0.27	0.1707	0.0213	0.1541		0.1415
10	110	0.30	0.1182	0.0198	0.2211	0.1182	0.32	0.1038	0.0175	0.1265	0.1038	0.1110
11	118	0.31	0.0871	0.0155	0.1674	0.0871	0.30	0.0916	0.0142	0.1034	0.0916	0.0893
12	127	0.30	0.0767	0.0126	0.1489	0.0767	0.32	0.0648	0.0132	0.0842	0.0648	0.0707
13	136	0.33	0.0515	0.0109	0.1175	0.0515	0.51	0.0208	0.0099	0.0715	0.0208	0.0362
14	147	0.65	0.0104	0.0088	0.0947	0.0104	0.40	0.0266	0.0080	0.0550	0.0266	0.0185
15	158	0.28	0.0460	0.0068	0.0843	0.0460	0.65	0.0083	0.0062	0.0451	0.0083	0.0272
16	170	0.33	0.0261	0.0054	0.0629	0.0261	0.57	0.0086	0.0050	0.0366	0.0086	0.0173

Table A.15b. *n*-Pentadecane + Cl (16 July A): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	50	265	266	4353	4353	0.1050		0.6630
2	53	299	300	310	348	0.0084	0.0094	0.5744
3	57	299	300	124	161	0.0039	0.0044	0.6107
4	61	299	300	177	263	0.0063	0.0070	0.4143
5	65	299	300	246	416	0.0100	0.0112	0.3699
6	69	299	300	213	405	0.0098	0.0109	0.3017
7	74	299	300	266	584	0.0141	0.0158	0.2471
8	79	299	300	441	1102	0.0266	0.0297	0.1912
9	85	299	300	735	2124	0.0512	0.0572	0.1613
10	91	299	300	1113	3686	0.0889	0.0993	0.1550
11	97	299	300	1631	6140	0.1480	0.1653	0.1319
12	104	299	300	3968	17168	0.4139	0.4624	0.0964
13	112	299	300	908	4558	0.1099	0.1228	0.0341
14	120	299	300	29	169	0.0041	0.0046	0.0377
Volume-weighted average κ								0.1233

Table A.16a. 1-Octene + O₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	50	0.38	0.7790	0.1810	1.4144	0.7790	0.45	0.5470	0.1708	1.0984	0.5470	0.6630
2	53	0.44	0.4882	0.1546	1.1726	0.4882	0.37	0.6606	0.1435	0.8961	0.6606	0.5744
3	57	0.36	0.5825	0.1229	0.9302	0.5825	0.34	0.6390	0.1152	0.7569	0.6390	0.6107
4	61	0.27	0.8359	0.1005	0.7602		0.38	0.4143	0.0938	0.5982	0.4143	0.4143
5	65	0.36	0.3891	0.0829	0.6202	0.3891	0.38	0.3506	0.0779	0.5020	0.3506	0.3699
6	69	0.37	0.2990	0.0690	0.5072	0.2990	0.37	0.3044	0.0651	0.4152	0.3044	0.3017
7	74	0.37	0.2450	0.0580	0.5003	0.2450	0.37	0.2493	0.0546	0.3863	0.2493	0.2471
8	79	0.38	0.1942	0.0480	0.4026	0.1942	0.39	0.1883	0.0446	0.3183	0.1883	0.1912
9	85	0.37	0.1616	0.0382	0.3264	0.1616	0.37	0.1610	0.0359	0.2609	0.1610	0.1613
10	91	0.25	0.3012	0.0312	0.2631		0.34	0.1550	0.0294	0.2119	0.1550	0.1550
11	97	0.35	0.1200	0.0258	0.2230	0.1200	0.32	0.1437	0.0243	0.1713	0.1437	0.1319
12	104	0.32	0.1161	0.0216	0.1757	0.1161	0.40	0.0767	0.0198	0.1424	0.0767	0.0964
13	112	0.48	0.0421	0.0171	0.1449	0.0421	0.61	0.0262	0.0158	0.1123	0.0262	0.0341
14	120	0.48	0.0341	0.0140	0.1167	0.0341	0.44	0.0413	0.0129	0.0926	0.0413	0.0377

