

KINETICS, PRODUCTS, AND OPTICAL PROPERTY CHANGES DURING THE
HETEROGENEOUS OXIDATION OF ORGANIC AEROSOLS

by

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(Under the Direction of Dr. Geoffrey D. Smith)

ABSTRACT

A series of laboratory measurements have been developed to study the kinetics and product formation of organic aerosol oxidation and the consequences of oxidation on the optical properties of organic aerosol. The rate of reactive uptake of radical species and the resulting product distributions from the radical initiated oxidation of model solid and liquid organic aerosols exhibited a clear particle phase dependence. In NO_x -free experiments, although small differences in the reactive uptake of radical species on solid versus liquid particles were observed, higher degrees of oxidative turnover of condensed phase species occurred in solid particles compared to liquid particles of the same chemical composition. In NO_x -containing experiments, organic nitrate formation was observed in the reactions of solid, but not liquid particles. These experiments have many implications for the optical and water-uptake properties organic aerosol will exhibit in the atmosphere. In order to study the changes in light scattering and absorption cross sections of organic aerosols as a function of oxidative age, a UV cavity ring-down spectrometer was constructed. Clear increases in light extinction due to UV absorption were observed for oxidatively aged aerosol in comparison to “fresh” organic aerosol. Lastly, a new technique for studying gas phase and heterogeneous

oxidation kinetics has been developed and this “virtual injector” has been used to explore the effect of radical and radical precursor concentrations on the reactive uptake of these radicals and evidence of Langmuir-type adsorption of precursor species was observed. These experiments have important consequences for studying heterogeneous reaction kinetics in a laboratory setting where high concentrations of radicals, and thus high concentrations of radical precursors, must be used to access atmospherically relevant radical exposures on a short timescale.

INDEX WORDS: organic aerosol, heterogeneous oxidation, reactive uptake coefficient, hydroxyl radical, nitrate radical, ozone, chlorine radical, cavity ring-down, optical properties, refractive index

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DEDICATION

This work is dedicated to my loving family. I am grateful to have been raised by a strong, supportive mother who is always willing to listen, a loving, intelligent father who is always willing to help and a sister, my best friend, who has supported and encouraged me throughout my entire life. The three of them have always made me feel like I could do whatever I set myself to. Secondly, I want to thank the other two most important women in my life, Tamzyn and Stephanie, who have been there for me and encouraged me in my personal and academic pursuits for the past 16 years. Lastly, I want to dedicate this work to my future family. My fiancée has been a patient and wonderful companion throughout these last few years and I look forward to moving on with our lives together.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	v
CHAPTER	
1 INTRODUCTION: CURRENT SCIENTIFIC UNDERSTANDING OF ORGANIC AEROSOLS IN THE TROPOSPHERE.....	1
2 THE IMPORTANCE OF PARTICLE PHASE IN THE RADICAL- INITIATED OXIDATION OF MODEL ORGANIC AEROSOLS	17
3 PHASE DEPENDENCE OF ORGANIC NITRATE FORMATION.	71
4 A “VIRTUAL INJECTOR” FLOW-TUBE APPROACH FOR MEASURING GAS PHASE AND HETEROGENEOUS OXIDATION KINETICS	100
5 ARTIFACTS IN MEASURING AEROSOL UPTAKE KINETICS: THE ROLES OF TIME, CONCENTRATION, AND ADSORPTION	140
6 DEVELOPMENT OF AN ULTRA-VIOLET CAVITY RING-DOWN SPECTROMETER FOR AEROSOL EXTINCTION MEASUREMENT....	169
7 CONCLUSIONS AND FUTURE DIRECTION.....	199
APPENDICES	
A COMPARISON OF THE COUNTING EFFICIENCIES OF BUTANOL AND WATER-BASED CONDENSATION PARTICLE COUNTERS.....	205
B TIME EVOLUTION OF A GLYOXAL-AMMONIUM SULFATE SOLUTION	207
C SOLID AND LIQUID PARTICLE SCATTERING AND SUPERCOOLING LIFETIMES AS MEASURED WITH NEPHELOMETRY	209

CHAPTER 1
INTRODUCTION: CURRENT SCIENTIFIC UNDERSTANDING OF ORGANIC
AEROSOLS IN THE TROPOSPHERE

1.1. Introduction to atmospheric chemistry

The field of atmospheric chemistry is a relatively new discipline although issues of air pollution have been of interest to humankind for many centuries.¹ In fact, concern over air pollution has been documented back to the first and second centuries A.D.² However, it wasn't until the 1940s-1950s during the famous "London Fog" or "pea soup fog" episodes in London and "LA smog" episodes in California that concern over the health effects of air pollution brought public attention to atmospheric chemistry. The worst of the London Fog episodes in the 1950's is estimated to have led to the deaths of at least 12,000 people.³ Since the 1950s, the field of atmospheric chemistry has developed into a multifaceted discipline. In the last 60 years, observation, lab measurements, and modeling have led atmospheric scientists to a better understanding of the role of urban air pollution on visibility and human health and also on the atmospheric constituents that may affect the Earth's climate in both urban and remote areas.

The Earth's climate may be affected by phenomena which occur in troposphere, the closest "layer" of the atmosphere to earth, as well as phenomena which occur in the stratosphere, which contains the protective ozone layer. Since the troposphere contains essentially all of the water vapor, clouds, and precipitation as well as the air we breathe, the

atmospheric chemistry of the troposphere is of particular interest for observational, lab measurements, and modeling studies.

1.2. Organic aerosols in the troposphere

Natural and anthropogenic aerosols are ubiquitous in the troposphere and play a key role in many atmospheric/climatic processes such as water uptake, cloud condensation nuclei (CCN) activity, and scattering and absorption of incoming solar radiation, and they may have a significant impact on human health. Understanding the role of organic aerosol in atmospheric/climatic processes is of particular interest as organic carbon species account for 10-90% of fine particulate mass in some areas.^{4, 5}

Organic aerosols are formed from primary sources such as combustion, biomass burning, or sea spray that carries organic matter from the surface of the ocean. Conversely, they may also be formed in the atmosphere through the photochemical oxidation of gas-phase species yielding low-vapor-pressure products that may then condense or partition to existing particles to form secondary organic aerosol. Once formed, the particles will react with tropospheric gas-phase oxidants such as hydroxyl radicals (OH), ozone (O₃), and nitrate radicals (NO₃) to form more-highly-oxygenated species which may, in turn, affect the physical properties of the aerosol. Understanding how such organic particles are transformed chemically in the atmosphere is essential to understanding their fates and their climatological and human health effects.

1.3. Importance of particle oxidation in the troposphere

The relative rates of reaction and deposition of organic aerosols determines whether oxidative processing is important during the lifetime of the particles in the troposphere. For instance, if the heterogeneous reactions between particles and oxidants are slow and

deposition rates are fast, the chemical transformations an organic aerosol would undergo during its lifetime in the atmosphere would be negligible. Deposition of organic aerosols, on the other hand, has important consequences for ecosystem contamination and is a major source of toxic organic species such as PAHs in aquatic and soil environments.^{6, 7} The ecosystem effects of deposition of organic aerosol species are beyond the scope of this work. However, one must keep in mind the interconnectedness of the biogeochemosphere if one is to study one part of that complex system such as the atmosphere. The focus of this work is aimed at a better understanding of aerosols in the atmosphere and their role in climate.

Atmospheric lifetimes of organic aerosols depend on particle size and conditions such as humidity and precipitation rates, among other factors, and range from several days to a week.^{4, 8-10} The reactive lifetimes of organic aerosols, on the other hand, depend on the concentration of oxidants, particle size and composition. Hydroxyl radicals (OH), although present in much lower concentrations in the troposphere than other oxidants such as O₃ and NO₃, is considered the most important tropospheric oxidant due to its high reactivity with gas and particle phase species. Recent studies of the OH initiated oxidation of ambient particles have suggested that enhanced oxidation of the organic matter in organic aerosol may occur after no more than four days at typical atmospheric OH concentrations.¹¹ Clearly, the reactive transformation of organic material in aerosols is able to occur on the timescale of an organic aerosol. The chemical transformations of organic aerosols, therefore, will play an important role in determining their physical properties and climate effects during their lifetime in the atmosphere.

The observation that many particulate phase organic species are oxidized rapidly in the troposphere has important consequences for source apportionment studies. Associated with

particulate organic matter emitted from certain sources are molecular markers which are characteristic of the source type. For example, the molecule levoglucosan which arises from the pyrolysis of cellulose is often used as a molecular marker for biomass burning aerosol,¹² while hopanes and steranes are often used as molecular markers for motor vehicle emissions,^{13, 14} and oleic acid has been used as a molecular marker for meat cooking aerosol.¹⁵ Many source apportionment models assume that markers are stable during transport and that oxidative transformation is negligible. However, much evidence has suggested the contrary - many molecular markers undergo efficient reactions with OH on timescales which are shorter than or comparable to the particle lifetimes in the troposphere. For example, one recent study reported oxidative lifetimes levoglucosan with OH to be 0.7-2.2 days.¹⁶ Other recent studies have shown that hopanes and steranes may have OH oxidation lifetimes of ~1-2 days under dry conditions.^{17, 18} Although ozonolysis reactions are generally slower than OH concentrations, typical ozone concentrations are higher than OH, thus the oxidative lifetime of some species such as unsaturated organics may be heavily influenced by their reaction rates with ozone. Oleic acid in meat cooking aerosol, for instance, is estimated to have an oxidative lifetime of less than one day from reactions with tropospheric ozone.¹⁹ These results suggest that treating molecular markers as unreactive in chemical transport models may introduce a large source of error in source apportionment studies. Clearly, there is a need for a firm understanding of the rates of heterogeneous reactions in the troposphere, not only to include in transport models but also in order to understand the rates at which the physical properties of the aerosols may be changing.

Although OH is often considered the most important tropospheric oxidant of organic species due to its nearly non-selective reactivity with organic carbon compounds, other

reactive species including NO_3 and O_3 are also considered important tropospheric oxidants. In marine environments, halogen atoms such as Cl, Br, and I may be considered significant oxidants of organic particulate matter. No matter the initiating oxidant, the end result of heterogeneous oxidation of organic aerosols is almost always the formation of more highly functionalized organic species. In radical initiated oxidation of organic particles, condensed phase, functionalized products are observed including carbonyls, alcohols, and organic nitrates as well as multigenerational products, the consequence of the primary oxidation products undergoing further oxidation. Recent studies of the OH initiated oxidation of a branched alkane, squalane, suggest that for every collision with OH, another oxygen atom is added to the molecule.²⁰ While many laboratory studies of organic aerosol oxidation have been carried out on model organic aerosols made of reduced organics such as hydrocarbons, atmospheric aerosols are often dominated by highly oxygenated constituents.^{5, 21-23} Recent experiments have shown that not only do reduced organics become more oxygenated after radical initiated oxidation, ambient particles and diesel exhaust aerosol also become more highly oxygenated upon exposure to OH.^{11, 24} The formation of highly functionalized products may alter the effect of the aerosol on climate processes such as their ability to scatter and absorb ultraviolet and visible light as well as their ability to act as nuclei for cloud condensation.

1.4. Climate effects of organic aerosol

Direct Effects

Aerosol particles in the troposphere directly influence the climate through their ability to scatter and absorb radiation. Organic aerosols have generally been considered purely scattering in the actinic window, the range of wavelengths which are able to reach the

troposphere. However, recent evidence for light absorbing organic compounds has surfaced and the scientific community still has little understanding of the sources and chemical composition of these “brown carbon” (BrC) species. Recent evidence suggests that light absorption by particulate organic matter increases during atmospheric aging due to the formation of BrC species.²⁵ Thus, as organic aerosols in the troposphere are undergoing oxidative aging, their ability to scatter and absorb solar radiation is constantly changing. The exact mechanisms of BrC formation and the chemical structure of BrC species is still an important unknown although much headway has been made.²⁶⁻³⁵ Some BrC species appear to be “Humic-Like Substances”^{30, 32} (oligomeric, multifunctionalized, high molecular weight species, HULIS) while other BrC species appear to be highly conjugated nitrogen containing species,²⁶ and yet others appear to be polyaromatic molecules.

Primary sources of BrC also exist. In the U.S. and other industrialized nations, diesel emissions are important sources of light absorbing organic carbon. However, in developing nations, biomass burning is an important fuel source for energy production, transportation, and home heating and cooking operations. Further, wild fires in boreal and tropical regions and prescribed and agricultural waste burning across the globe also represent large sources of combustion-derived aerosol. These fuels and combustion processes emit both black carbon (“soot”) and large quantities of organic carbon aerosol. However, different fuels, fuel conditions, and combustion phases emit widely differing aerosols, including some BrC species with unknown chemical composition, although most appear to be humic-like.³⁶

The formation of absorbing constituents in organic aerosol has important atmospheric consequences as an aerosol’s ability to scatter and absorb radiation determines its role in the aerosol direct effect. Radiative forcing is a measure of the change in net irradiance at the

tropopause and can be ascribed to atmospheric constituents to describe their effect on global radiation budgets. Negative radiative forcing is associated with attenuation of light at the tropopause and thus with cooling while positive radiative forcing is associated with warming. The International Panel on Climate Change estimates the direct global radiative forcing of aerosols (organic and inorganic) to be $-0.50 \pm 0.40 \text{ W m}^{-2}$.³⁷ Large error bars on these estimates represent the large uncertainty in the aerosol direct effect, much of which is due to current uncertainty of the role of organic aerosol in scattering and absorption processes.

The ability of particles to scatter and absorb solar radiation not only affects climate by affecting the amount of radiation that reaches the Earth's surface but also has important consequences for visibility impairment, especially when the particle sizes are on the same order of magnitude as the wavelength of light. Organic aerosol components have been found to contribute to light extinction properties of ambient aerosols in both urban and remote areas.^{38, 39}

Indirect Effects

Microphysical interactions between aerosols and clouds may alter cloud cover and cloud albedo (a measure of a cloud's reflectivity) and thus impact the amount of solar radiation that reaches the Earth's surface through a variety of aerosol indirect effects.³⁷ The indirect effects of aerosol particles on cloud cover and precipitation are complex and it is difficult to quantify the magnitude of each different effect that an aerosol particle will exert in the atmosphere. However, what is understood about aerosol particles and their role in the indirect effects is that the size and chemical composition of the initial cloud condensation nuclei (CCN, e.g. sulphates, nitrates, dust, organic carbon, black carbon, and brown carbon) are essential in the activation and early growth of cloud droplets, particularly the water-soluble fraction of

aerosols including water soluble organic species and compounds that affect the surface tension of the aerosol particle.⁴⁰ The hygroscopicity of ambient aerosol particles will determine their ability to act as CCN and thus their ability to affect cloud formation and precipitation rates. Many recent studies have shown that the hygroscopicity of particulate organic matter is directly correlated to increasing degree of oxidation of the aerosol.^{25, 41, 42} These studies suggest that as organic aerosols undergo reactions with OH and other reactive species in the troposphere and form more highly oxygenated products, their potential effect on climate through their ability to act as CCN is increasing.

1.5. Goals of this work

Kinetics and products of model organic aerosol oxidation

In order to better understand the impact of organic aerosol oxidation on the chemistry of the troposphere and the impact oxidized organic aerosol will have on climatic processes, elucidation of heterogeneous reaction rates and the important reaction pathways that have the potential to alter particle physical properties is a necessity. Although much recent effort has been aimed at elucidating the important reaction pathways of radical initiated heterogeneous oxidation, there appears to be no clear consensus on the importance of functionalization versus fragmentation.

Hydrogen abstraction by radical species including OH, Cl, and NO₃ is efficient and after initial abstraction, alkyl radicals rapidly react with O₂ to form peroxy radicals. These peroxy radicals then undergo self-reactions to form carbonyl and alcohol products or may undergo β -scission reactions that result in the formation of volatile aldehydes. The relative importance of these mechanisms has important consequences for the fate of the organic aerosol and its climatic properties. For instance, if scission reactions dominate - forming low molecular

weight, volatile products - the particle oxidation state will not drastically change, as the majority of oxidation products will leave the particle phase. Conversely, if functionalization reactions dominate, the particles will become more heavily oxygenated and their physical and climatic properties may be altered.

While several experiments including both laboratory generated, single-component aerosol studies and ambient aerosols studies have suggested that functionalization is the primary channel for radical initiated oxidation with little to no contribution from the β -scission,^{11, 43-47} others have suggested the importance of the β -scission channel though the few measurements of their yields span a wide range.⁴⁸⁻⁵¹ It is not clear from a review of the existing experiments how prevalent the β -scission channel is or under what conditions volatilization may occur on organic aerosols. Furthermore, it is not evident whether the phase and morphology of the organic particle or film influences the important RO₂ reaction channels.

In Chapters 2 and 3, the effect of particle phase on RO₂ chemistry is explored in simulated “clean” and “polluted” atmospheres where oxidation reactions of solid and liquid particles of the same chemical composition were studied at room temperature in the presence and absence of NO_x (NO + NO₂). These experiments may elucidate some of the sources of controversy in the ongoing discussion of the relative importance of fragmentation and functionalization as well as provide interesting information on the phase dependence of RO₂ chemistry and product diffusion.

Design of a new method for studying organic aerosol oxidation kinetics

A better understanding of heterogeneous reaction kinetics is necessary in order to predict the oxidative lifetimes of particulate organic matter in the atmosphere. In order to study the

kinetics of aerosol oxidation in a laboratory setting, much higher concentrations of oxidants than those present in the atmosphere must be used. Otherwise, the collection of a single reactive decay would take as long as the reactive lifetime of particles in the atmosphere which is anywhere on the scale of hours to more than a week. Using higher oxidant concentrations, the oxidative decay of particle phase species may be observed in a few seconds to minutes using flow-tube apparatus.

In converting between laboratory and atmospheric conditions, it is often simpler to think of oxidant “exposure”, the product of oxidant concentration and time. For instance, a heterogeneous reaction of a theoretical condensed-phase unsaturated organic with OH with an effective bimolecular rate constant of 1×10^{-11} cm³/molecule/sec. would take almost 1.2 days to decay by one lifetime in the atmosphere with 1×10^6 molecules/cm³ OH, but may be studied in only 100 seconds with 1×10^{10} molecules/cm³ OH in a reaction flow-tube.

Many flow-tubes studies have used a thin film or flow-tube coating of the condensed phase organic species as a surrogate for organic aerosol.^{47, 52-56} In those studies, the decay of the gas phase oxidant is observed as it is allowed to interact with the film of condensed phase organic. Recent advancements, especially in mass spectral detection of aerosol species, have led to the development of aerosol flow-tube designs whereby the decay of the aerosol species is observed as the particles are exposed to a gas phase oxidant.^{20, 44, 51, 57, 58} The kinetics derived from the decay of the condensed phase species will differ from the kinetics derived from the decay of the gas phase oxidant if there are any additional loss mechanisms in the condensed phase such as secondary reactions between radical intermediate species and the condensed phase organic. The distinction between kinetics obtained by these two approaches, therefore, is important.