Table A.16b. 1-Octene + O₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	1E+05	106339	0.2371		0.2684
2	64	299	300	35211	40062	0.0893	0.1170	0.2483
3	67	299	300	9913	12361	0.0276	0.0362	0.2492
4	71	299	300	25297	35422	0.0790	0.1035	0.1855
5	76	299	300	43799	70272	0.1567	0.2053	0.1371
6	80	299	300	41888	74467	0.1660	0.2175	0.1188
7	85	299	300	32152	64527	0.1439	0.1886	0.1086
8	91	299	300	16389	37699	0.0841	0.1102	0.1054
9	96	299	300	2779	7115	0.0159	0.0208	0.1172
10	103	299	300	91	268	0.0006	0.0008	0.1225
Volume-weighted average κ								0.1459

Table A.17a. *n*-Pentadecane + Cl (8 July B): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.23	1.1982	0.1261	1.0876		0.49	0.2684	0.1176	0.8495	0.2684	0.2684
2	64	0.46	0.2479	0.1059	1.0009	0.2479	0.46	0.2487	0.0978	0.7254	0.2487	0.2483
3	67	0.42	0.2641	0.0977	0.8646	0.2641	0.44	0.2344	0.0869	0.7385	0.2344	0.2492
4	71	0.44	0.2015	0.0805	0.8601	0.2015	0.48	0.1695	0.0747	0.5281	0.1695	0.1855
5	76	0.47	0.1437	0.0657	0.5832	0.1437	0.49	0.1305	0.0606	0.4052	0.1305	0.1371
6	80	0.47	0.1226	0.0556	0.4625	0.1226	0.48	0.1150	0.0516	0.3950	0.1150	0.1188
7	85	0.45	0.1112	0.0432	0.6281	0.1112	0.46	0.1061	0.0413	0.3431	0.1061	0.1086
8	91	0.42	0.1042	0.0369	0.3950	0.1042	0.41	0.1066	0.0345	0.2598	0.1066	0.1054
9	96	0.38	0.1101	0.0323	0.2923	0.1101	0.35	0.1244	0.0297	0.2020	0.1244	0.1172
10	103	0.33	0.1156	0.0263	0.2171	0.1156	0.31	0.1293	0.0242	0.1685	0.1293	0.1225

Table A.17b. *n*-Pentadecane + Cl (8 July B): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	85977	85977	0.1894		0.4061
2	64	299	300	32763	37277	0.0821	0.1013	0.2471
3	67	299	300	9146	11404	0.0251	0.0310	0.2420
4	71	299	300	23902	33470	0.0737	0.0909	0.1968
5	76	299	300	43516	69820	0.1538	0.1898	0.1435
6	80	299	300	44825	79689	0.1756	0.2167	0.1241
7	85	299	300	36392	73037	0.1609	0.1985	0.1118
8	91	299	300	21686	49884	0.1099	0.1356	0.1096
9	96	299	300	4910	12571	0.0277	0.0342	0.1279
10	103	299	300	242	712	0.0016	0.0020	0.1341
Volume-weighted average κ								0.1463

Table A.18a. *n*-Pentadecane + Cl (8 July A): Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.34	0.5371	0.1273	1.0242	0.5371	0.48	0.2752	0.1159	0.8148	0.2752	0.4061
2	64	0.45	0.2552	0.1059	0.9362	0.2552	0.47	0.2389	0.0959	0.6381	0.2389	0.2471
3	67	0.43	0.2483	0.0895	0.7399	0.2483	0.44	0.2356	0.0838	0.5506	0.2356	0.2420
4	71	0.42	0.2152	0.0774	0.6226	0.2152	0.46	0.1785	0.0703	0.4447	0.1785	0.1968
5	76	0.45	0.1520	0.0632	0.5305	0.1520	0.48	0.1351	0.0573	0.3525	0.1351	0.1435
6	80	0.45	0.1309	0.0531	0.4073	0.1309	0.48	0.1173	0.0484	0.2826	0.1173	0.1241
7	85	0.44	0.1143	0.0427	0.3254	0.1143	0.45	0.1094	0.0390	0.2448	0.1094	0.1118
8	91	0.41	0.1070	0.0342	0.2543	0.1070	0.40	0.1123	0.0315	0.2087	0.1123	0.1096
9	96	0.37	0.1151	0.0293	0.2482	0.1151	0.33	0.1407	0.0271	0.2032	0.1407	0.1279
10	103	0.32	0.1207	0.0246	0.2336	0.1207	0.29	0.1475	0.0227	0.1542	0.1475	0.1341