In both aerosol flow-tube and coated flow-tube or thin film experiments, a variety of techniques exist for studying heterogeneous oxidation kinetics which vary in the way that the oxidant exposure is changed to simulate oxidative aging. In the atmosphere aging occurs as a function of time at more-or-less steady state concentrations of radicals. In some flow-tube designs, oxidant concentrations are held constant while a movable injector is used to increase or decrease the amount of contact time between the particles and oxidant while other laboratory studies take advantage of the relationship between reaction time and oxidant concentration and simulate aging by changing the radical concentration at a fixed reaction time. In Chapter 4, an aerosol flow tube is introduced which acts as a “virtual injector” flow-tube. Using this design, both gas phase and the heterogeneous kinetics of both single component and complex particles may be studied as a function of time at steady state radical concentrations while overcoming some of the disadvantages of movable injector designs.

Understanding experimental artifacts of flow-tube experiments

Although laboratory experiments utilize the relationship between oxidant concentration and reaction time in order to study reactions on the timescale of a few minutes which may occur in the troposphere on the timescale of hours to days, it is still not clear whether in heterogeneous reactions these two parameters are truly interchangeable. In Chapter 5, the relationship between concentration and time is addressed using the virtual injector flow-tube introduced in Chapter 4 and a smaller volume flow-tube where oxidant concentration rather than reaction time was used to alter the exposure to OH and Cl radicals. Also, the effect of radical precursor concentrations on the reactive uptake of OH and Cl is also explored. These experiments have important consequences for studying reactive uptake kinetics in a laboratory setting.

Optical characterization of oxidized organic aerosol

As discussed in Section 1.4, many organic aerosol oxidation mechanisms exist that may lead to the formation of brown carbon species, organic compounds which are able to absorb strongly in the UV and visible regions of the electromagnetic spectrum. A better understanding of the oxidation mechanisms which may lead to brown carbon formation as well as the magnitude of the predicted optical changes upon formation of these brown carbon species is needed in order to gain a better understanding of the role of brown carbon in climate forcing. In Chapter 6, the design of a cavity ring-down instrument for the highly sensitive detection of aerosol absorption is discussed. Although this instrument is still in the developmental stages, experiments are presented that show promising evidence of the sensitivity of this technique. Experimental parameters which may affect the accuracy of the cavity ring-down instrument are also discussed.

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CHAPTER 2

THE IMPORTANCE OF PARTICLE PHASE IN THE RADICAL-INITIATED OXIDATION OF MODEL ORGANIC AEROSOLS¹

2.1. Introduction

Particle phase may significantly alter the reactivity of the particle and the products that are formed in reactions with gas phase oxidants. It is imperative to distinguish between heterogeneous reactions occurring on solid and liquid particles in order to gain a better understanding of the effect of aerosol phase in oxidation reactions in the atmosphere. Some evidence exists that suggests particle phase may significantly affect organic aerosol reactivity with gas phase oxidants. For example, it has been shown that the rate of reactive uptake of ozone on liquid oleic acid particles may be more than an order of magnitude faster than on mixed particles containing a solid component, such as myristic acid, stearic acid, hexadecanoic acid, or *n*-docosane.²⁻⁵ In these cases significant differences in reactive uptake are observed because ozone diffusion and/or solubility in the solid domains of the particles limit the rate of reaction. Reactions with other species, such as Cl, OH, and NO₃, have also been studied, but there does not yet appear to be a clear picture of how the particle phase affects the rates and products of these radical-initiated heterogeneous reactions.

In particular, reactions of OH radicals with liquid and solid organic aerosols are of interest since OH is the primary oxidant in the troposphere. The analogous gas-phase reactions of OH with volatile organic compounds have been studied extensively and provide a framework for understanding the heterogeneous reactions.⁶ The generally accepted

mechanism in the gas phase is as follows: the OH radical efficiently abstracts a hydrogen atom from the hydrocarbon chain and in the presence of atmospherically relevant concentrations of O₂, an alkylperoxy radical (RO₂) is formed. Under low-NO_x (NO + NO₂) conditions, two RO₂ radicals can react to form either two alkoxy radicals (RO) or a carbonyl–alcohol pair with a branching ratio of approximately 50%. Alternatively, the RO₂ radical may react with HO₂ to generate hydroperoxides. The RO radicals formed may then react further to produce a variety of products either through 1,4-H-shift isomerization, β-scission leading to decomposition into a smaller aldehyde and an alkyl radical, or by reaction with O₂ to form a ketone and HO₂. These reactions are summarized in Fig. 2.1.

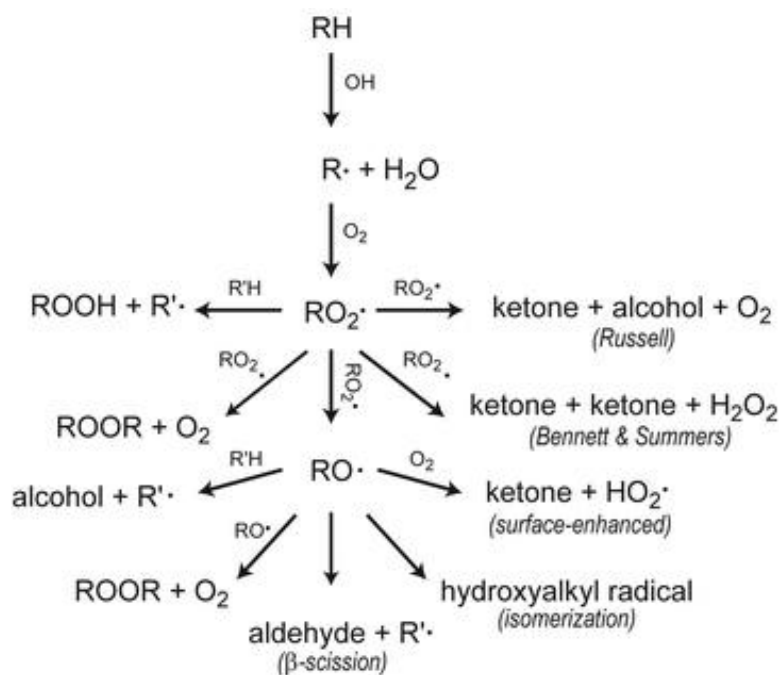


Figure 2.1. Reaction mechanism for the radical-initiated oxidation of organic species in the absence of NO_x.

In heterogeneous reactions of OH with organic species, hydrogen abstraction is efficient⁷⁻⁹ and leads to the creation of RO₂ radicals in the presence of O₂, but their fates to produce various ketones, aldehydes, and alcohols is not clear. In bulk liquids it is known that primary

and secondary RO₂ radicals do not react to form RO radicals, in general, but instead form the carbonyl–alcohol pair and O₂.^{10, 11} However, recent work from this lab has indicated that this may not be the case for heterogeneous (*i.e.* interfacial) reactions since carbonyl products are formed in larger yields than are alcohol products.¹² Additionally, several researchers have found evidence of the β -scission channel in which the RO radical decomposes to form volatile aldehydes,^{9, 12-18} though the few measurements of their yields span a wide range. Such volatilization could alter the particle substantially through the loss of organic mass, and it has been suggested that in the atmosphere this channel could limit the lifetime of some organic particles¹⁴ and be a source of volatile organic compounds.¹⁹ However, it is not yet understood under what conditions or for what types of reactions this channel may be important. Interestingly, George *et al.*¹⁸ recently found that the oxidation of ambient particles by OH leads to increased functionalization of the organic fraction and that only a minor fraction of the particle mass is lost through volatilization when reacted with high concentrations of OH (equivalent to nine days with [OH] = 2×10^6 radicals per cm³ in the atmosphere). However, the complexity of ambient aerosols makes it difficult to determine the mechanisms of oxidation that are responsible and therefore how these results can be extrapolated to atmospheric conditions with much lower OH concentrations. For this reason, many have studied the oxidation of model organic aerosols or proxies for organic aerosols such as thin films and self-assembled monolayers.

For example, Hearn *et al.*¹² and George *et al.*⁹ saw negligible decreases in particle size in the Cl- and OH-initiated oxidation reactions of liquid dioctyl sebacate (DOS) particles, respectively, suggesting that volatilization is of minor importance. In each study the formation of ketone and alcohol products was also observed in the condensed phase, but the

yields of these two products were not equal as would be the case if they originated from the Russell mechanism²⁰ (known to occur in bulk liquids to produce a carbonyl–alcohol pair of products), and so it was concluded that some of the ketone product was created from additional channels.¹² The observation of H₂O₂ suggested that the RO₂ + RO₂ → ketone + ketone + H₂O₂ reaction (the Bennett & Summers mechanism²¹) may be one such channel, while the dependence of the ketone yield on O₂ concentration indicated the presence of a surface-enhanced RO + O₂ → ketone + HO₂ reaction. The large yield of condensed-phase products (86%) along with the absence of low-*m/z* species in the mass spectrum of reacted DOS and the negligible particle size change suggested that particle volatilization from the formation of VOCs through β-scission is insignificant in these particles.^{9, 12}

Likewise, Knopf *et al.*¹⁶ and Docherty and Ziemann²² saw little or no volatilization in the NO₃-initiated oxidation of organic films and particles, as did Moise and Rudich²³ using Br and Cl radicals. Using X-ray photoelectron microscopy (XPS) to investigate the surface of octadecanethiol self-assembled monolayers (SAMs) during reaction with NO₃, Knopf *et al.*¹⁶ observed increased functionalization of the SAM surface with spectral features indicative of C–O groups, carbonyls such as aldehydes or ketones, or carboxylic acids. However, the exact identity of the functionalized products was not determined. Also, they found that even at very large NO₃ exposures (equivalent of one week at [NO₃] = 50 ppt in the atmosphere), less than 10% of the carbon was lost leading them to conclude that volatilization of the surface through reaction with NO₃ was not efficient. Docherty and Ziemann²² studied the reaction of liquid oleic acid particles with NO₃ in an environmental chamber, and although the initial step involves NO₃ addition across the double bond rather than proton abstraction, RO₂ radicals are subsequently formed and the primary products are the hydroxy-nitrates and

carbonyl-nitrates. These results suggest that the major products of radical-initiated oxidation of saturated and unsaturated compounds are alcohol- and ketone-substituted parent compounds rather than small, volatile decomposition products. Moise and Rudich²³ used FTIR, XPS, and contact angle measurements to characterize the surface after Br and Cl radical-initiated oxidation of organic thin films and found increased functionality and hydrophilicity of the surface with some carbon loss suggesting the formation of oxygenated condensed-phase products and perhaps a minor contribution from the decomposition channel.

On the contrary, Molina *et al.*¹⁴ observed the efficient volatilization of octadecyltrichlorosilane (OTS) self-assembled monolayers during OH-initiated oxidation. Among the volatile products observed were various low-molecular-weight aldehydes, acids, and peroxides. They estimated that volatilization of these monolayers is so efficient that for every 2–3 collisions of OH with the surface, one OTS chain is removed. These results suggest that decomposition of the alkoxy radical through C–C bond scission is the primary mechanism of reaction following radical initiation by OH and that volatilization is efficient enough to compete with wet and dry deposition in the atmosphere. Eliason *et al.*¹⁵ also observed the formation of low-molecular-weight aldehydes resulting from the β -scission channel of the RO radical in the OH-initiated oxidation of thin films of liquid hexadecane. In addition, they detected low-molecular-weight carboxylic acids although the mechanism of their formation is unclear. Furthermore, in the oxidation of dodecane films they observed the formation of ketone products and no alcohol products suggesting that the RO₂ self-reaction to form a carbonyl–alcohol pair (Russell mechanism) is negligible.

In their study of the OH-initiated oxidation of solid palmitic acid particles, McNeill *et al.*¹⁷ found that volatilization of the surface of the particles was efficient enough to

continuously expose sub-surface layers to OH, thus leading to a constant renewal of the surface and a continued loss of palmitic acid. Although the alcohol and ketone condensed-phase products were observed, they also detected a variety of carboxylic acid products with molecular weights smaller than palmitic acid suggesting the importance of the β -scission channel of the RO radical. They also report a decrease of up to 10% in the particle mobility diameter upon reaction with OH supporting volatilization as a potential pathway in palmitic acid oxidation; however, changes in particle shape or morphology could be responsible for the observed changes in mobility diameter. In a similar study of the OH-initiated oxidation of solid stearic acid particles, Vlasenko *et al.*¹³ measured the yields of VOCs to be as high as 34%; conversely, they measured much smaller yields for the oxidation of liquid DOS (10%), solid *n*-hexane soot (3%), and solid pyrene (1%) particles.

Thus, there appears to be no clear consensus on how prevalent the β -scission channel is or under what conditions volatilization may occur on organic aerosols. Furthermore, it is not clear whether the phase and morphology of the organic particle or film influences this β -scission channel, in particular, or the chemistry of the RO₂ radicals, in general. While there has been a lack of experiments to test the effect of phase on radical-initiated oxidation directly, Moise and co-workers did determine that the uptake of NO₃ radicals can be slowed by up to a factor of five on some organic films when they were frozen whereas other films showed no such phase effect.²⁴ However, it is still not well understood how radical-initiated oxidation proceeds on liquid and solid organic particles and how phase may influence the aging of organic aerosols in the atmosphere.

Towards this end, we have investigated the Cl-initiated oxidation of single component particles containing erucic acid (cis-13- docosenoic acid, EA), brassidic acid (trans-13-

docosenoic acid, BA), nervonic acid (*cis*-15-tetracosenoic acid, NA), *trans*-11-eicosenoic acid (TEA), and elaidic acid (*trans*-9-octadecenoic acid, ELA), stearic acid (SA, octadecanoic acid), arachidic acid (AA, eicosanoic acid), behenic acid (BHA, docosanoic acid), and lignoceric acid (LA, tetracosanoic acid), and gondoic acid (GA, *cis*-11-eicosenoic acid). Particles of BA, NA, TEA, ELA, and EA are able to exist as supercooled (*i.e.* liquid) particles and solid particles allowing the determination of the importance of particle phase in the kinetics and product formation pathways for solid and liquid particles of the same chemical composition. Here, the Cl radical is used as a surrogate for the OH radical because it is simpler to generate and introduces fewer experimental complications. The unsaturated acids in this study are used here as a proxy for unsaturated organic fatty acids, which can be significant components of organic aerosol matter and are associated with aerosols in both urban and remote areas.^{25, 26} Oleic acid (*cis*-9-octadecenoic acid), for example, is found in particulate matter from urban atmospheres at mean annual concentrations of 17.3–26 ng/m³,²⁵ and in remote atmospheres at concentrations of 2.5–33 ng/m³,²⁷ and is known to originate from a variety of sources including the broiling of meat.²⁸ In a broader sense, the organic acids employed in this study were used as a proxy for aerosol hydrocarbons, in general, since many of the oxidation reactions in these model organic aerosols are not unique to molecules containing a carboxylic acid moiety; thus studying these model systems may provide insight into the importance of particle phase in the oxidation of organic aerosols in general.

Using a flow tube reactor coupled to a chemical ionization mass spectrometer, the Cl-initiated oxidation reactions of solid and supercooled liquid organic acid particles were investigated at room temperature. Organic acids which were used to form both solid and supercooled liquid aerosols include erucic acid (*cis*-13- docosenoic acid), brassidic acid

(trans-13-docosenoic acid), nervonic acid (*cis*-15-tetracosenoic acid), trans-11-eicosenoic acid, and elaidic acid (trans-9-octadecenoic acid). For the first time radical-initiated oxidation reactions of liquid and solid organic particles of identical chemical composition were performed making it possible to probe the effect of phase on reaction kinetics and product distributions. The lack of significant slowing upon solidification suggests that the surface is continuously renewed, perhaps by evaporation of volatile products or mixing of underlying solid particle constituents at a surface melt layer. The initial oxidation products were found to be the keto-acid and the alcohol-acid for both solid and liquid particles, and they account for as much as two thirds of the reacted acid. The distribution of other products, however, was found to be quite different in the two phases. For equivalent Cl radical exposures, more multiply-oxidized species as well as low-molecular-weight species were created from the oxidation of solid particles. These observations, as well as the greater decrease in particle volume observed from the reaction of solid brassidic acid particles, are consistent with a loss of mass through evaporation of small, volatile oxidation products. The findings from this study suggest that slower diffusion of the oxidation products in solid particles confines the products to the surface where they continue to react with Cl radicals producing more-highly-functionalized products which may decompose more readily. Thus, the solid particles react nearly as efficiently as the liquid ones, but the manner in which they “age” chemically is substantially different. The product trends observed in the direct comparison of radical-initiated oxidation of solid and liquid particles of the same chemical composition were also observed in the oxidation of other solid and liquid single component aerosols. These experiments with these model systems indicate that particle phase could be important in

determining how organic aerosols evolve chemically through radical-initiated oxidation in the atmosphere.

2.2. Materials and methods

2.2.1. Particle generation

Organic acid particles were generated through homogeneous nucleation by flowing 0.9 slpm (standard liters per minute) of N₂ through a reservoir containing the organic acid of interest and heated to the temperature listed in Table 1 under “vapor well temperature.” Upon exiting the reservoir the organic vapor cooled to room temperature and spontaneously nucleated forming supercooled liquid droplets. The aerosol was then reheated as it flowed through a heated section of 1/2 inch o.d. glass tubing to narrow the distribution of particle sizes. The reheater temperatures used for the generation of each particle type were approximately the same for each particle type and ranged from 140-150 °C. After they exited this stage the particles cooled to room temperature and the particle diameters which were generated are given in Table 1. The geometric standard deviation of the particles was less than or equal to 1.25, as measured using a scanning mobility particle sizer (SMPS) (model 3936L85, TSI, Inc.).

Table 2.1. Summary of vapor well temperatures, resulting particle diameters, melting points and solid/liquid phase capability of the organic acids studied herein.

Organic Acid	Vapor well temperature (°C)	Average particle diameter (nm)	Melting point (°C, ref. 29 unless noted)	Phase capability
BA	146	60.9	61.9	solid/liquid
NA	134	44.0	43	solid/liquid
TEA	126	75.0	51.9 ³⁰	solid/liquid
ELA	119	87.9	45	solid/liquid
EA	136	75.5	34 ³¹	solid/liquid
SA	152	80.5	69.3	solid
AA	156	82.7	76.5	solid
BHA	155	88.3	81.5	solid
LA	158	98.0	87.5	solid
GA	126	66.6	22 ³²	liquid

Previous experiments have shown that particles of other organic acids formed by homogeneous nucleation can be supercooled by up to 32 °C below the freezing point and may remain supercooled for at least half an hour.² Because BA, EA, NA, TEA, and ELA have relatively low melting points (see Table 1) these particles also remained supercooled even when cooled to room temperature and while in the flow tube reactor (residence time ~2 seconds). Alternatively, the droplets were sent through a cold trap held at –80 °C where they froze to solid particles and then were warmed to room temperature before entering the flow tube reactor. In this way it was possible to generate liquid or solid organic acid particles. To ensure that BA was able to form supercooled liquid droplets (as the freezing point is slightly greater than 32 °C above room temperature and is thus approaching the limits of supercooling lifetimes that are useful in these experiments), the phase of the particles was confirmed by observing the slowing in the rate of reaction of BA with O₃ upon freezing, as described later. For the saturated acids, which have much higher melting points, supercooling is not feasible and solid particles were formed after the particles leaving the homogeneous nucleation source cooled to room temperature. The GA, on the other hand, melts at room temperature

and the liquid particles which exited the homogeneous source remained liquid throughout the flow tube.