Table A.18b. *n*-Pentadecane + Cl (8 July A): Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	24037	24037	0.2788		0.5848
2	63	299	300	6329	6977	0.0809	0.1122	0.2474
3	67	299	300	1692	2110	0.0245	0.0340	0.2551
4	71	299	300	4515	6323	0.0734	0.1018	0.1972
5	75	299	300	8762	13690	0.1588	0.2202	0.1471
6	79	299	300	11292	19577	0.2271	0.3149	0.1352
7	83	299	300	5721	10948	0.1270	0.1761	0.1423
8	88	299	300	1000	2152	0.0250	0.0347	0.1545
9	93	299	300	161	386	0.0045	0.0062	0.1509
Volume-weighted average κ								0.1628

Table A.19a. *m*-Xylene + OH with NO_x: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.26	0.9688	0.1162	1.2505	0.9688	0.56	0.2007	0.1064	0.7968	0.2007	0.5848
2	63	0.47	0.2542	0.1015	1.1107	0.2542	0.48	0.2406	0.0920	0.6684	0.2406	0.2474
3	67	0.44	0.2420	0.0826	0.8825	0.2420	0.41	0.2682	0.0762	0.5719	0.2682	0.2551
4	71	0.42	0.2159	0.0708	0.7872	0.2159	0.46	0.1786	0.0637	0.4674	0.1786	0.1972
5	75	0.45	0.1604	0.0602	0.6807	0.1604	0.49	0.1338	0.0545	0.4031	0.1338	0.1471
6	79	0.45	0.1361	0.0520	0.5816	0.1361	0.46	0.1343	0.0467	0.3161	0.1343	0.1352
7	83	0.42	0.1337	0.0456	0.5204	0.1337	0.40	0.1509	0.0405	0.2804	0.1509	0.1423
8	88	0.38	0.1398	0.0379	0.4180	0.1398	0.35	0.1691	0.0341	0.2423	0.1691	0.1545
9	93	0.34	0.1449	0.0318	0.3716	0.1449	0.33	0.1568	0.0290	0.2099	0.1568	0.1509

Table A.19b. *m*-Xylene + OH with NO_x: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	50	265	266	26950	26950	0.0878		0.4158
2	53	299	300	7987	8974	0.0292	0.0320	0.3051
3	57	299	300	1330	1728	0.0056	0.0061	0.3342
4	61	299	300	8309	12368	0.0403	0.0442	0.2621
5	65	299	300	21059	35590	0.1160	0.1272	0.1775
6	69	299	300	45662	86958	0.2834	0.3107	0.1586
7	74	299	300	36889	80801	0.2633	0.2887	0.1449
8	79	299	300	16777	41881	0.1365	0.1497	0.1517
9	85	299	300	2996	8658	0.0282	0.0309	0.1582
10	91	299	300	745	2466	0.0080	0.0088	0.1292
11	97	299	300	121	456	0.0015	0.0016	0.1398
Volume-weighted average κ								0.1661

Table A.20a. 1,2-Dimethyl cyclohexene + O₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	50	0.43	0.6094	0.1858	1.3983	0.6094	0.71	0.2222	0.1742	1.1190	0.2222	0.4158
2	53	0.54	0.3139	0.1551	1.2180	0.3139	0.56	0.2963	0.1467	0.9919	0.2963	0.3051
3	57	0.48	0.3285	0.1256	0.9717	0.3285	0.47	0.3399	0.1182	0.7904	0.3399	0.3342
4	61	0.44	0.3088	0.1028	0.7957	0.3088	0.53	0.2153	0.0970	0.6495	0.2153	0.2621
5	65	0.52	0.1875	0.0845	0.6699	0.1875	0.55	0.1674	0.0796	0.5333	0.1674	0.1775
6	69	0.51	0.1632	0.0708	0.5558	0.1632	0.52	0.1540	0.0663	0.4257	0.1540	0.1586
7	74	0.48	0.1459	0.0591	0.4463	0.1459	0.49	0.1439	0.0542	0.3623	0.1439	0.1449
8	79	0.43	0.1494	0.0472	0.3725	0.1494	0.43	0.1540	0.0444	0.2981	0.1540	0.1517
9	85	0.39	0.1486	0.0380	0.2961	0.1486	0.37	0.1678	0.0356	0.2358	0.1678	0.1582
10	91	0.35	0.1472	0.0308	0.2433	0.1472	0.41	0.1113	0.0291	0.1872	0.1113	0.1292
11	97	0.33	0.1398	0.0255	0.1979	0.1398	0.29	0.1842	0.0242	0.1622		0.1398

Table A.20b. 1,2-Dimethyl cyclohexene + O₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	50	265	266	89160	89160	0.1866		0.5248
2	53	299	300	41767	46929	0.0982	0.1207	0.2659
3	57	299	300	14376	18683	0.0391	0.0481	0.2490
4	61	8	9	269	400	0.0008	0.0010	
5	50	298	301	48279	48279	0.1010	0.1242	0.2011
6	53	299	300	75261	84563	0.1770	0.2176	0.1690
7	55	2	3	-2	-2	0.0000	0.0000	
8	60	298	302	63247	91075	0.1906	0.2343	0.1438
9	64	299	300	40950	67092	0.1404	0.1726	0.1304
10	67	299	300	13159	23629	0.0495	0.0608	0.1584
11	71	299	300	1705	3438	0.0072	0.0089	0.1817
12	76	299	300	371	857	0.0018	0.0022	0.1542
13	80	299	300	200	513	0.0011	0.0014	0.1835
14	85	299	300	740	2138	0.0045	0.0055	0.1315
15	90	299	300	319	1034	0.0022	0.0027	0.0525
16	96	299	300	10	35	0.0001	0.0001	0.0337
Volume-weighted average κ								0.1749

Table A.21a. *n*-Decane + Cl, 2nd irradiation: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	50	0.38	0.7605	0.1904	1.8416	0.7605	0.62	0.2891	0.1769	1.2101	0.2891	0.5248
2	53	0.58	0.2791	0.1593	1.5310	0.2791	0.61	0.2528	0.1487	1.1037	0.2528	0.2659
3	57	0.54	0.2553	0.1291	1.2149	0.2553	0.55	0.2426	0.1193	0.9052	0.2426	0.2490
4	61											
5	50	0.70	0.2243	0.1889	1.7697	0.2243	0.80	0.1727	0.1779	1.3545	< 0.1779	0.2011
6	53	0.70	0.1888	0.1600	1.4999	0.1888	0.80	0.1454	0.1493	1.1147	< 0.1493	0.1690
7	55											
8	60	0.62	0.1650	0.1101	1.0157	0.1650	0.72	0.1227	0.1037	0.7707	0.1227	0.1438
9	64	0.63	0.1328	0.0901	0.8383	0.1328	0.64	0.1279	0.0849	0.6557	0.1279	0.1304
10	67	0.55	0.1525	0.0795	0.7327	0.1525	0.53	0.1642	0.0738	0.5599	0.1642	0.1584
11	71	0.46	0.1842	0.0661	0.6138	0.1842	0.46	0.1792	0.0622	0.4744	0.1792	0.1817
12	76	0.42	0.1797	0.0544	0.5141	0.1797	0.49	0.1287	0.0505	0.3886	0.1287	0.1542
13	80	0.36	0.2019	0.0463	0.4305	0.2019	0.40	0.1651	0.0439	0.3270	0.1651	0.1835
14	85	0.39	0.1440	0.0384	0.3590	0.1440	0.43	0.1191	0.0363	0.2779	0.1191	0.1315
15	90	0.50	0.0744	0.0326	0.3034	0.0744	0.80	0.0300	0.0306	0.2267	< 0.0306	0.0525
16	96	0.62	0.0409	0.0268	0.2514	0.0409	0.77	0.0264	0.0251	0.1886	0.0264	0.0337

Table A.21b. *n*-Decane + Cl, 2nd irradiation: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	10980	10980	0.0345		0.2972
2	63	299	300	2531	2790	0.0088	0.0091	0.3059
3	67	299	300	1528	1905	0.0060	0.0062	0.3050
4	71	299	300	6802	9525	0.0300	0.0311	0.2572
5	75	299	300	63761	99626	0.3133	0.3245	0.2501
6	79	299	300	17676	30643	0.0964	0.0998	0.2153
7	83	299	300	45563	87190	0.2742	0.2840	0.1864
8	88	299	300	25125	54047	0.1700	0.1761	0.1485
9	93	299	300	7813	18771	0.0590	0.0611	0.1439
10	99	299	300	806	2193	0.0069	0.0071	0.1325
11	104	299	300	95	285	0.0009	0.0009	0.0765
Volume-weighted average κ								0.2042