2.2.2. Flow tube reactions

Reactions were carried out at atmospheric pressure and room temperature in a glass flow tube (1.1 cm i.d., 90 cm length). The BA, TEA, NA, ELA or EA particles (0.9 slpm N₂ flow) and either Cl₂ and O₂ (0.5 slpm flow) or O₃ were carried into the rear end of the flow tube in a 1.1 slpm N₂ carrier flow. The total flow of 2.5 slpm thus contained 20% O₂, and the total reaction time was about 2 seconds. While the OH radical is the primary oxidant in the troposphere, the Cl radical was used in this study to initiate the oxidation of the unsaturated fatty acids particles instead because it is possible to generate a larger steady-state concentration of Cl radicals (the self-reaction rate coefficient is smaller for Cl than for OH), and the Cl₂ precursor is unreactive and does not interfere with the oxidation chemistry in the particles. Chlorine radicals were generated by photodissociation of Cl₂ using the third harmonic (355 nm) from a 10-Hz pulsed Nd:YAG laser (QuantaRay PRO-250, Spectra-Physics). The chlorine radical concentration was controlled by either adjusting the laser power or by adjusting the flow of Cl₂ through the flow reactor, and was measured using a gas phase reference compound, methanol, for which the gas phase rate constant with Cl is firmly established ($k = 5.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)³³. Typical Cl concentrations used in these studies range were between 10^{10} – 10^{11} radicals per cm³ which corresponds to an equivalent OH radical exposure of approximately 5.5–55 hours in the atmosphere assuming an average OH radical concentration of 10^6 molecules per cm³.

2.2.3. Chemical ionization and detection

The flow tube eluent containing aerosol was sampled into the ion tube region through a stainless steel orifice (0.5 mm i.d.) in a heated (230-240 °C) stainless steel vaporizer tube (1/4 inch o.d., 4 inches long). The vaporized aerosol flow then entered the heated (160 °C) stainless steel ion tube (1/2 inch o.d., 8 inches long, 40 Torr) of the CIMS instrument where it mixed with a 2 slpm flow of N₂ containing reagent ions generated from a radioactive ²¹⁰Po source (NRD). The reagent ions ionized the vaporized particle constituents, and the ions were then sampled into the high vacuum region through a 200-μm orifice by means of a small potential gradient (2–5 V) and differential pumping. Ions were filtered using a quadrupole mass spectrometer (ABB Extrel) and detected using a Channeltron electron multiplier (model 4816, Burle).

A few different reagent ions were employed depending on the type of experiment being conducted. For the product yield studies, which were performed with BA and EA particles only, negative ion chemical ionization was used with Cl[−] and Cl₂[−] reagent ions generated from the Cl₂ exiting the flow tube. The BA and EA and the oxidation products were detected through proton abstraction (*e.g.* [M − H][−]) or Cl[−]-adduct formation (*e.g.* [M + Cl][−]). The proton abstraction peaks were particularly useful in measuring the yields of the oxidation products since Cl[−] will abstract a proton preferentially from the carboxylic acid functional group of the reactants and the oxidation products. Consequently, the ionization rate constants, and thus the detection sensitivities, are expected to be nearly identical for the reactants and the products making it possible to calculate product yields. The Cl[−]/Cl₂[−] ratio was adjusted to enhance Cl[−]-adduct formation by adding a trace amount of O₂ in the N₂ flow through the ²¹⁰Po radioactive source. Positive reagent ions, H⁺(H₂O)_{*n*} (*n* = 2 or 3), were used

in the kinetics studies and product trend studies since 1) the large concentrations of O_3 required for the ozonolysis reactions interfere with negative ion chemical ionization 2) the relative ionization efficiencies of the organic acids and their oxidation products is not important in determining the trends in product formation in solid and liquid particles and 3) methanol, the gas phase reference compound, used to ensure solid and liquid particles have been exposed to the same radical concentrations, is not ionized by Cl^- or Cl_2^- . The $H^+(H_2O)_n$ reagent ions were generated by sending trace amounts of O_2 and residual water along with the N_2 through the ^{210}Po source. The organic acid and oxidation products were then detected as the corresponding protonated molecular ion, $[M + H]^+$. A schematic diagram of the experimental setup is shown in Fig. 2.2.

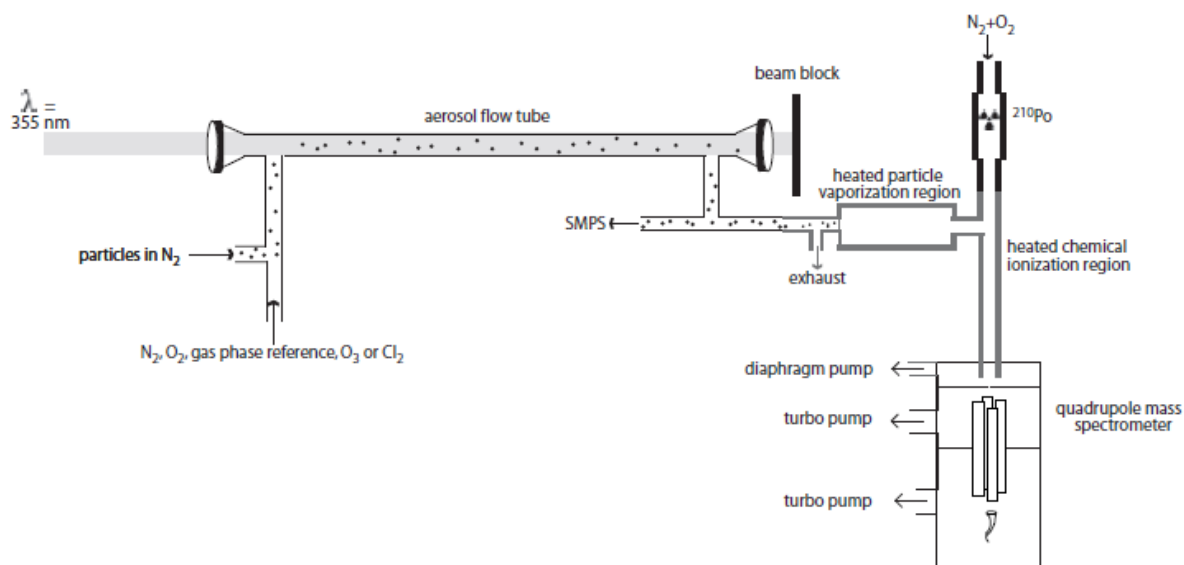


Figure 2.2. Schematic diagram of the flow tube reactor and Aerosol CIMS instrument used in these experiments.

2.2.4. Gases and chemicals

Gases used were nitrogen (99.99%, National Welders), chlorine (UHP grade, National Welders), and oxygen (industrial grade, National Welders). Ozone was generated using a commercial ozone generator (Model L11, Pacific Ozone Technology) and stored on silica gel at $-80\text{ }^{\circ}\text{C}$ as described elsewhere.³⁴ Brassidic acid (98%), nervonic acid ($\geq 99\%$), trans-11-eicosenoic acid ($\geq 98\%$), elaidic acid ($>99\%$), erucic acid ($\geq 99\%$), arachidic acid ($>98\%$), lignoceric acid ($\geq 99\%$), stearic acid ($\geq 99\%$), behenic acid (98%), gondoic acid (99%), butyric acid ($>99\%$), and 2-butanone ($>99.7\%$) were purchased from Sigma Aldrich and used without further purification.

2.3. Results and discussion

2.3.1. Confirmation of particle phase

In numerous studies, a clear difference in the rate of reaction has been observed for ozonolysis of unsaturated species depending on whether they exist in liquid or solid states.^{2, 3, 5, 35-37} For example, Moise and Rudich measured a decrease of approximately an order of magnitude in the uptake coefficient of ozone on oleic acid and linoleic acid surfaces when they were frozen.³⁶ Furthermore, Hearn and Smith have measured a decrease of more than an order of magnitude in the rate of ozonolysis of frozen mixed oleic acid–myristic acid particles compared to supercooled particles of the same chemical composition.² In those experiments, organic acid particles formed by homogeneous nucleation, displayed supercooling up to $32\text{ }^{\circ}\text{C}$ below the freezing point and remained supercooled for at least a half an hour.² All of the organic acids used here have melting points which are above room temperature with the exception of GA, which has a melting point at the laboratory temperature. For those species with melting points less than $32\text{ }^{\circ}\text{C}$ but significantly above

room temperature, the ability to form supercooled particles was assumed. Brassidic acid, which has a melting point $\sim 42^{\circ}\text{C}$ above room temperature, is on the brink of what is considered likely to form supercooled particles. Therefore, in order to determine whether BA was able to exist as either supercooled or solid particles, the relative rates of reaction with O_3 were used as ozone reaction kinetics exhibit a clear phase dependence where up to an order of magnitude decrease in reactivity may be observed upon freezing. As shown in Fig. 2.3, the concentration of BA in the particles, measured using the $[\text{BA} + \text{H}]^+$ signal from the mass spectrometer, decreases when O_3 is introduced into the flow tube and recovers when O_3 is removed. The magnitude of the decrease is clearly smaller when the particles have been sent through the cold trap (*i.e.* “pre-cooled”) thus initiating their solidification. In fact, approximately eight times as much BA reacts in the liquid particles compared to the solid ones even though the reaction time and O_3 concentration were equal for both reactions. The observed decrease in the rate of ozonolysis can be attributed to reduced O_3 solubility or reduced O_3 and/or BA diffusion in the solid particles. This experiment was repeated several times alternating between supercooled and solid particles by simply bypassing the cold trap or sending the particles through it, and each experiment demonstrated the same change in reactivity. We have confirmed, therefore, that BA may remain supercooled over the residence time in the reaction flow tube. It is assumed that the other species which have melting points closer to room temperature than BA are also able to form supercooled particles that are able to remain supercooled over the reaction time.

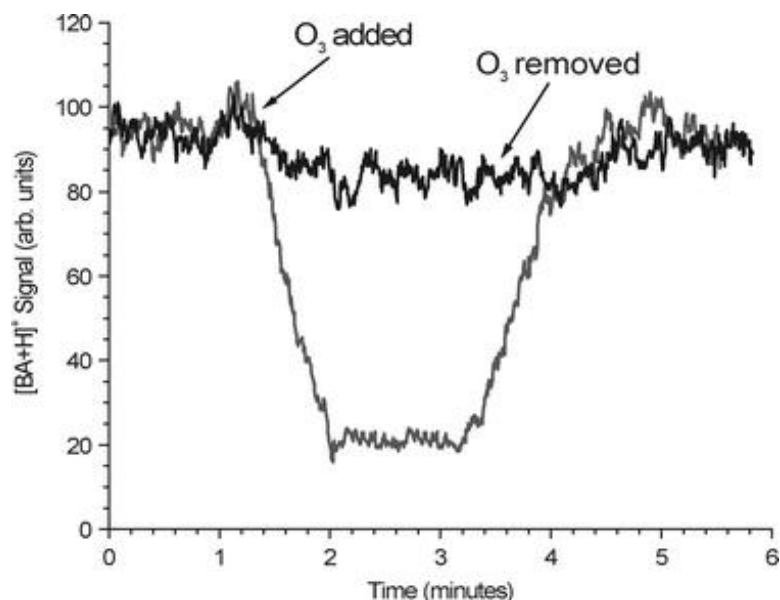


Figure 2.3. Particle phase of brassidic acid is confirmed by performing ozonolysis reactions. Supercooled liquid brassidic acid (BA) droplets (grey line) react approximately eight times as much as solid particles (black line) with the same ozone concentration and reaction time.

2.3.2. Chlorine radical relative kinetics

The rates of reaction of the organic acid aerosols were determined relative to a gas-phase reference, methanol, which has an established rate constant with Cl ($k = 5.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)³³. Because the effective rate constants obtained from the observed loss of the particle species depend on many factors, including surface area and volume, it is useful to express the efficiency of a heterogeneous reaction in terms of a reactive uptake coefficient, γ . This uptake coefficient is unitless and represents the fraction of gas-particle collisions that results in reactive loss. The effective uptake coefficient, γ_{part} , which is determined using the loss of the particle phase species rather than the gas phase oxidant, can be calculated from the measured fractional rate of loss of the particle species, X:

$$\gamma_{\text{part}} = \left[\frac{d([X]/[X]_o)}{d[Y] \bullet t} \right] \frac{4RT}{\bar{c}} \frac{V}{S_A} [X]_o \quad 2-1$$

where $[Y]$ is the concentration of the gas-phase reactive species (in this case Cl), R is the gas constant, T is the temperature, $\bar{c}$ is the mean speed of the gas-phase reactant and V/S_A is the volume-to-surface-area ratio and $[X]_o$ and $[X]$ are the concentration of particle phase species before and after reaction. For discrete measurements, the term in brackets is approximated by $\frac{\Delta([X])/([X])_o}{\Delta[Y]t}$. The term, $[Y]t$, is determined using the gas phase reference using

$$[Y]t = \left(-\ln \frac{[R]}{[R]_o} \right) / k_{ref} \text{ where } [R]_o \text{ and } [R] \text{ are the intensities of the gas phase reference}$$

before and after reaction, and k_{ref} is the room temperature rate constant for the gas phase reference with the gas phase reactive species. For these experiments, discrete measurements were performed where $[R]_o$ and $[X]_o$ were the methanol and organic acid mass spectrum signal intensities before the initiation of the Cl reaction by introduction of the photolysis laser, and $[R]$ and $[X]$ were the methanol and organic acid signal intensities after the initiation of the Cl reaction by introduction of the photolysis laser. The Cl concentration generated upon introduction of the laser light was changed by adjusting the 355 nm flux or by adjusting the concentration of Cl_2 . Particle size was determined using a scanning mobility particle sizer which sizes particles based on their electrical mobility diameter. As discussed in detail in below, this method of particle sizing may be affected by particle shape as well as size.

The effective reactive uptake coefficients, γ_{part} , of Cl on the solid and liquid (supercooled) particles studied here have been determined and are summarized in Figure 2.4. For particles which may form supercooled liquid or solid particles, discrete measurements were made while alternating between directly introducing the supercooled particle stream into the flow tube and forcing solidification of the particles using a cold trap (~ -80 °C) prior to

introduction into the flow tube. The methanol + Cl reaction was used in order to determine the Cl radical exposure and an SMPS was used to determine the particle size. The results in Figure 2.4 suggest that particle solidification causes only a factor of two or less change in the particle reactivity.

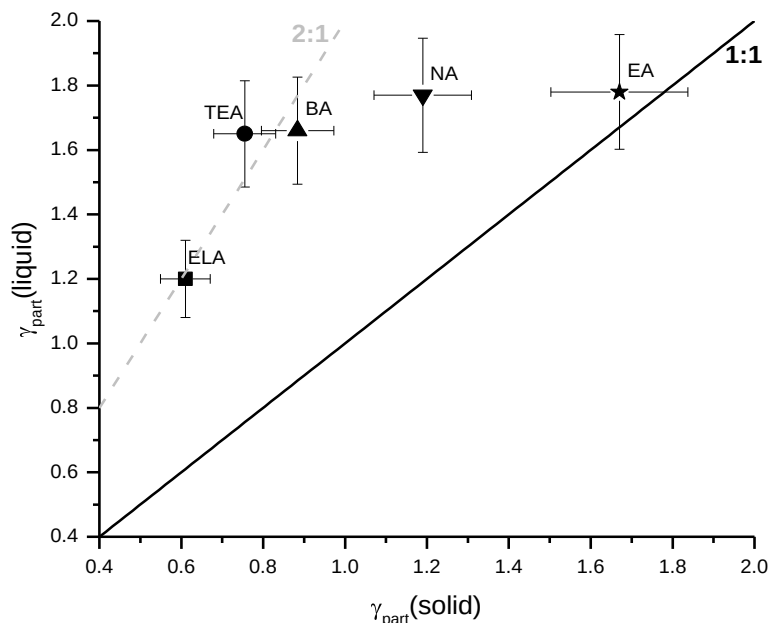


Figure 2.4. Effective reactive uptake coefficient, γ_{part} for liquid (y-axis) and solid (x-axis) particles of the same chemical composition. The error bars represent 10% error, a conservative estimation of the absolute error. A 1:1 line is added to show where the points would fall if no difference in the rate of reaction of solid and liquid particles were observed and a 2:1 line is added in order to show that in all five solid-liquid comparisons, the liquid never reacts more than about twice as fast as the solid particles.

The slope of the linear fit to each data point in Fig. 2.4 provides a measure of the relative rate of reaction in liquid and solid particles of identical chemical composition. This slope is $1.97 (\pm 0.28)$, $2.18 (\pm 0.31)$, $1.88 (\pm 0.26)$, $1.49 (\pm 0.21)$ and $1.07 (\pm 0.15)$ for ELA, TEA, BA, NA, and EA, respectively. EA shows almost no difference in reactivity upon solidification, and will be discussed in detail, later. However, BA, NA, ELA, and TEA all show evidence of a measureable decrease in the rate of reaction upon solidification. Though some of the difference in solid and liquid reactivity may be attributed to reduced Cl solubility and

reduced Cl and/or organic acid diffusion in the solid, it may also result from the buildup of product species at the surface. If, for example, the products cannot diffuse and mix with the rest of the particle, then they will stay at the surface and compete for Cl radicals effectively reducing the rate of reaction between the organic acid and Cl. In that case, the products should prevent more than just a few monolayers of BA from reacting which would drastically slow the rate of BA loss after only a small fraction of it has reacted. However, during the Cl-initiated reaction of solid particles, as much as 50-60% of the of the BA, TEA, NA, ELA, and EA reacts in the frozen particles, suggesting that product buildup at the surface of solid particles cannot, alone, explain the drop in reactivity upon solidification. Evidently, there must be some mechanism by which the particle components can still react with the Cl at the surface despite the decreased transport within the solid, or the solid particles are reacting faster than would be expected due to increased surface area compared to the liquid particles. These possibilities are discussed in further detail, below.

One way in which the surface may be renewed is through the formation of a surface liquid layer which could increase the accessibility of underlying organic acid molecules by mixing at the solid-liquid interface. The existence of a thin layer of a melt liquid at the surface of a solid below the melting temperature is known to occur commonly for many types of solids.³⁸ This liquid layer is the result of a wetting phenomenon whereby the free energy of the system is lowered by converting some of the solid to liquid, and it is therefore a thermodynamically stable system. Even the existence of a liquid layer a few nanometers thick could help propagate the reaction such that a large fraction of the organic acid reacts. The thickness of this liquid layer depends on many factors including how far below the melting point the temperature is. Interestingly, EA, which has the lowest melting point of the

organic acids studied here, displays almost no difference in the reaction kinetics when solid and liquid particles are compared however it is not clear whether this is due to the formation of a thicker liquid layer compared to the other organic acids studied here. The case of EA will be addressed in detail in the discussion section as many of the trends observed for these particles stand apart from the other solid/liquid systems studies here. It may be possible in future studies to confirm the existence of a liquid layer by studying particle reactivity at a colder temperature at which the layer is not thick enough to help the reaction to proceed at rates that are comparable to liquid particle reactions.

Another way in which the reaction could continue to proceed is for the surface of the particle to be renewed continuously such that the reaction with Cl is not halted, an idea which has been proposed recently for the OH-initiated oxidation of solid palmitic acid particles.¹⁶ In that work it was suggested that such a renewal may occur if volatile oxidation products evaporate from the surface exposing underlying layers of the particle. Indeed, we observe indirect evidence for the production of some volatile species in the Cl-initiated oxidation of BA, NA, TEA, ELA, and EA in the form of small products/fragments and aerosol volume decrease (see Section 2.3.3 for small-molecular-weight peaks and particle volatility). In any case, there is some mechanism by which the solid particles react with Cl at almost the same rate and to the same extent as the liquid droplets, and discerning what this mechanism is and evaluating whether it might occur in ambient aerosols will require further study.

A third way in which the reaction of solid unsaturated fatty acid aerosols may proceed as if it were liquid is through the formation of disordered solid structures that appear “liquid-like” in terms of reactivity. Almost all fatty acids possess two or more solid phases (polymorphisms) under a given set of thermodynamic conditions.^{31, 39-42} These solid phases

differ in terms of unit cell dimensions which arise from differences in molecular chain packing and conformation. The number of polymorphs a certain fatty acid may exist at and the transition temperatures between these different polymorphs are highly variable and involve much discussion. However, take for instance the case of erucic acid, which shows almost no difference in reactivity between solid and liquid particles. According to Suzuki et al.³¹, from a melt-grown crystal, there are two accessible solid phases of erucic acid: α_1 and γ_1 . Creating EA from a melt which is then frozen and warmed back to room temperature, as the particles were created in these studies, the erucic acid would ultimately be expected to be present as the α_1 polymorph, a relatively ordered solid. If this were the case, the reaction would be expected to slow considerably upon solidification. The results in Fig. 2.4 show less than a factor of two difference in reactivity between solid and liquid particles and nearly no difference in solid and liquid EA reactivity. However, because solid crystal formation is dependent on the rate of cooling, the possibility of forming an amorphous solid cannot be excluded as an explanation of the EA results and may also exist for the other unsaturated acids studied here.

Lastly, the relatively small difference observed in the solid and liquid organic acid aerosol reactivity with Cl may be due to the formation of solid crystal structures which have a larger surface area to volume ratios than the liquid, spherical particles. By comparing γ_{part} for solid and liquid particles, the effect of the particle size, as determined by SMPS, on the rate of reactive uptake of Cl is accounted for. However, because the SMPS operates on electrical mobility, alone, the shape of the particle and the surface area to volume ratios are not accounted for in the sizing process. Therefore, if the actual rate of reaction of the organic acids in the solid particles were an order of magnitude slower, but the surface area to volume

ratio were an order of magnitude larger, no difference in γ_{part} would be observed even if a large difference in reactivity existed. A large change in surface area to volume ratio may still be possible while maintaining the same electrical mobility diameter. For instance, if the solid particles were smaller in diameter than the liquid particles but had spindle-like structure that caused a greater drag inside the DMA, the electrical mobility diameter would be the same and therefore the reported particle diameter would be the same (see Table 2.1)

2.3.3. Oxidation products and yields

First-generation products

As has been observed in the radical-initiated oxidation of other organic aerosol species,^{9, 12} the predominant products of BA, TEA, NA, ELA, and EA oxidation are those corresponding to the addition of a ketone or alcohol functional group. These ketone and alcohol products are referred to here as “1st-generation” products since they result from a single radical reaction. Products containing several ketone and/or alcohol functional groups resulting from multiple oxidations and/or radical isomerization are also observed, and these are referred to “2nd-, 3rd-, and 4th-generation” products. These products can be seen in Fig. 2.5 in which a difference spectrum of liquid BA droplets is constructed by subtracting an unreacted spectrum (*i.e.* with the photodissociation laser off) from a reacted spectrum. The negative-going peaks represent the loss of BA and the positive-going peaks represent the rise of oxidation products ionized by proton transfer by $(\text{H}_2\text{O})_n\text{H}^+$.

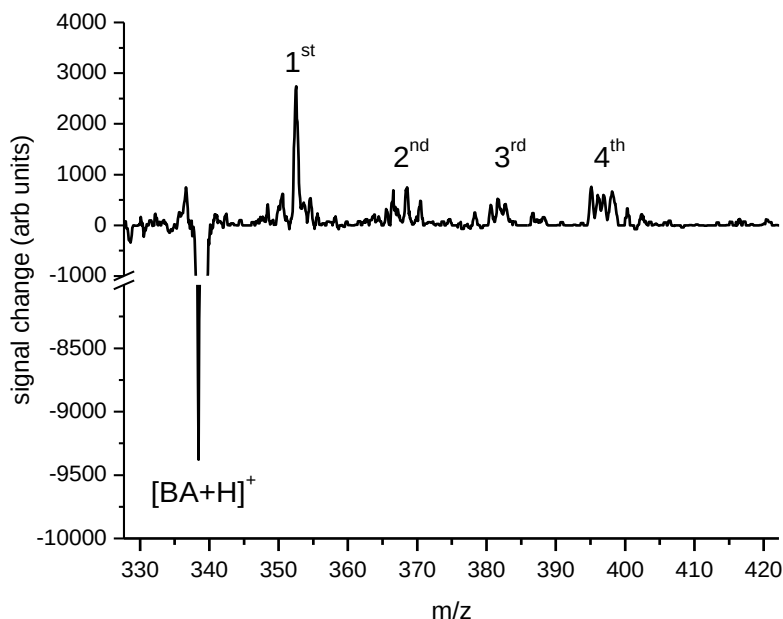


Figure 2.5. $(\text{H}_2\text{O})_n\text{H}^+$ ionization difference mass spectrum of supercooled liquid brassidic acid particles. The mass spectrum of unreacted particles is subtracted from that of reacted particles. Positive-going peaks represent increases in 1st-, 2nd-, 3rd-, and 4th-generation products of oxidation, while the negative-going peak represents loss of brassidic acid.

The trends in the production of 1st generation oxidation products from the reactions of solid and liquid BA, TEA, NA, ELA, and EA particles were determined using the proton transfer peaks (*i.e.* $[\text{M}+\text{H}]^+$) from $(\text{H}_2\text{O})_n\text{H}^+$. The ketone and alcohol signal increase during the reaction was normalized to the signal decrease of organic acid during the reaction and the Cl radical exposure was determined using methanol as the gas phase reference. The relative ionization efficiencies of the organic acids and the ketone and alcohol products are not equivalent using H^+ transfer ionization and so these data were not used to quantify reaction yields. Rather, in order to compare ketone and alcohol product formation differences between solid and liquid particle reactions, the ketone and alcohol product signals from the reaction of solid and liquid particles were normalized to the amount of organic acid that reacted away at each Cl exposure and these “normalized product signals” were compared as a function of Cl

radical exposure. These data are summarized in Fig. 2.6a-e where the normalized ketone and alcohol product formation from the reaction of solid and liquid BA, NA, TEA, ELA, and EA are plotted against Cl radical exposure.

The trends in the normalized first generation product signals show that in each system, the ketone product was more abundant in the liquid particles compared to the solid particles. The alcohol product, however, seems to be formed in equal amounts, regardless of particle phase. As will be discussed in more detail below, even at low Cl radical exposures ($\sim 5 \times 10^9$ molecules/cm³ *sec), the 1st generation products formed from the reaction of solid particles have already begun oxidizing into even higher generation products. This complicates the elucidation of important ketone and alcohol formation pathways as the products are being formed from the oxidation of the organic acid precursor and lost through reaction with Cl simultaneously. While it is possible, for instance, that there are ketone-forming mechanisms that are enhanced in liquid compared to solid particles, the differences in the ketone product formation may also be due to faster oxidative turnover of the ketone product in solid compared to liquid particles. The alcohol product formation does not exhibit a clear phase dependence. However, again, it is not clear whether the alcohol product is formed in equal amounts regardless of particle phase or if initially (at radical exposures too low to access in these experiments), the alcohol product formation differed between the two phases and sequential oxidation altered the measured normalized alcohol product signal.

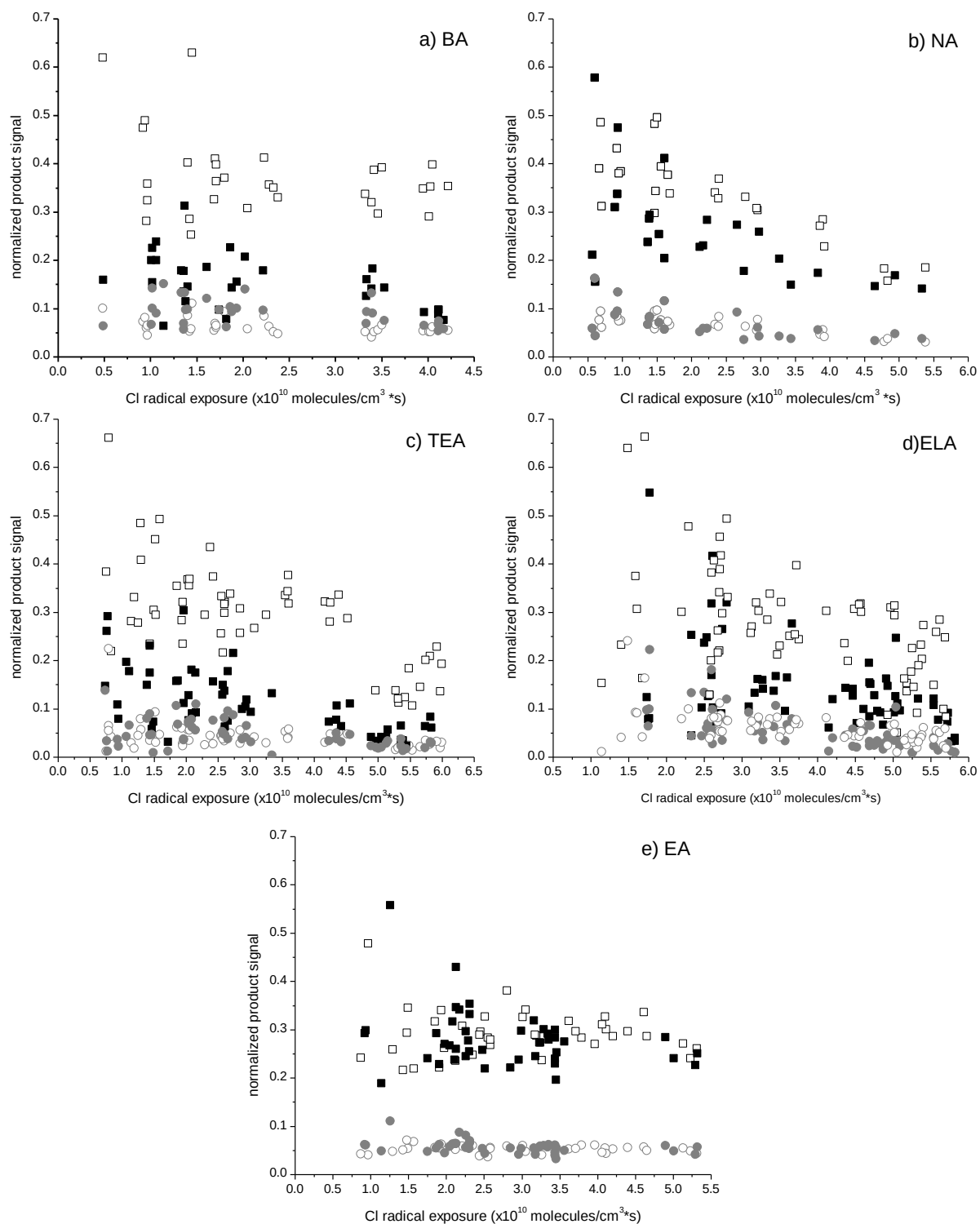


Figure 2.6 a-e. normalized ketone (black squares) and alcohol (gray circles) product signal from the Cl initiated oxidation of solid (filled symbol) and liquid (empty symbol) **a)** BA, **b)** NA, **c)** TEA, **d)** ELA, and **e)** EA as a function of Cl radical exposure.

Although the yields of the ketone and alcohol products could not be determined from the data above due to non-uniform ionization efficiency between the reactant organic acids and the resulting ketone and alcohol products, much useful information about the important oxidation pathways may be gained from knowledge of the yields of these products. In particular, the ketone: alcohol ratio may elucidate some of the important mechanisms at play in the oxidation of solid and liquid particles. Using proton abstraction ionization from $\text{Cl}^-/\text{Cl}_2^-$ it is possible to quantify the yields of the ketone and alcohol products formed during the radical initiated oxidation of the organic acid particles studied here. Methanol, used as a gas phase reference in the reactions discussed above, is not readily ionizable using proton abstraction and thus in gaining the ability to quantify reaction yields, the ability to track Cl exposure is lost. However, by maintaining a constant Cl_2 flow and constant laser flux, it is possible to rapidly switch between solid and liquid particles while assuming the Cl radical concentration stays constant and compare the ketone and alcohol yields using $\text{Cl}^-/\text{Cl}_2^-$ ionization. Because no Cl radical exposure data can be gathered simultaneously while using $\text{Cl}^-/\text{Cl}_2^-$ ionization and we must assume a steady radical concentration the particle source is changed, this experiment was performed for solid and liquid BA and EA particles only.

The proton abstraction peaks were used to quantify the ketone and alcohol yields from the reaction of solid and liquid BA and EA particles because Cl^- is expected to abstract a proton from the carboxylic acid moiety of each product and BA with equal efficiency regardless of whether additional carbonyl or alcohol groups are present. In order to verify that this is indeed the case, a gas mixture consisting of a carboxylic acid, butyric acid, and a ketone, 2-butanone, was ionized using Cl^- . It was found that the detection sensitivity to the carboxylic acid was 160 times larger than for the ketone using the corresponding $[\text{M} - \text{H}]^-$

signals, thus confirming that Cl^- abstracts a proton preferentially from the C(O)OH functional group rather than from the α -hydrogen of the ketone functional group. Tiernan *et al.*⁴³ have also found that proton abstraction using a similar ion, F^- , occurs at the C(O)OH group for polyfunctional organic acids containing multiple accessible hydrogens. Furthermore, they also showed that proton abstraction using F^- does not occur for aliphatic alcohols due to their weak acidity. Because Cl^- has a lower proton affinity (1393 kJ mol^{-1}) than F^- (1548 kJ mol^{-1}), it is even less favorable for Cl^- to abstract a proton from the $-\text{OH}$ group of an aliphatic alcohol. Thus, it is reasonable to assume that proton abstraction will occur preferentially at the carboxylic acid group leading to the formation of the carboxylate anion for all of the oxidation products as well as BA and EA. Consequently, the detection sensitivities for each product and BA or EA can be assumed to be equal, and the yield of each product can be calculated by comparing the corresponding signal rise with the BA or EA signal decrease.

The ketone and alcohol products as well as the higher generation oxidation products of BA oxidation can be seen in Fig. 2.7 in which a difference spectrum of liquid BA droplets is constructed by subtracting an unreacted spectrum (*i.e.* with the photodissociation laser off) from a reacted spectrum. The negative-going peaks represent the loss of BA: $[\text{BA} - \text{H}]^-$ ($m/z = 337 \text{ amu}$) from proton abstraction by Cl^- and $[\text{BA} + \text{Cl}]^-$ ($m/z = 373 \text{ amu}$) from Cl^- -adduct formation by both Cl^- and Cl_2^- . The positive-going peaks represent the rise of oxidation products ionized by both Cl^- and Cl_2^- .

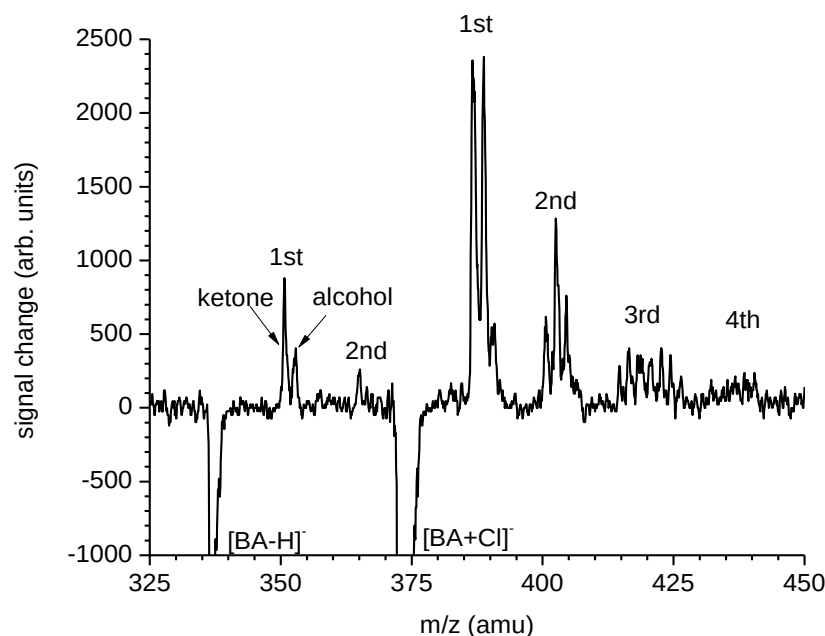


Figure 2.7. $\text{Cl}^-/\text{Cl}_2^-$ ionization difference mass spectrum of supercooled liquid brassidic acid particles. The mass spectrum of unreacted particles is subtracted from that of reacted particles. Positive-going peaks represent increases in 1st-, 2nd-, 3rd-, and 4th-generation products of oxidation, while negative-going peaks represent loss of brassidic acid. Note that ions resulting from both proton abstraction and Cl^- -adduct formation are present.

The measured product yields for reaction of liquid and solid BA and EA are shown in Fig. 2.8 in which the ketone yield is plotted *versus* the corresponding alcohol yield. The wide range of yields observed results from the range of Cl concentrations used in the flow tube, presumably due to subsequent loss of the products through further reaction with Cl radicals at the higher concentrations. These two products alone account for as much as 70-85% of the reacted BA and EA indicating that these are the primary products of the initial oxidation reaction. Recall, from Fig. 2.6, these products decrease with increasing Cl radical exposure. Since these products are larger and more heavily oxidized than BA and EA, they remain in the particles rather than vaporizing.