Table A.22a. Cyclooctene + O₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.31	0.6790	0.0934	0.6334		0.46	0.2972	0.0853	0.5297	0.2972	0.2972
2	63	0.43	0.3007	0.0795	0.5433	0.3007	0.42	0.3112	0.0732	0.4543	0.3112	0.3059
3	67	0.40	0.2875	0.0657	0.4487	0.2875	0.38	0.3225	0.0613	0.3820	0.3225	0.3050
4	71	0.39	0.2572	0.0572	0.3827	0.2572	0.33	0.3576	0.0550	0.3389		0.2572
5	75	0.34	0.2782	0.0489	0.3444	0.2782	0.38	0.2220	0.0450	0.2710	0.2220	0.2501
6	79	0.37	0.1991	0.0414	0.2873	0.1991	0.35	0.2315	0.0380	0.2502	0.2315	0.2153
7	83	0.36	0.1864	0.0365	0.2472	0.1864	0.33	0.2233	0.0325	0.2181		0.1864
8	88	0.37	0.1485	0.0304	0.2524	0.1485	0.33	0.1820	0.0274	0.1669		0.1485
9	93	0.34	0.1439	0.0258	0.1967	0.1439	0.31	0.1806	0.0240	0.1560		0.1439
10	99	0.33	0.1325	0.0216	0.1719	0.1325	0.33	0.1277	0.0191	0.1181		0.1325
11	104	0.31	0.1237	0.0181	0.1224		0.40	0.0765	0.0165	0.0997	0.0765	0.0765

Table A.22b. Cyclooctene + O₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	48678	48678	0.1704		0.5266
2	63	299	300	28858	31816	0.1114	0.1343	0.3389
3	67	299	300	21115	26330	0.0922	0.1111	0.3082
4	71	299	300	16738	23438	0.0820	0.0988	0.2324
5	75	299	300	54172	84644	0.2963	0.3572	0.1934
6	79	299	300	30168	52300	0.1831	0.2207	0.1513
7	83	299	300	6097	11668	0.0408	0.0492	0.1417
8	88	299	300	2928	6299	0.0220	0.0265	0.1358
9	93	299	300	211	508	0.0018	0.0022	0.1274
Volume-weighted average κ								0.2160

Table A.23a. Cyclohexene + O₃: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.30	0.6858	0.0910	0.7607	0.6858	0.42	0.3674	0.0832	0.5190	0.3674	0.5266
2	63	0.43	0.2993	0.0800	0.5285	0.2993	0.38	0.3786	0.0716	0.4456	0.3786	0.3389
3	67	0.38	0.3227	0.0643	0.4410	0.3227	0.39	0.2936	0.0593	0.3591	0.2936	0.3082
4	71	0.39	0.2472	0.0539	0.3676	0.2472	0.42	0.2177	0.0498	0.3062	0.2177	0.2324
5	75	0.41	0.1958	0.0463	0.3091	0.1958	0.41	0.1910	0.0421	0.2541	0.1910	0.1934
6	79	0.42	0.1594	0.0396	0.2618	0.1594	0.44	0.1432	0.0361	0.2147	0.1432	0.1513
7	83	0.42	0.1384	0.0343	0.2269	0.1384	0.41	0.1450	0.0313	0.1943	0.1450	0.1417
8	88	0.42	0.1155	0.0284	0.1937	0.1155	0.36	0.1560	0.0261	0.1561	0.1560	0.1358
9	93	0.37	0.1273	0.0242	0.1619	0.1273	0.37	0.1275	0.0223	0.1366	0.1275	0.1274

Table A.23b. Cyclohexene + O₃: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	50	265	266	29219	29219	0.4005		0.3972
2	53	299	300	4247	4772	0.0654	0.1091	0.3415
3	57	299	300	1074	1396	0.0191	0.0319	0.3638
4	61	299	300	2836	4221	0.0578	0.0964	0.2823
5	65	299	300	5203	8794	0.1205	0.2010	0.2099
6	69	299	300	5338	10166	0.1393	0.2324	0.1885
7	74	299	300	3772	8263	0.1133	0.1890	0.1909
8	79	299	300	1490	3720	0.0510	0.0851	0.1864
9	85	299	300	632	1826	0.0250	0.0417	0.1793
10	91	299	300	177	585	0.0080	0.0133	0.1542
Volume-weighted average κ								0.2236

Table A.24a. Cyclooctane + OH without NO_x: Similar to Table A.1a.

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	50	0.44	0.5742	0.1922	1.6238	0.5742	0.71	0.2202	0.1792	1.2368	0.2202	0.3972
2	53	0.53	0.3329	0.1614	1.3512	0.3329	0.51	0.3501	0.1513	1.0258	0.3501	0.3415
3	57	0.46	0.3515	0.1311	1.0840	0.3515	0.44	0.3760	0.1218	0.8667	0.3760	0.3638
4	61	0.44	0.3153	0.1079	0.8957	0.3153	0.49	0.2493	0.0999	0.6773	0.2493	0.2823
5	65	0.47	0.2274	0.0881	0.7340	0.2274	0.51	0.1925	0.0826	0.5734	0.1925	0.2099
6	69	0.46	0.1991	0.0746	0.6247	0.1991	0.49	0.1780	0.0695	0.4693	0.1780	0.1885
7	74	0.42	0.1915	0.0641	0.5070	0.1915	0.42	0.1903	0.0585	0.3923	0.1903	0.1909
8	79	0.39	0.1808	0.0505	0.4139	0.1808	0.38	0.1919	0.0486	0.3170	0.1919	0.1864
9	85	0.36	0.1758	0.0395	0.3254	0.1758	0.35	0.1828	0.0365	0.2512	0.1828	0.1793
10	91	0.32	0.1761	0.0316	0.2692	0.1761	0.37	0.1322	0.0293	0.2106	0.1322	0.1542

Table A.24b. Cyclooctane + OH without NO_x: Similar to Table A.1b.

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	75	265	266	9544	9544	0.0316		0.1242
2	79	299	300	2497	2771	0.0092	0.0095	0.1892
3	83	299	300	621	760	0.0025	0.0026	0.1756
4	87	299	300	3874	5213	0.0172	0.0178	0.1494
5	92	299	300	19235	28944	0.0957	0.0988	0.1188
6	97	299	300	20943	35031	0.1158	0.1196	0.1171
7	102	299	300	45288	83766	0.2770	0.2860	0.0594
8	108	299	300	30106	62428	0.2064	0.2131	0.0352
9	114	299	300	27666	63918	0.2114	0.2183	0.0260
10	120	299	305	3366	8616	0.0285	0.0294	0.0383
11	127	299	300	420	1203	0.0040	0.0041	0.0494
12	134	299	300	63	200	0.0007	0.0007	0.0384
Volume-weighted average κ								0.0622

Table A.25a. α -Pinene + O₃ A: Similar to Table A.1a. This experiment was excluded from the study (see Figure B7).

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	75	0.68	0.0707	0.0483	0.4577	0.0707	0.43	0.1777	0.0442	0.3272	0.1777	0.1242
2	79	0.38	0.1932	0.0406	0.391	0.1932	0.39	0.1852	0.0379	0.2821	0.1852	0.1892
3	83	0.39	0.1623	0.0349	0.3317	0.1623	0.36	0.1889	0.0325	0.2404	0.1889	0.1756
4	87	0.38	0.1475	0.0304	0.2714	0.1475	0.37	0.1513	0.0283	0.2109	0.1513	0.1494
5	92	0.37	0.1289	0.0258	0.2374	0.1289	0.4	0.1086	0.024	0.1756	0.1086	0.1188
6	97	0.36	0.1194	0.0220	0.2007	0.1194	0.36	0.1148	0.0206	0.1492	0.1148	0.1171
7	102	0.42	0.0737	0.0190	0.1735	0.0737	0.54	0.0451	0.0177	0.1317	0.0451	0.0594
8	108	0.54	0.0374	0.0161	0.1474	0.0374	0.58	0.0331	0.0151	0.1083	0.0331	0.0352
9	114	0.68	0.0202	0.0139	0.1239	0.0202	0.54	0.0318	0.0129	0.0924	0.0318	0.0260
10	120	0.47	0.0368	0.0122	0.1065	0.0368	0.45	0.0398	0.0107	0.0674	0.0398	0.0383
11	127	0.39	0.0444	0.0102	0.0882	0.0444	0.35	0.0544	0.009	0.0579	0.0544	0.0494
12	134	0.38	0.0396	0.0087	0.0747	0.0396	0.39	0.0372	0.0077	0.0487	0.0372	0.0384

Table A.25b. α -Pinene + O₃ A: Similar to Table A.1b. This experiment was excluded from the study (see Figure B.7).