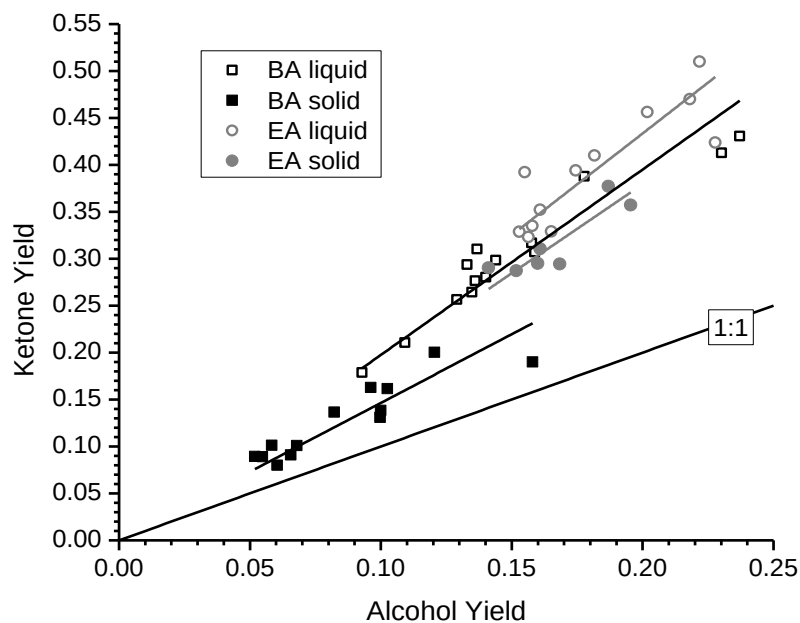


Figure 2.8. Yields of the 1st-generation products, the ketone and alcohol, calculated from the corresponding proton-abstraction peaks for both supercooled liquid BA and EA droplets ($\square$ and $\circ$, respectively) and solid BA and EA particles ($\blacksquare$ and $\bullet$, respectively). The larger ketone yield indicates a ketone source other than the Russell reaction (from which both the ketone and alcohol products are created).

It is evident from the difference spectrum of BA and from the product yield data of BA and EA that the ketone product is generated in a higher yield than is the alcohol product. In fact, the ketone–alcohol ratio is approximately 2:1 for liquid BA and EA particle reactions regardless of the extent of reaction. We have measured similar ketone: alcohol yield ratios in the reaction of other liquid organic species, including dioctyl sebacate (DOS),¹² and oleic acid indicating that the larger yield of the ketone product may be a general result of radical-initiated oxidation of organic aerosols. Since much of the literature on condensed-phase RO_2 radical chemistry indicates the Russell mechanism (in which both a ketone and an alcohol are generated concurrently) to be the primary fate of secondary RO_2 radical self-reaction,¹⁰ the larger observed ratio suggests the existence of additional ketone-forming pathways. These

channels, including: (1) the Bennett and Summers mechanism in which two RO_2 radicals react to form two ketones and H_2O_2 ,²¹ and (2) the reaction of RO with O_2 to generate a ketone and HO_2 radical, may be enhanced at or even specific to the gas–particle interface of aerosol particles. However, it is not clear what causes this surface specificity. For solid BA particle reactions, the ratio of ketone to alcohol is less than 2:1 but still greater than 1:1. There are no logical mechanisms that may be responsible for increased alcohol formation in solid compared to liquid particles. However, if 1) decreased O_2 solubility in the solid BA reduces the branching ratio for the $\text{RO} + \text{O}_2 \rightarrow \text{ketone} + \text{HO}_2$ reaction or 2) the ketone products were preferentially oxidized over the alcohol product in the solid particle reactions, the ketone: alcohol ratio would decrease. As the ketone yields are greater than the alcohol yields, when another Cl radical collides with the particle, it will be more likely to “see” a ketone product and sequential oxidation will cause the ketone: alcohol ratio to decrease. In liquid particles, the 1st generation products may mix within the particle and thus decrease the surface concentration of these species, preventing sequential oxidation whereas in solid particles, the 1st generation oxidation products may be confined to the surface where sequential oxidation is likely. As discussed in detail below, this picture of decreased product diffusion in solid compared to liquid particles is consistent with a greater degree of oxidative turnover in solid compared to liquid particles.

Higher-generation products

In addition to the 1st-generation products, others containing multiple ketone and/or alcohol functional groups are created when BA is oxidized. These higher-generation products are generated from the subsequent Cl -initiated oxidation of the 1st-generation (ketone and alcohol) products and can be seen in the Cl^- -adduct peaks of the difference spectrum of

reacted BA droplets in Fig. 2.7 as well as in the proton transfer peaks of the difference spectrum of reacted BA droplets in Fig. 2.5. While the high generation product signal intensities are greater using Cl^- adduct ionization, recall that methanol is not readily ionizable with $\text{Cl}^-/\text{Cl}_2^-$ ionization and thus the Cl radical exposure could not be simultaneously traced during these studies. However, using proton transfer ionization, the formation of these products could be traced at known Cl radical concentrations. For BA particles, the trends in the high generation oxidation products were observed using both ionization schemes by: 1) maintaining constant but unknown Cl radical concentrations by maintaining Cl_2 concentrations and laser power and rapidly switching between frozen and supercooled particles using $\text{Cl}^-/\text{Cl}_2^-$ ionization and 2) by observing the product formation using proton transfer with $(\text{H}_2\text{O})_n\text{H}^+$ for either liquid or solid particles as a function of $[\text{Cl}]$ measured using methanol as a gas phase reference and comparing liquid and solid particle product yields by correlating the yield data based on Cl exposure. These data are shown in Figs. 2.9a and 2.9b, respectively, where a 1:1 line is plotted to show where the data would fall if no difference in the products were observed between solid and liquid particle oxidation. As can be seen in Figure 2.9, although the absolute normalized product signal depending on the ionization technique used due to differences in ionization efficiencies of the products relative to BA, the trends observed are the same; namely, the first generation products are formed to a greater degree in liquid particles compared to solid particles and the 2nd-4th generation products are formed to a greater degree in solid compared to liquid particles.

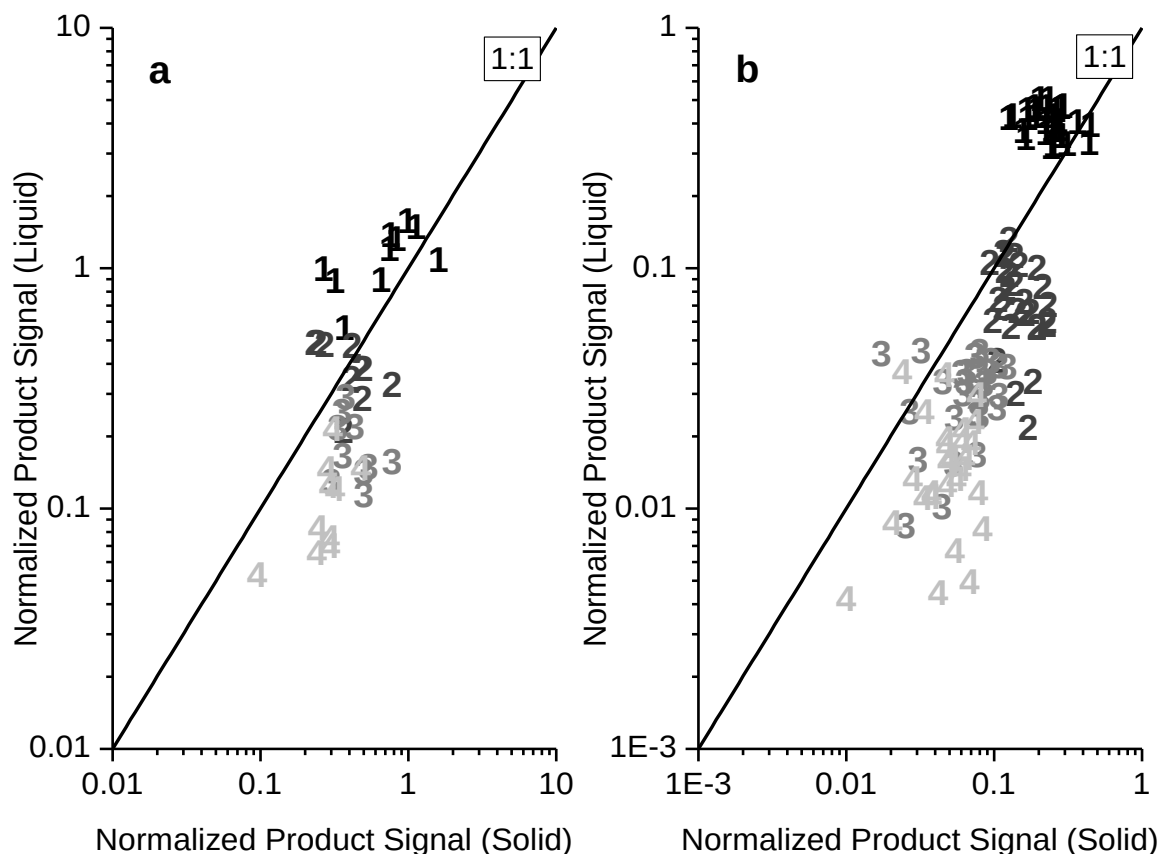


Figure 2.9. a) Integrated product signals ($[M + Cl]^-$) for the 1st-, 2nd-, 3rd-, and 4th-generation products normalized by the brassidic acid signal ($[BA + Cl]^-$) loss. Solid particles are more highly oxidized than supercooled liquid droplets with similar Cl radical concentrations and reaction times. **b)** Integrated product signals ($[M + H]^+$) for the 1st-, 2nd-, 3rd-, and 4th-generation products normalized by the brassidic acid signal ($[BA + H]^+$) loss. Solid particles are more highly oxidized than supercooled liquid droplets with same radical exposure, as measured by the loss of methanol.

Using technique 2, above (where the trends in the protonated high generation products of liquid and solid particles as a function of $[Cl]$ were measured and liquid and solid particle product formation was correlated based on Cl exposure), the trends in the 1st through 4th generation products of TEA, NA, ELA and EA were also determined and are shown in Fig 2.10 a-d, respectively.

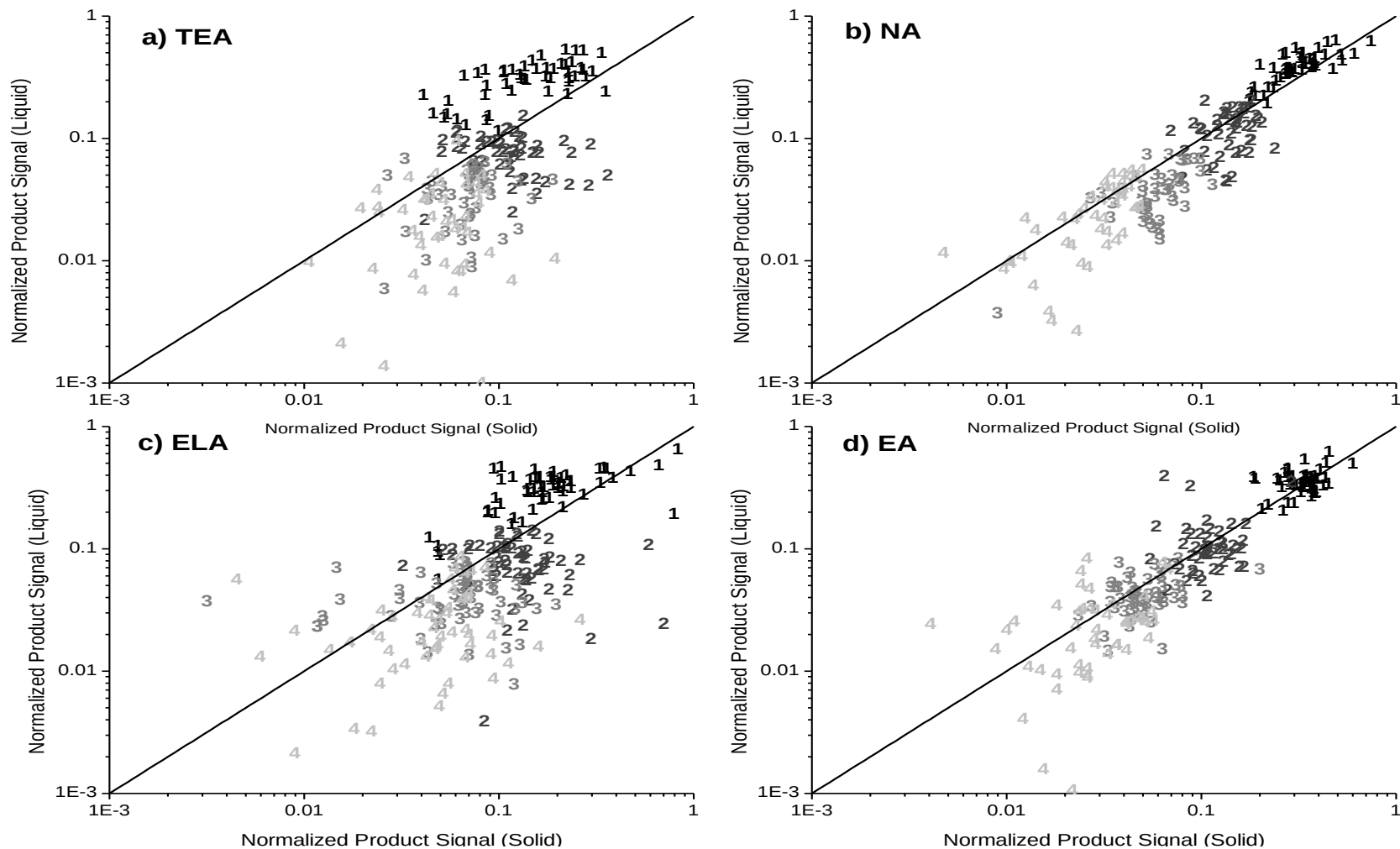


Figure 2.10 a-d. Integrated product signals ($[M + H]^+$) for the 1st-, 2nd-, 3rd-, and 4th-generation products normalized by the organic acid signal ($[M + H]^+$) loss for (a) TEA, (b) NA, (c) ELA, and (d) EA. Solid particles are more highly oxidized than supercooled liquid droplets with same radical exposure, as measured by the loss of methanol with the exception of EA which shows no apparent difference in solid and liquid product formation.

It is found that upon freezing, more of the higher-generation products are created at the expense of the 1st-generation products, shown in Fig. 2.9 a-b and 2.10 a-d. With the exception of Figure 2.9 a, for which $\text{Cl}^\cdot/\text{Cl}_2^\cdot$ ionization was used, each data point represents the integrated signal for all of the $\text{H}^\cdot$ -transfer peaks in a given generation of products normalized to the organic acid $[\text{M} + \text{H}]^+$ signal decrease made once for liquid droplets and once for solid particles at the same Cl radical exposure. Strictly speaking, this normalized signal should not be considered a yield because the detection sensitivities for the various products are not known. However, the sensitivity of each product will be the same whether it originates from a liquid or a solid particle, so the ratio of the normalized liquid and solid signals should be equivalent to the ratio of the liquid and solid yields. Since each measurement is made with a gas phase reference in order to measure Cl radical exposure, the effect of phase change can be determined under identical conditions (*i.e.* Cl concentration and reaction time). Such changes are evident in Fig. 2.9 b and 2.10 a-c for BA, TEA, NA, and ELA, respectively, in which the 1st-generation signal decreases and the higher-generation signals increase when the particles are frozen. This shift is believed to be a consequence of the reduced diffusion of the products in the solid particles where they remain on the surface and react further with Cl to create higher-generation products. The high generation product formation from the reaction of solid and liquid EA appears to be equivalent from the data in Fig 2.10d. Close inspection of the data in Fig. 2.10d shows some slight enhancement of the 2nd through 4th generation products in solid compared to liquid particles but the difference is minimal in comparison to those observed for BA, TEA, NA, and ELA. The small differences observed between solid and liquid EA particles will be discussed in greater detail in the discussion.

As might be expected, the extent of oxidation is a function of the Cl radical exposure. This correlation is shown in Fig. 2.11 a-e for BA, TEA, NA, ELA, and EA in which the “average generation” of the products are plotted as a function of Cl exposure. Here, the average generation is calculated by weighting the integrated signal for each generation by the order of the generation (1, 2, 3 or 4). It should be pointed out that this measure describes the distribution of 1st–4th-generation products only and does not account for any other products that are formed. The fact that the average generation increases with Cl radical exposure is consistent with the idea that the oxidation products continue to react adding more functional groups for both solid and liquid particles. The much larger average generation values for the solid organic acid particles indicate that they are much more heavily oxidized than the liquid organic acid droplets. Even at the lowest Cl radical exposures studied here, the average generation of the solid particle reaction products of BA, TEA, NA, and ELA oxidation are significantly greater for solid particles compared to liquid particles of the same composition suggesting this oxidative turnover in the solid particles occurs readily and is not dependent on high Cl radical exposures. Again, this observation is consistent with the products being confined to the surface of the solid because of the inhibited transport into and mixing with the rest of the particle. Erucic acid, while exhibiting no difference in the kinetics, exhibits a slight enhancement in the average generation of oxidation products in solid compared to liquid particles. However, whereas the average generation of the oxidation products of BA, TEA, NA, and ELA was ~50-80% greater for solid compared to liquid particles, solid EA oxidation showed only a 10-20% increase in the average generation of products formed compared to liquid EA oxidation. Again, EA will be discussed in detail in the discussion, below.

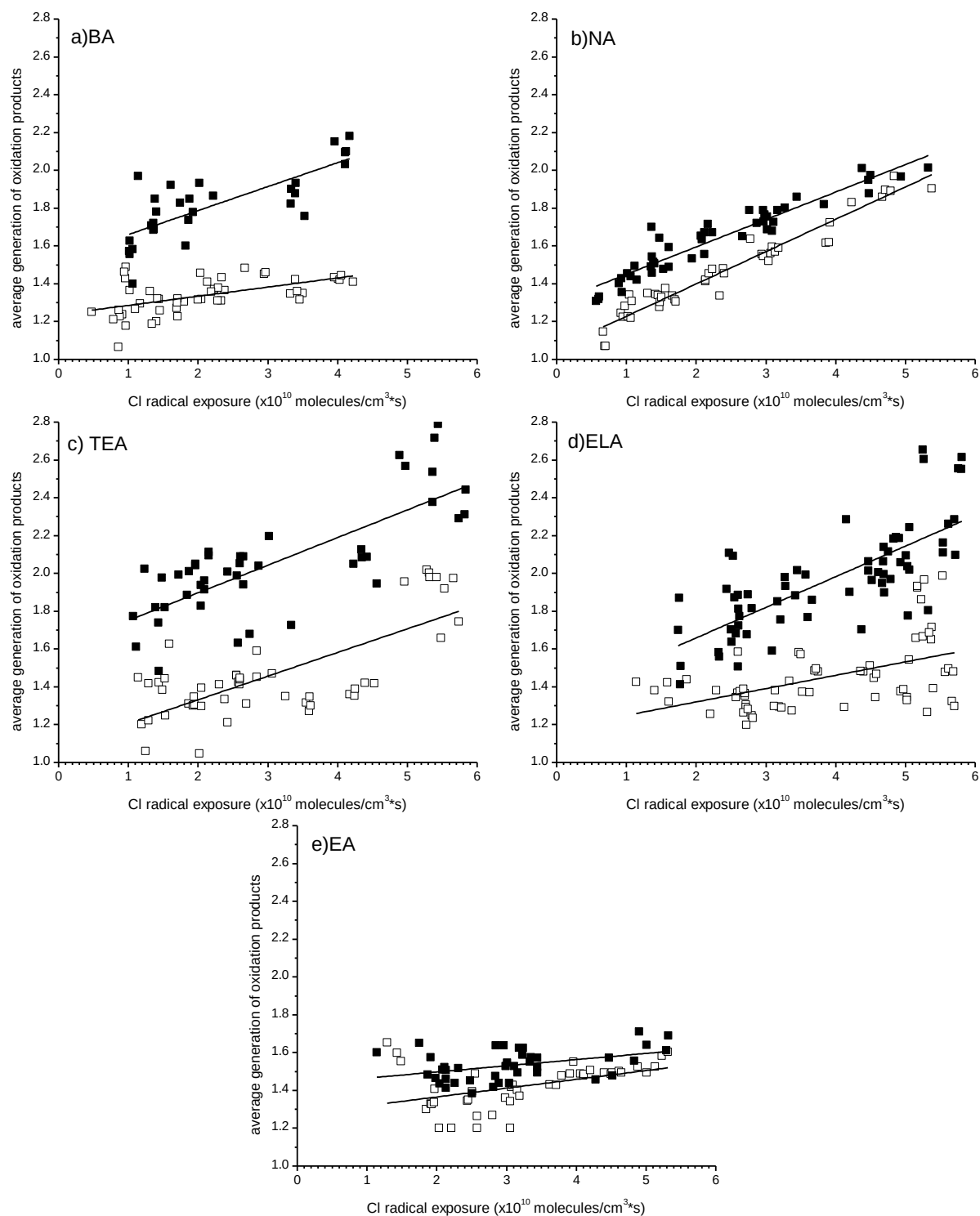


Figure 2.11 a-e “Average generation” of the 1st–4th-generation products. The immobility of products at the surface of the solid particles (■) results in their further oxidation as compared to supercooled liquid droplets(□) for (a) BA, (b) NA, (c) TEA, (d) ELA, and (e) EA.

Small-molecular-weight peaks and particle volatility

In addition to the 1st–4th-generation products with mass-to-charge ratios larger than the organic acid components, some products with smaller mass-to-charge values were observed. These peaks were not as well resolved as the larger ones, and it was not possible to identify individual peaks with specific products or fragments conclusively. Additionally, many of these peaks were present in the difference spectra even in the absence of particles indicating that they originated from reactions occurring on the walls of the flow tube. To identify the contribution to these peaks made by the particle reactions alone it was necessary to collect “difference–difference” spectra in the following way: mass spectra were obtained before (1) and during (2) reaction with organic acid particles and also when no particles were present with (3) and without (4) Cl radicals. From these individual spectra, a difference–difference spectrum could be constructed by first subtracting spectrum 1 from spectrum 2 and then subtracting from that the difference between spectra 3 and 4. In doing so, the only positive-going peaks which are observed are attributed to the particle reaction and not to reactions with species on the walls of the flow tube. An example of such a difference-difference spectrum is shown in Fig. 2.12 for the reaction of solid BA particles.

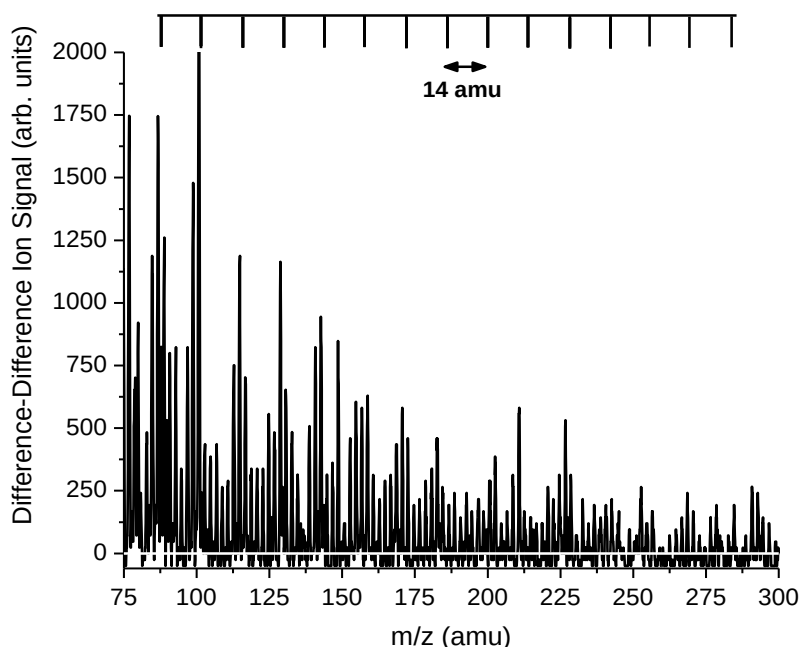


Figure 2.12. “Difference–difference” mass spectrum from reacted solid brassidic acid particles. Positive-going peaks represent products and/or fragments of particle oxidation in excess of any originating from flow tube wall reactions.

This procedure of collecting difference–difference spectra is sensitive to changes in many factors including the Cl concentration, the reaction time, and the identity/aging of the coating on the flow tube walls. Consequently, it was found that the signal rise of individual, positive-going peaks in the difference–difference spectra was not always reproducible. However, it is evident in the difference–difference spectrum in Fig. 2.12 that there is more signal above the zero (white) line than below it indicating that low- m/z species are formed from the particle reaction. These difference-difference spectra were collected at a radical exposure of $\sim 4 \times 10^{10}$ molecules/cm³*s for each of the five solid-liquid systems studied here including BA, TEA, NA, ELA, and EA and are summarized in Fig. 2.13a in which each data point represents the integrated low m/z signal ($m/z = 80\text{--}300$ amu) divided by the signal loss of the organic acid species. These signals are not necessarily directly proportional to the yields since the

detection sensitivities for all of the individual products are not known. However, they do provide a way to quantify and compare the magnitudes of these low- m/z signals. It is evident from Fig. 2.13a that low- m/z species are detected from the reaction of both liquid and solid particles, but this signal is larger for solid BA, TEA, NA, and ELA than for liquid particles of the same composition suggesting that the immobility of products on the surface of solid BA particles somehow leads to more low- m/z products or fragments. Perhaps some smaller-molecular-weight products are created from the initial oxidation of BA in both the liquid and the solid, for example through the β -scission decomposition channel of the RO radicals. Then, as the products react further and become more-highly-functionalized, especially in the solid particles, they decompose more readily⁴⁴ giving rise to an enhancement in the low- m/z signal for solid particles. These data are consistent with previous data collected with $\text{Cl}^-/\text{Cl}_2^-$ ionization of BA and EA reactions at different, but unmeasured Cl radical exposures, shown in Fig. 2.13b. The disparity observed here for the two phases suggests that liquid and solid particles in the atmosphere may also “age” differently through radical-initiated oxidation. The data in Figure 2.13a suggest that EA shows the opposite effect of the other organic acids, with more low m/z product formation in liquid particles than solid particles at a Cl radical exposure of 4×10^{10} molecules/ $\text{cm}^3 \cdot \text{s}$. However, at only slightly lower exposure (3×10^{10} molecules/ $\text{cm}^3 \cdot \text{s}$), the low mass product formation from solid and liquid particle oxidation appears nearly equal, with slightly more low mass product formation in the solid compared to liquid particles (shown as empty grey squares in Fig. 2.13 a). The data in Figure 2.13b show nearly equal low mass product formation from the reaction of solid and liquid EA particles at various Cl radical exposures. Again, the case of EA will be addressed in the discussion section below.

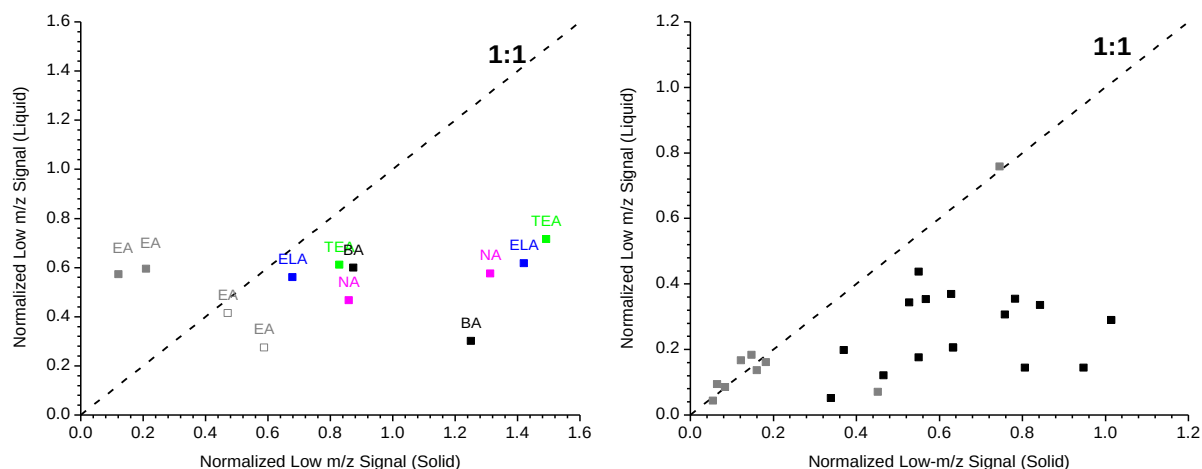


Figure 2.13. a) Integrated signals from the $(\text{H}_2\text{O})_n\text{H}^+$ spectra for $m/z = 80\text{--}300$ amu normalized to organic acid loss $[\text{M}+\text{H}]^+$ from the difference-difference spectra where low mass product formation was compared at the same exposure **b)** Integrated signals from the $\text{Cl}^-/\text{Cl}_2^-$ spectra for $m/z = 80\text{--}300$ amu (excluding $m/z = 105\text{--}109$ amu, the Cl_3^- peaks) normalized to brassidic acid loss $[\text{BA}-\text{H}]^-$ and erucic acid loss $[\text{EA}-\text{H}]^-$ from difference-difference spectra and the black and grey squares represent the BA and EA low mass product data, respectively. The differences observed in **a** and **b** are consistent with there being a greater degree of volatilization from the solid particles, with the exception of EA.

One implication of the formation of low- m/z species is that some of them may be small enough and volatile enough to evaporate from the particles. This hypothesis has been proposed recently by Molina and co-workers as a potentially important route by which organic particulate matter is removed through volatilization.¹⁴ In that study it was suggested that the formation of RO radicals produced from RO_2 self-reaction leads to the creation of smaller aldehydes through a β -scission channel analogous to the one known to occur with gas-phase RO radicals. Indeed, some studies have found that small-molecular-weight species are formed from the radical-initiated oxidation of solid particles and surfaces.^{13, 14, 17} However, other studies have suggested that volatilization of liquid dioctyl sebacate (DOS) particles is negligible even at relatively high Cl or OH exposures.^{9, 12} Is it possible that solid particles are more efficiently volatilized than are liquid ones?

Since the difference–difference spectra contain species from both the particles and the gas phase it is not possible to use them to answer this question directly. However, the size distribution of liquid and solid BA particles was measured using a scanning mobility particle sizer (SMPS) both before and during reaction with Cl. In the event that volatile products are created, the mobility diameter of the aerosol should decrease during reaction assuming that other factors, such as particle density and shape, are constant. The results of these experiments are shown in Fig. 2.14 in which the fractional change in the mean mobility diameter after reaction is plotted for liquid vs. solid particles. Since each data point represents a pair of measurements made with identical Cl concentration and reaction time—one for liquid particles and one for solid particles—the difference is a result of the change in phase only. While there is a sizeable decrease in diameter of up to 11% (or 30% in volume) for the liquid droplets, an even bigger decrease (up to 14% in diameter) is observed for the solid particles. Because the liquid BA particles are spherical droplets to begin with, their reaction probably does not alter their shape in such a way as to decrease the mobility diameter so we can be confident that the geometric diameter of those droplets does decrease after reaction consistent with evaporation of volatile products. Studies of the oxidation of dioctyl sebacate (DOS) droplets by Cl and OH showed similar volume decreases (up to 17%⁹ and 20%,¹² respectively) at the largest radical exposures. The large decrease in mobility diameter for solid BA particles, however, cannot necessarily be attributed to a decrease in geometric diameter since they could change shape after reaction;⁴⁵ if, for example, the particles become more spherical because of a liquid layer that forms from the oxidation reactions, then the observed mobility diameter may decrease even if the volume of the particle does not change. Thus, it is only possible to conclude that the measured size decreases for the solid particles

could result from the evaporation of volatile products consistent with the volatilization observed from the radical-initiated oxidation of other solid/monolayer systems.^{13, 14, 16, 17, 23}

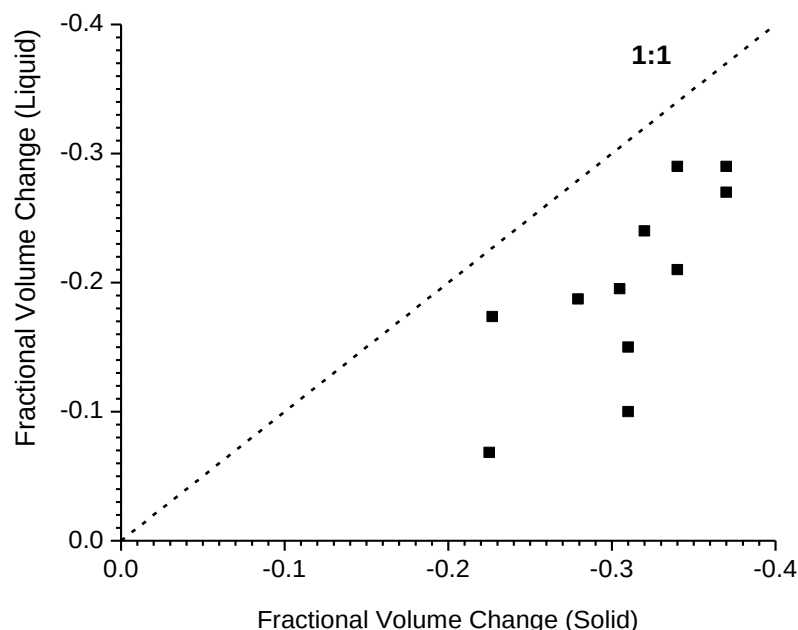


Figure 2.14. Fractional change in mean mobility diameter of supercooled liquid and solid BA particles after Cl-initiated oxidation. Each point represents measurements made with identical Cl radical concentrations and reaction times for each phase. The size decreases are consistent with volatilization of both liquid and solid particles.

Taken together, the difference-difference spectra of BA, TEA, NA, and ELA and the size change data of BA appear to support the creation of some small, volatile products from the oxidation of both liquid and solid, though their yields could not be determined. Furthermore, it appears as if there may be more of this volatilization for solid particles than for liquid ones which could be linked to the greater degree of oxidation at the surface of solid particles. It is possible that this difference is, at least in part, a consequence of the high concentration of Cl radicals (10^{10} – 10^{11} radicals per cm^3) leading to large concentrations of RO_2 and RO radicals at the surface. Ambient organic particles exposed to much lower OH concentrations (*ca.* 10^6

radicals per cm^3) may react much differently, and additional experiments are needed to determine whether volatilization is a function of the rate of radical-initiated oxidation. Also, experiments in which individual volatile products from the particle reactions could be identified would provide further insight into the chemical mechanism for their creation.

2.3.4. Other solid and liquid systems

In addition to the organic acids which were able to form either supercooled liquid or solid particles at room temperature, various organic acids were studied which were able to form either liquid or solid particles, only, at room temperature. The solid particle reactions which were studied include SA, AA, BHA, and LA. The oxidation of GA particles which are present as liquid particles at room temperature, were also studied. In Fig. 2.15a-e, the ketone and alcohol product formation for SA, AA, BHA, LA and GA are shown as a function of Cl radical exposure, respectively. In figure 2.16, the average generation of products formed from the reaction of Cl radicals with SA, AA, BHA, LA, and GA are shown as a function of Cl radical exposure.

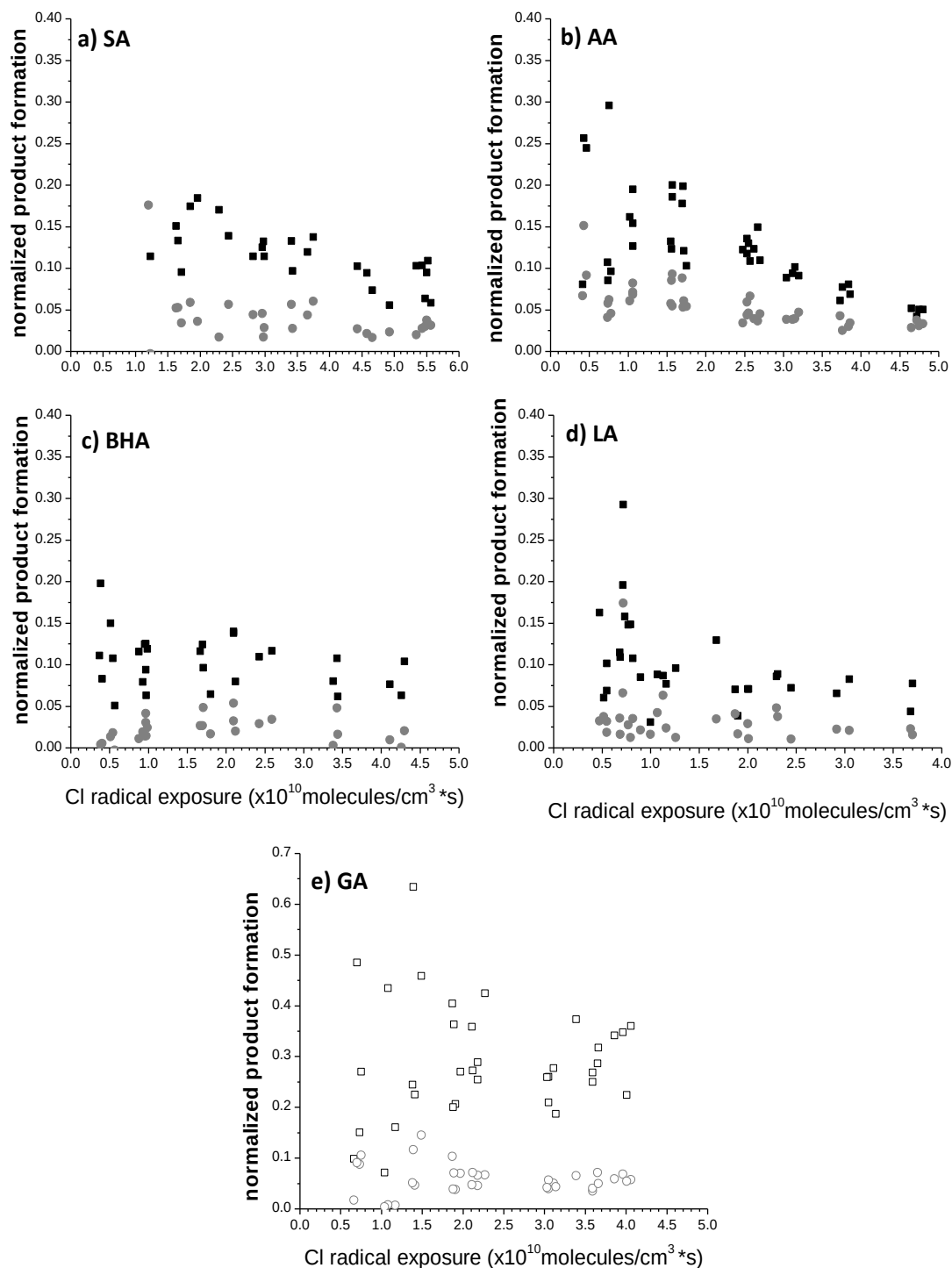


Figure 2.15 a-e. normalized ketone (black filled squares) and alcohol (gray filled circles) product signal from the Cl initiated oxidation of solid (a) SA, (b) AA, (c) BHA, and (d) LA particles as a function of Cl radical exposure. (e) normalized ketone (black empty squares) and alcohol (gray empty circles) product signal from the Cl initiated oxidation of liquid GA particles as a function of Cl radical exposure.