Scan #	D _d [nm]	Datapoints	Δt [s]	CN [#]	CN at D _{ref} [#]	Number fraction	Adjusted fraction	Average κ for scan
1	60	265	266	21729	21729	0.0203		0.3205
2	64	299	300	11055	12578	0.0118	0.0120	0.2730
3	68	299	300	2799	3595	0.0034	0.0035	0.2467
4	72	299	300	13636	19636	0.0184	0.0188	0.2053
5	76	299	300	51145	82059	0.0767	0.0783	0.2142
6	81	299	300	85949	156641	0.1465	0.1495	0.1939
7	86	299	300	128955	264932	0.2478	0.2529	0.1696
8	92	299	300	94193	221458	0.2071	0.2114	0.1455
9	98	299	300	72265	192787	0.1803	0.1840	0.1129
10	104	299	300	23047	69243	0.0648	0.0661	0.0922
11	111	299	300	5726	19597	0.0183	0.0187	0.0944
12	118	299	300	1312	5074	0.0047	0.0048	0.0774
Volume-weighted average κ								0.1564

Table A.26a. α -Pinene + O₃ B: Similar to Table A.1a. This experiment was excluded from the study (see Figure B.7).

Scan #	D _d [nm]	Upscan					Downscan					Average κ
		s_c	κ_{orig}	envelope		κ_{final}	s_c	κ_{orig}	envelope		κ_{final}	
1	60	0.43	0.3449	0.1176	1.0162	0.3449	0.46	0.2962	0.1101	0.8051	0.2962	0.3205
2	64	0.42	0.3018	0.0972	0.8558	0.3018	0.46	0.2443	0.0904	0.6570	0.2443	0.2730
3	68	0.41	0.2586	0.0804	0.6996	0.2586	0.43	0.2349	0.0807	0.6898	0.2349	0.2467
4	72	0.40	0.2308	0.0717	0.6908	0.2308	0.45	0.1798	0.0661	0.4999	0.1798	0.2053
5	76	0.34	0.2640	0.0591	0.5225	0.2640	0.44	0.1644	0.0548	0.4231	0.1644	0.2142
6	81	0.36	0.2033	0.0497	0.4608	0.2033	0.37	0.1846	0.0456	0.3333	0.1846	0.1939
7	86	0.34	0.1850	0.0421	0.3842	0.1850	0.37	0.1542	0.0383	0.2848	0.1542	0.1696
8	92	0.35	0.1420	0.0343	0.3110	0.1420	0.34	0.1490	0.0318	0.2564	0.1490	0.1455
9	98	0.34	0.1271	0.0285	0.2599	0.1271	0.39	0.0986	0.0275	0.1994	0.0986	0.1129
10	104	0.34	0.1073	0.0228	0.2056	0.1073	0.40	0.0772	0.0213	0.1702	0.0772	0.0922
11	111	0.34	0.0894	0.0191	0.1685	0.0894	0.32	0.0995	0.0178	0.1402	0.0995	0.0944
12	118	0.31	0.0887	0.0160	0.1395	0.0887	0.36	0.0660	0.0149	0.1160	0.0660	0.0774

Table A.26b. α -Pinene + O₃ B: Similar to Table A.1b. This experiment was excluded from the study (see Figure B.7)

APPENDIX B

Chromatograms for HPLC experiment pairs

Figure B.1. 1,5-Cyclooctadiene + NO₃: timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). Two HPLC experiments, A and B, were performed for the same filter extract. The bottom plot shows measured κ -values (circle for experiment A, triangle for experiment B) and the envelope of measureable κ -values during the experiments (dotted lines; lavender for experiment A, grey for experiment B). The particle dry diameter is noted below the symbol for each κ -value.

Figure B.2. *n*-Pentadecane + Cl (8 July): similar to Figure B.1. The ratio of Cl atoms to *n*-pentadecane molecules determines the extent of oxidation.

Figure B.3. *n*-Pentadecane + Cl (9 July): timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). Two HPLC experiments, A and B, were performed for the same filter extract. The bottom plot shows measured κ -values (circle for experiment A, triangle for experiment B) and the envelope of measureable κ -values during the experiments (dotted lines; lavender for experiment A, grey for experiment B). The particle dry diameter is centered above (experiment B) or below (experiment A) the set of κ envelopes associated with each upscan-downscan cycle. The ratio of Cl atoms to *n*-pentadecane molecules determines the extent of oxidation.