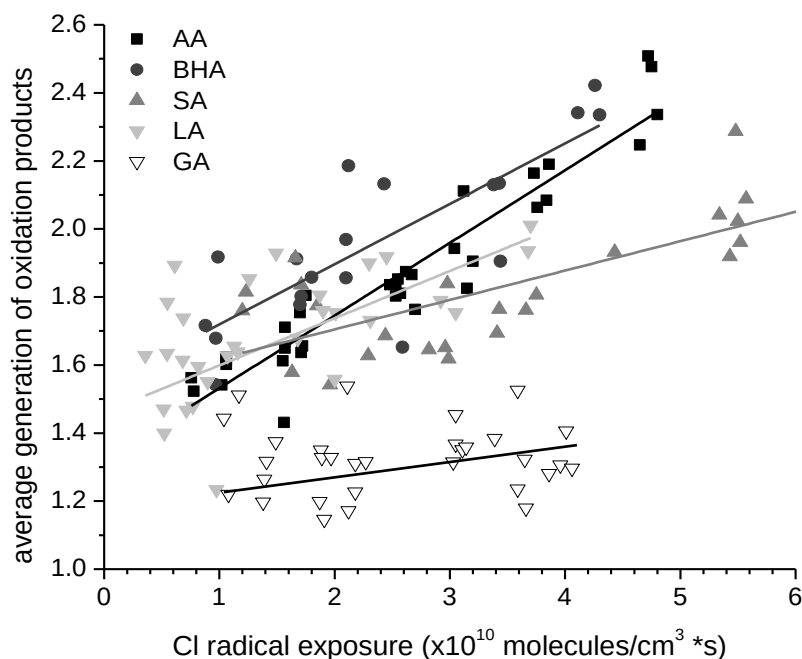


Figure 2.16 “Average generation” of the 1st–4th-generation products of solid AA, solid BHA, solid SA, solid LA, and liquid GA as a function of Cl radical exposure. These data are consistent with the solid and liquid data in Figs. 2.11a-e.

The data in Figures 2.15a-e and 2.16 show that the oxidation of these solid and liquid particles display similar trends as observed above for BA, NA, TEA, ELA and EA (see Fig. 2.6 a-e and 2.11a-e) where the normalized ketone signal is greater for liquid than solid particle oxidation, and solid particle reactions yield more high generation products than do liquid particle reactions. This is presumably due to the higher oxidative turnover of the products of Cl initiated oxidation of solid particles compared to liquid particles. Whereas in liquid particles, the first generation products are able to diffuse into the particle, and thus become diluted, in solid particles, the oxidation products are confined to the surface where they are more likely to undergo further oxidation reactions initiated by Cl. The lower ketone product formation in solid particles may be explained by this oxidative turnover, where the

ketone product, even at low radical exposures, has already begun being converted into higher generation oxidation products.

In addition to tracking the oxidation products of SA, AA, BHA, LA, and GA, the low molecular weight product formation was also quantified by collecting difference-difference spectra to account for low mass product formation from the reactions of Cl with species on the flow tube wall. Recall, from above, that this procedure of collecting difference–difference spectra is sensitive to changes in many factors including the Cl concentration, the reaction time, and the identity/aging of the coating on the flow tube walls and is therefore not always reproducible and are not to be considered a true yield since the ionization efficiencies differences between reactant and products are unknown. Nonetheless, the normalized low molecular weight product formation was quantified in order to compare solid SA, AA, BHA, and LA particles to liquid GA particles at a Cl exposure of 4×10^{10} molecules/cm³*s. The average low molecular weight product formation of two consecutive measurements of SA, AA, BHA, and LA particles were 0.44, 0.77, 0.75, 1.25, respectively. The normalized low molecular weight product formation from the oxidation of liquid GA particles was 0.29. The solid SA, AA, BHA, and LA particle reactions all resulted in more low molecular weight product formation than the oxidation of liquid GA particles, consistent with the results discussed above for solid and liquid BA, TEA, NA, and ELA. These results are consistent with the idea that in solid particles, the highly functionalized oxidation products are confined to the surface. Since these functionalized products may decompose more readily, low molecular weight product formation is enhanced in solid compared to liquid particles. The observation that solid SA, AA, BHA, and LA and liquid GA particles follow the same trends in ketone and alcohol formation, higher generation oxidation product formation, and low

mass product formation as the direct solid-liquid comparison studies of BA, TEA, NA, ELA, and EA suggest that the trends reported herein may be used to predict the behavior of other solid and liquid organic aerosols.

2.4. Discussion

Erucic Acid

The differences in solid and liquid EA reactions differ significantly from those observed for BA, TEA, NA, and ELA. In short, very small differences were observed in the solid and liquid EA kinetics, first generation product formation, 1st -4th generation product trends, and average generation of oxidation products. Is it possible that EA, although it has a melting point above room temperature, does not form solid particles when passing through the cold trap? In order to address this question, the ozonolysis reaction was performed on 110 nm EA particles which were either sent through the cold trap or allowed to remain supercooled.

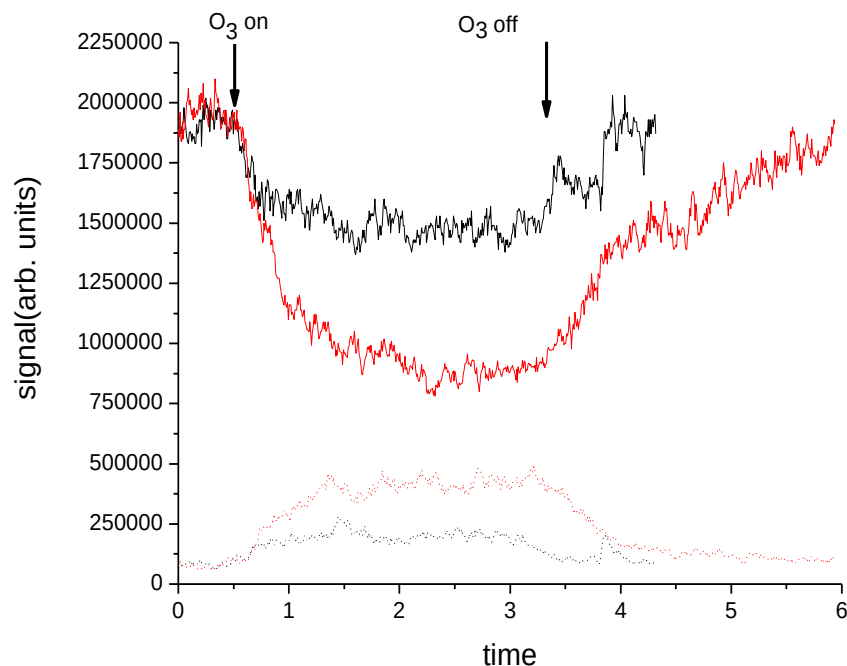


Figure 2.16. Particle phase of erucic acid (EA) is confirmed by performing ozonolysis reactions. Supercooled liquid EA droplets (red line) react approximately 2 times as much as solid particles (black line) with the same ozone concentration and reaction time. An ozonolysis product at m/z 229 is also shown and displays similar phase dependence.

While the difference in the reactivity of these particles with ozone was not as pronounced as observed for BA, the EA room-temperature reactivity with O_3 decreased by a factor of ~ 2 after being forced to solidify, suggesting there is a phase change in the EA upon sending the particles through the cold trap. However, if the solid particles were to have a thick liquid layer, or if the radical reaction were to cause a melt layer to form due to the enthalpy of mixing, the lack of significant differences in the kinetics and products of particles which were allowed to remain supercooled or forced to solidify may be explained. Erucic acid has a melting point that is closest to room temperature of any of the organic acid species studied here. As the formation of a liquid melt layer depends on how far below the melting point the

temperature is, EA is most likely of the acids studied here to form a thick liquid melt layer. The presence of a liquid layer may still allow differences in the O_3 reaction to be observed while not allowing much difference in the radical reaction to be observed, as the reacto-diffusive length of O_3 is longer than that of Cl. The reacto-diffusive length of O_3 in liquid oleic acid (an unsaturated fatty acid like those studied here) is $\sim 5\text{-}6$ nanometers,^{36, 46} A liquid layer with a thickness of a few nanometers would be sufficient for the radical reaction to appear as if the particle were liquid even if a solid core were present. Therefore, ozone may react differently with the particle depending on whether the particle is liquid or solid with a liquid melt layer whereas the particle will always “look” like a liquid to Cl, which never diffuses past the liquid layer before reacting.

In order to determine whether the liquid-like reactivity of solidified EA particles was due to a liquid layer or due to a liquid-like morphology of the solid EA particles, the ozonolysis of solid and liquid EA was determined as a function of flow tube temperature as each of these phenomena was expected to display a temperature dependence. The flow tube temperature was varied from $-10\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ by circulating a chilled methanol–water solution using a constant-temperature refrigerated bath (Caron Products and Services, Model 2050 W). These results are summarized in Fig. 2.18. It is still not clear from the data in Fig. 2.18 whether changes in the flow tube temperature change the thickness of the melt layer or if the solid structure changes morphology between the γ_1 to α_1 polymorphs. However, at a temperature very near the γ_1 to α_1 transition of $9\text{ }^{\circ}\text{C}$, the ratio of liquid: solid particle reactivity with O_3 seems to start declining from an average ratio of about 3.5 from $-10\text{ }^{\circ}\text{C}$ to $8\text{ }^{\circ}\text{C}$ to a factor of ~ 2 at room temperature. Although a much sharper drop in reactivity would be expected for a pure material (the transition temperatures are very well defined and occur

over a few degrees Celsius), these oxidized particles are not pure and the transition temperatures may be broadened.

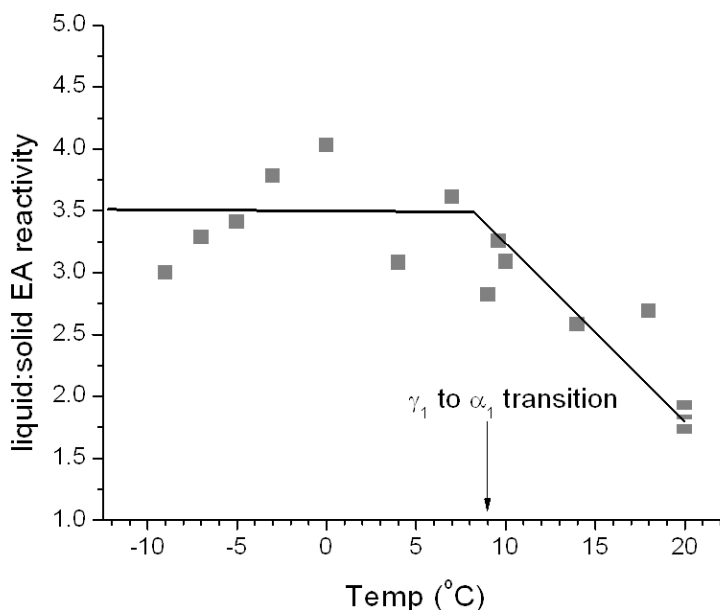


Figure 2.18. ratio of reactivity of liquid and solid EA particles with O_3 as a function of flow tube temperature.

While little is understood about the physical characteristics of solidified EA particles and how these characteristics may cause the solidified particles to behave very much like the supercooled liquid particles in the Cl- radical initiated oxidation reactions described in detail above, it is feasible that EA either has a thick liquid layer or is present at room temperature as a more disabled solid than the other eight solid organic acids studied herein.

2.5. Conclusions

In this study it was found that solid and liquid brassidic, nervonic, trans-11-eicosenoic, elaidic, and erucic acid particles do not differ greatly in how efficiently they react with Cl in the presence of O_2 . Erucic acid displayed almost no difference in the reaction kinetics of solid and liquid particles with Cl. In some respects, the finding that the kinetics of radical

initiated oxidation of solid and liquid particles of the same chemical composition do not vary greatly is counterintuitive since reduced solubility and diffusion in the solid particles would be expected to slow the observed rate of reaction considerably. However, renewal of the solid surface through volatilization of reaction products or surface melting could serve to bring the organic acid to the surface where it can continue to react with Cl radicals nearly as quickly as in the liquid. On the other hand, with the exception of erucic acid, which may have a considerable liquid melt layer, the distribution of oxidation products is quite different for the two phases. Whereas in liquid particles the organic acids and their oxidation products can diffuse and mix freely, this process is hindered in solid particles. Consequently, the products are confined to the surface region where they continue to react with Cl to create multiply-functionalized species which may be more likely to decompose. The trends in the ketone and alcohol product formation and higher generation oxidation products observed in the five systems where solid and liquid particles of the same chemical composition were studied were also apparent in the oxidation of other solid and liquid systems, suggesting that the trends observed here may occur in solid and liquid organic aerosol particles, in general. The liquid and solid particles react with Cl at similar rates but “age” differently with possible implications for volatilization and chemical transformation of organic aerosols in the atmosphere. Further research is needed to evaluate whether particle phase plays a similar role in the radical-initiated oxidation of organic aerosols of more complex composition.

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CHAPTER 3

PHASE DEPENDENCE OF ORGANIC NITRATE FORMATION¹

3.1. Introduction

Tropospheric gas-phase oxidants such as hydroxyl radicals (OH), ozone (O₃), and nitrate radicals (NO₃) react with organic constituents in aerosol particles to form more-highly-oxygenated species. In polluted atmospheres, where NO_x (NO + NO₂) is abundant, organic nitrates may also be formed. Nitric oxide (NO) and nitrogen dioxide (NO₂) are emitted from fossil fuel combustion and are interconverted through photochemical reactions involving volatile organic compounds in the atmosphere.² Atmospheric NO is also generated from natural processes including biomass burning and soil release.³ Typical concentrations of both NO and NO₂ range from a few ppt in remote, rural areas² to as high as 200 ppb in polluted urban areas.⁴⁻⁶ Organic nitrates have been observed in ambient atmospheric aerosols⁷⁻⁹ and in secondary organic aerosols (SOA) formed from the oxidation of various volatile organic compounds in the presence of NO_x.¹⁰⁻¹³ It is clear that at least some of these organic nitrates are formed in the gas phase after which they partition to aerosols as a result of their reduced volatility. Furthermore, reactions between NO₃ radicals and organic aerosol constituents are known to lead to the incorporation of –ONO₂ functional groups.¹⁴⁻¹⁸ However, it is not clear to what extent radical-initiated oxidation followed by reaction with NO or NO₂ in the particle leads to organic nitrate formation.

The formation of organic nitrates on aerosol particles may have many important atmospheric implications; for example, the addition of a polar nitrate group to condensed phase organics in the aerosol may change the hygroscopicity of the aerosol and may thus alter the CCN activity of the particle. In addition, because organic nitrates absorb UV radiation, formation of particle phase organic nitrates may significantly alter the radiative properties of the aerosol particle and may ultimately affect the UV actinic flux to Earth's surface. Organic nitrate formation may also act as an efficient reservoir of NO_x, thus allowing long-range transport into rural areas and also vertical transport through the troposphere.

The gas-phase mechanism of organic nitrate formation under tropospheric conditions is well understood and provides a useful starting point for understanding analogous reactions in organic aerosols: gas-phase organics (RH) react with OH radicals to form alkyl radicals (R) which then react rapidly with O₂ to form alkylperoxy radicals (RO₂):



The RO₂ radicals can react with one another:



Alternatively, in the presence of NO, RO₂ reacts with NO to form a peroxyxynitrite, ROONO*, which can either isomerize to form an organic nitrate (RONO₂) or decompose to an alkoxy radical (RO) and NO₂:^{19, 20}





where the nitrate yield increases with the size of the peroxy radical²¹ (ranging from <0.01 for ethyl peroxy¹⁹ to 0.23 for n-decyl peroxy radicals²²). Alkoxy radicals may also react with NO₂ to form organic nitrates:



but in the gas phase this reaction is slow ($\sim 75 \text{ s}^{-1}$ at 100 ppb NO₂) compared to the reaction of RO with O₂ ($\sim 4 \times 10^4 \text{ s}^{-1}$), RO decomposition ($\sim 3 \times 10^4 \text{ s}^{-1}$), and RO isomerization ($\sim 2 \times 10^5 \text{ s}^{-1}$) for a simple alkoxy radical such as 3-alkoxy hexane in air.² Therefore, in the gas phase, the primary fate of RO radicals is isomerization, reaction with O₂, and decomposition.

In this work, aerosol chemical ionization mass spectrometry was used to investigate the radical-initiated oxidation reactions between Cl and model solid and liquid aerosols consisting of brassidic acid (BA, *trans*-13-docosenoic acid) erucic acid (EA, *cis*-13-docosenoic acid), nervonic acid (NA, *cis*-15-tetracosenoic acid), *trans*-11-eicosenoic acid (TEA), and elaidic acid (ELA, *trans*-9-octadecenoic acid) in the presence of O₂ and NO_x. While these acids have not been observed in ambient aerosol, they are used here as a proxy for unsaturated organic fatty acids, which can be significant components of organic aerosol matter and are associated with aerosols in both urban and remote areas,^{23, 24} as well as for aerosol hydrocarbons, in general. More importantly, because these particles have melting points close to, but above, room temperature it is possible to generate both solid particles and supercooled liquid droplets. Consequently, it is possible to study the reaction of both solid and liquid particles of identical chemical composition at room temperature, as described, in the absence of NO_x.²⁵ Here, these model systems were used to (1) determine whether organic nitrates are formed from heterogeneous oxidation reactions in the presence of NO_x, (2)

determine if there is a particle phase dependence of organic nitrate yields for particles of equivalent chemical composition, and (3) elucidate the mechanism of nitrate formation in heterogeneous oxidation reactions.