Figure B.4. *n*-Pentadecane + Cl (16 July): similar to Figure B.3.

Figure B.5. 1-Decene +O₃: timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (first and third plots). The second and fourth plots show measured κ -values (circle for RH = 20%, triangle for RH = 82%) and the envelope of measureable κ -values during the experiments (dotted lines). The particle dry diameter is noted near the symbol for each κ -value. The fifth plot shows a comparison between both experiments of the timeseries of κ -values (circle for RH = 20%, triangle for RH = 82%). Two experiments were performed for the 1-decene + O₃ system with different relative humidity present during the chamber reaction.

Figure B.6. *n*-Decane + Cl: similar to Figure B.5. The *n*-decane + Cl system was irradiated twice, and a filter sample was taken after each irradiation.

Figure B.7. α -Pinene + O_3 : similar to Figure B.5. Two HPLC experiments, A and B, were performed for the same filter extract. This data was excluded from the study – some of the CCN measured in experiment A seem to be multiply charged particles, which are larger than the prescribed D_d and thus would be expected to have a higher κ -value. The κ -value was lower for experiment A than for experiment B, throughout all retention times, despite multiply charged particles. Experiment A was the first experiment performed during the study.

APPENDIX C

Chromatograms for individual HPLC experiments

Figure C.1. 1,2-Dimethyl cyclohexene + O₃: timeseries of CN (black lines) and CCN (grey lines) with HPLC retention time (top and middle plots). The bottom plot shows measured κ -values and the envelope of measureable κ -values during the experiments (dotted lines). The particle dry diameter is noted above the symbol for each κ -value. The fraction of total eluting material is plotted vs. its associated κ -value, for each dry diameter measured (inset bar plot). The volume-weighted average κ -value is noted above the bars.

Figure C.2. 1,3,5,7-Cyclooctatetraene + NO₃: similar to Figure C.1.

Figure C.3. 1,3-Cyclohexadiene + NO₃: similar to Figure C.1.

Figure C.4. 1-Octene + O_3 : similar to Figure C.1.

Figure C.5. Cyclodecane + OH with NO_x ; similar to Figure C.1.

Figure C.6. Cyclohexene + O_3 : similar to Figure C.1.

Figure C7. Cyclooctane + OH with NO_x : similar to Figure C.1.

Figure C.8. Cyclooctene + O₃: similar to Figure C.1.

Figure C.9. Methyl furan + OH with NO_x: similar to Figure C.1.

Figure C.10. *m*-Xylene + OH with NO_x: similar to Figure C.1.

Figure C.11. Ocimene + NO₃: similar to Figure C.1.

Figure C.12. *n*-Pentadecane + Cl (13 July): similar to Figure C.1

APPENDIX D

Atomized droplet size distribution

Collision-type atomizers produce a lognormal size distribution of droplets. If the solute is completely dissolved, then its concentration is identical in each droplet. As the solvent is evaporated from the droplets, the size distribution is shifted to smaller diameters but the total particle number and standard deviation are preserved. Concentration, c , is the volume fraction of solute with respect to solvent, or the ratio of residual particle size to droplet size:

$$c = \frac{v_{solute}}{v_{solute} + v_{solvent}} = \frac{D_d}{D}$$

where v is volume, D_d is residual diameter, and D is droplet diameter. The residual size distribution mode diameter is shifted by $D_d = c^{1/3}D$.

Figure D.1 shows the wet droplet size distribution with the size distribution or residual particles. We estimate the concentration of solute to reconstruct the fraction of total material that elutes at any given time. As a proxy for concentration, we use the number concentration of dry particles, which is a function of solute concentration. If the diameter is much larger than the mode diameter, this function is nearly linear (Figure D.1).

Figure D.1. (left) Lognormal size distribution of atomized droplets with a mode diameter of 300 nm, and the size distributions of residual particles for three concentrations of solute. The standard deviation is 1.58, which was obtained from the pentadecane size distribution in Figure 4.4. Mode diameters of the residual size distributions are noted above the distributions. (right) The number concentration of particles as a function of the solute concentration, for four different diameters within the range of diameters selected in this study. Note that the mode diameter axis is not monotonically spaced.