3.2. Materials and methods

3.2.1 Particle generation

Particles of BA, NA, TEA, ELA, and EA were generated through homogeneous nucleation by flowing 0.9 slpm (standard liters per minute) of N₂ through a reservoir containing the organic acid of interest. Upon exiting the reservoir the organic vapor cooled to room temperature and spontaneously nucleated forming supercooled liquid droplets. The aerosol was then reheated as it flowed through a heated section of 1/2" o.d. glass tubing to narrow the distribution of particle sizes. The temperatures of the reservoir and reheater regions used to generate a narrow distribution (geometric standard deviation ≤ 1.25) of particle sizes are described in Chapter 2.

Previous experiments have shown that particles of other organic acids formed by homogeneous nucleation can be supercooled by up to 32 °C below the freezing point and may remain supercooled for at least a half an hour.²⁶ It was shown that BA, with melting point of 62 °C, is able to form supercooled liquid particles (Ref. ²⁵ and Chapter 2). The existence of supercooled BA particles was evident in both the ozonolysis reaction and in the product formation from Cl-initiated oxidation reactions, suggesting at least on the time scale of the flow tube experiments, that supercooling 42 °C below the freezing point is feasible. It was also shown that NA, TEA, ELA, and EA are able to form supercooled particles, as is expected since the melting points are between that of BA and room temperature. In these experiments, supercooled liquid particles of BA, NA, TEA, ELA, and EA were generated by

homogeneous nucleation and solid particles were generated when the droplets were sent through a cold trap held at $-80\text{ }^{\circ}\text{C}$ and were allowed to warm to room temperature before entering the flow tube reactor. In this way it was possible to generate liquid or solid BA particles.

3.2.2. Flow tube reactions

All reactions were carried out in an atmospheric-pressure jacketed glass flow tube (1.1 cm internal diameter (i.d.), 90 cm length) coupled to a chemical ionization mass spectrometer, as has been described previously.^{25, 27} For the temperature dependence experiments, the flow tube temperature was varied from $-14\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ by circulating a chilled methanol–water solution using a constant-temperature refrigerated bath (Caron Products and Services, Model 2050 W). The BA particles (0.9 slpm N_2 flow), the O_2 (0.5 slpm), the 1% Cl_2 – N_2 mixture (1–5 sccm, standard cubic centimetres per minute) and nitric oxide (NO) and/or nitrogen dioxide (NO_2) (0–1.5 sccm) were carried into the rear end of the flow tube by a 1.1 slpm N_2 carrier flow. The total flow of 2.5 slpm thus contained 20% O_2 , and the total reaction time was about two seconds.

While the OH radical is the primary oxidant in the troposphere, the Cl radical was used in this study to initiate the oxidation of the BA, NA, TEA, ELA, and EA particles instead because it is possible to generate a larger steady-state concentration of Cl radicals (the self-reaction rate coefficient is smaller for Cl than for OH), and the Cl_2 precursor is unreactive and does not interfere with the oxidation chemistry in the particles. The use of OH, instead, would be more difficult because the large concentration of O_3 commonly used as a precursor for OH would quickly react with the double bond in BA and convert most of the NO to NO_2 making the experiments with NO impossible. Furthermore, OH reacts with NO and NO_2 to

form HONO and HNO₃, respectively. The chlorine radicals were generated by photodissociation of Cl₂ using up to 100 mJ per pulse of the third harmonic (355 nm) from a 10 Hz pulsed Nd:YAG laser (QuantaRay PRO-250, Spectra-Physics). The chlorine radical concentration was varied by either adjusting the laser power or by adjusting the flow of Cl₂ through the flow reactor and was between 1.5×10^9 and 3.5×10^{10} radicals cm⁻³, as measured from the observed loss of gas-phase methanol and using $k = 5.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for the Cl + methanol reaction.^{28, 29}

The flow tube eluent containing aerosol was sampled into the ion tube region through a stainless steel orifice (0.5 mm i.d.) in a heated (200–380 °C) stainless steel vaporizer tube (1/4" o.d., 4" long). The vaporized aerosol flow then entered the heated (160 °C) stainless steel ion tube (1/2" o.d., 8" long, 40 Torr) of the CIMS instrument where it mixed with a 2 slpm flow of N₂ containing reagent ions generated from a radioactive ²¹⁰Po source (NRD). The reagent ions ionized the vaporized particle constituents, and the ions were then sampled into the high vacuum region through a 200 μm orifice by means of a small potential gradient (2–5 V) and differential pumping. Ions were filtered using a quadrupole mass spectrometer (ABB Extrel) and detected using a Channeltron electron multiplier (model 4816, Burle).

H⁺(H₂O)_{*n*} reagent ions were generated by sending trace amounts of O₂ and residual water along with the N₂ through the ²¹⁰Po source. The H⁺(H₂O)_{*n*} (*n* = 2 or 3) reagent ions were used in the nitrate product yield studies because ionization occurs preferentially at the carboxylic acid moiety of the BA and the BA-nitrate product. It was confirmed that this is indeed the case in a separate experiment in which *n*-docosane particles reacted with Cl in the presence of O₂ and NO to form the corresponding nitrate product (see results section). In that experiment, the BA and oxidation products were also detected as the corresponding Cl⁻-

adduct ions using Cl^- and Cl_2^- reagent ions generated from the addition of Cl_2 from the flow tube to the ion region.

3.2.3. Gases and chemicals

Gases used were nitrogen (99.99%, National Welders), chlorine (UHP grade, National Welders), oxygen (industrial grade, National Welders), nitric oxide ($\geq 99.5\%$, National Welders), and nitrogen dioxide ($\geq 99.5\%$, National Welders). Brassidic Acid ($\geq 99\%$) was purchased from Nu-Chek Prep, Inc, nervonic acid ($\geq 99\%$), trans-11-eicosenoic acid ($\geq 98\%$), elaidic acid ($> 99\%$), erucic acid ($\geq 99\%$), *n*-Docosane ($> 98\%$) were purchased from Sigma Aldrich.

3.3. Results

3.3.1. Formation of organic nitrates

The formation of the BA-nitrate product was observed when BA particles reacted with Cl in the presence of both O_2 and NO. Fig. 3.1 shows a difference mass spectrum created by subtracting the mass spectrum obtained with no radical reaction (light off) from the mass spectrum obtained during reaction (light on). Here, the loss of BA is observed at $m/z = 339$ (as $[\text{BA} + \text{H}]^+$) and the formation of the BA-nitrate product at $m/z = 400$ (as $[\text{BA-H} + \text{ONO}_2 + \text{H}]^+$). In addition to the BA-nitrate product, so-called “first-generation” products at $m/z = 353$ and 355 are also observed, corresponding to the addition of a ketone or alcohol group to BA, respectively; these are known to result from the self-reactions of peroxy radicals [and alkoxy radicals with species other than NO_x , as detailed previously.^{25, 27, 29} These are, in fact, the primary products and they can account for as much as 2/3 of the BA that reacts (in the absence of NO_x).²⁵ Likewise, the “second-generation” products observed at $m/z = 367$, 369

and 371 originate from the subsequent oxidation (or isomerization) of the first-generation products leading to the addition of another ketone or alcohol group. No other product peaks are observed at larger mass-to-charge ratios.

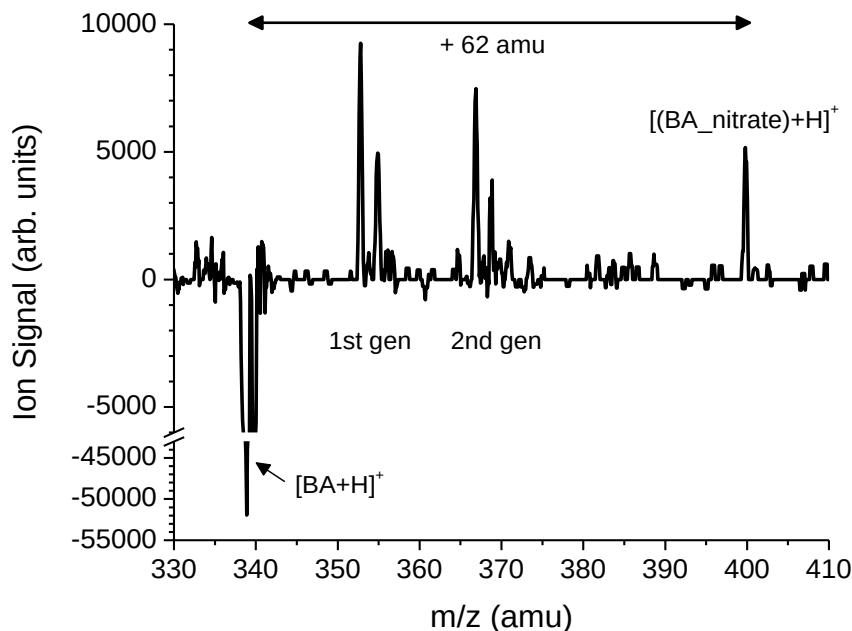


Figure 3.1. Difference mass spectrum showing loss of brassidic acid (BA) and appearance of organic nitrate (BA_nitrate) initiated by Cl radical reaction of solid particles in the presence of O₂ and NO. First- and second-generation products representing addition of one or two carbonyl or alcohol groups are also observed.

The organic nitrate yields were determined by dividing the increase in the acid-nitrate product signal (in the case of BA, $m/z = 400$ for $[(BA_nitrate)H]^+$) by the loss of the organic acid signal (in the case of BA, $m/z = 339$ for $[BA]H^+$) and correcting for the lower transmission efficiency of the quadrupole for the larger BA-nitrate. This factor was interpolated from measurements of the relative transmission efficiencies for various carboxylic acids in which the rise in their individual peak signals was compared to the losses of the reagent ions, $H^+(H_2O)_2$ and $H^+(H_2O)_3$. The best fit equation to describe the correction factor as a function of m/z (what each signal intensity must be multiplied by in order to

represent what the signal should be if all masses were equally transmitted through the quadrupole) for the particular set of voltages on the ion optics, quadrupole, and extraction plates used in these studies is given by $CF = 1.92e^{(\mu/237.36)} - 1.00$ where $\mu = m/z$. The correction factor for the organic nitrate product of each acid species was then divided by the correction factor for each of the respective acid species in order to determine the correction factor needed after normalizing the organic nitrate formation to the amount of acid reacted. The correction factors for BA, EA, NA, are 1.33 and the correction factors for TEA, and ELA are 1.34 and 1.35, respectively. Implicit in this approach is the assumption that the acid and the acid-nitrate are ionized by the $H^+(H_2O)_n$ reagent ions with equal efficiency; this seems reasonable since the proton transfer is expected to occur at the carboxyl group in each molecule. However, it is also possible that proton transfer could occur at the nitrate group resulting in an enhanced sensitivity to the organic nitrate product compared to the parent acid. To confirm that this is not the case, a separate experiment was conducted in which particles composed of a normal alkane, *n*-docosane, reacted with Cl in the presence of O₂ and NO to form the corresponding organic nitrate and 1st-generation products (ketone and alcohol). As shown in Fig. 3.2, both the nitrate and the ketone are detected using Cl^- ionization (as the corresponding Cl^- -adducts) but only the ketone is detected using $H^+(H_2O)_n$ ionization. The alcohol product was also detected with both methods of ionization, but for clarity it is not shown in Fig. 3.2. From this test we conclude that proton transfer ionization does not occur at the nitrate functional group; consequently, the carboxylic acid-nitrate (for instance, as shown in Fig. 3.1 for BA) must be ionized through proton transfer at the carboxylic acid moiety just as the carboxylic acid itself is.

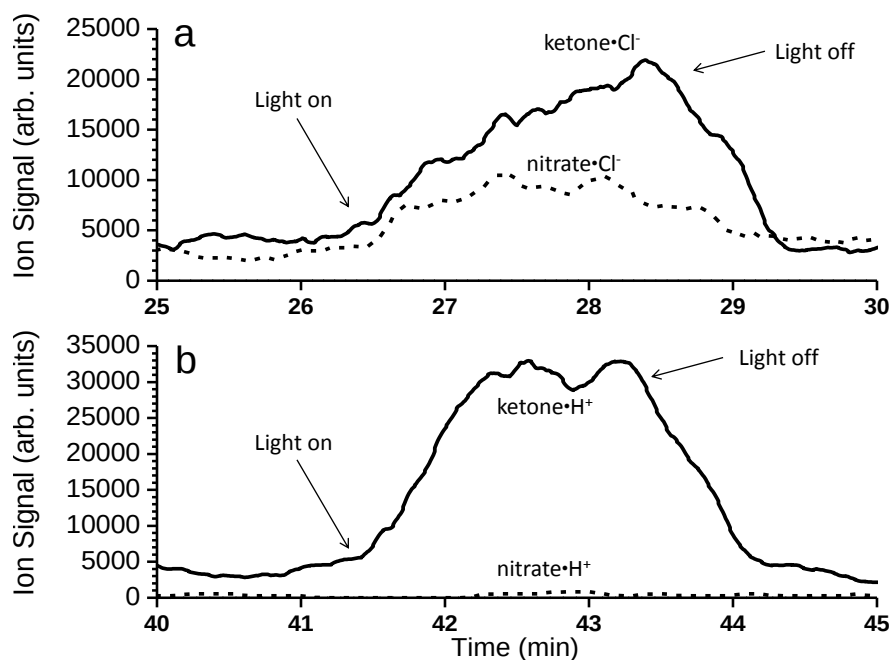


Figure 3.2. Single-ion traces of products from the reaction of Cl radicals with solid *n*-docosane particles in the presence of O₂ and NO. (a) The creation of both the ketone and nitrate products is confirmed with Cl⁻-adduct ionization. (b) The absence of nitrate signal confirms that proton transfer ionization does not occur at the -ONO₂ moiety.

The organic nitrate yields measured in this way are shown as a function of [NO] in Fig. 3.3a-e with the filled and empty squares representing the nitrate yields from the reaction of solid and liquid particles, respectively. The organic nitrate yields are significantly larger for solid particles (up to 6%) than for liquid particles ($\leq 0.5\%$) over the entire range of [NO]. The average chlorine radical concentrations in these experiments varied from 5×10^9 to 2×10^{10} radicals cm⁻³ as determined from the observed loss of gas-phase methanol. The observation that organic nitrates are formed on solid but not liquid organic aerosol particles suggests that the particle phase plays a fundamental role in determining the products which are formed from the radical-initiated oxidation reactions of organic aerosol species in polluted atmospheres containing NO_x. The nitrate yield increases with [NO] until it appears to level off at [NO] ≥ 0.3 ppm at which point the solid surface may be saturated with NO. Since NO

concentrations in the troposphere are typically lower than this, even in polluted environments, the nitrate yield is expected to depend linearly on NO concentration. However, extrapolation to atmospheric conditions would require also taking into account the lower concentration of RO₂ radicals, but this is beyond the scope of the present study.

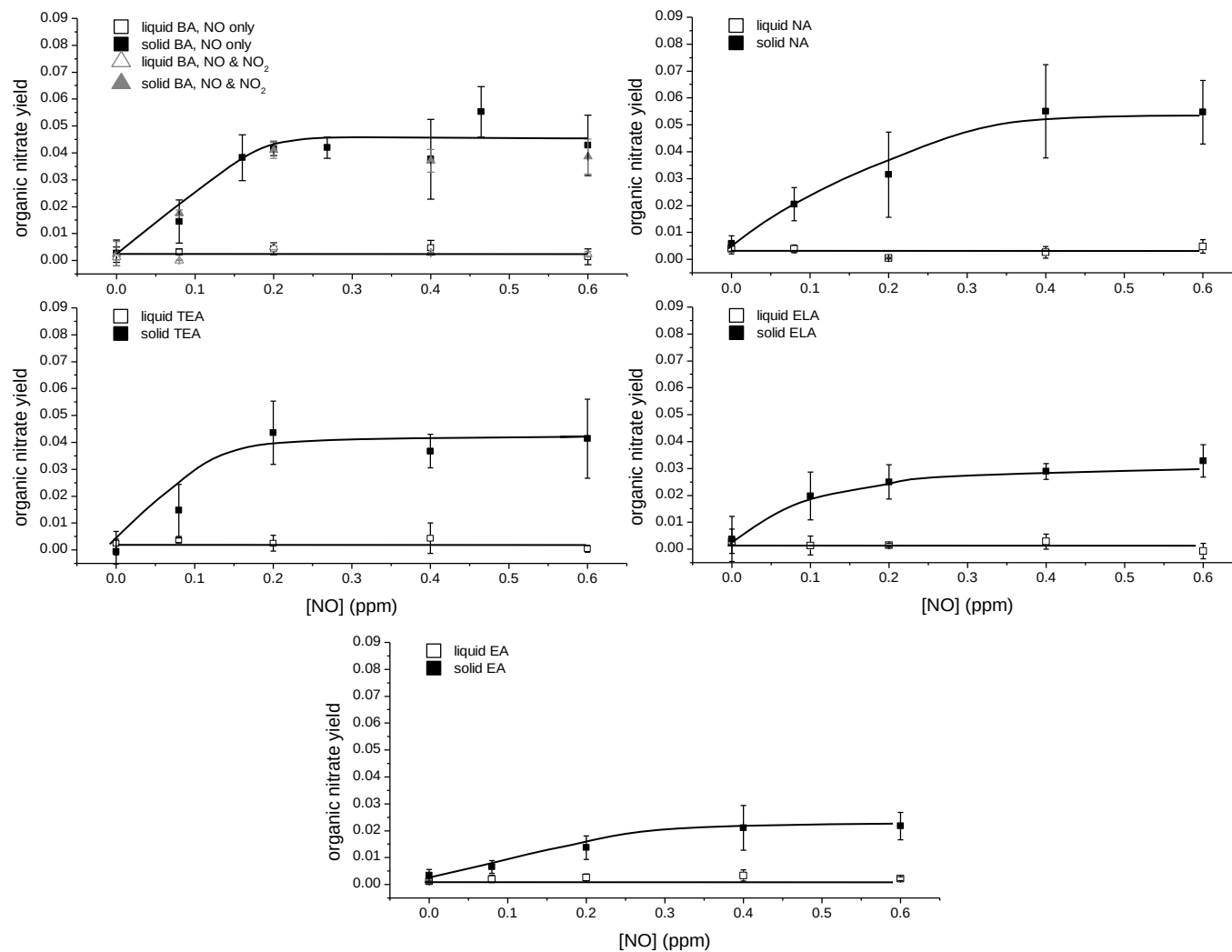


Figure 3.3 a-e. Organic nitrate yield as a function of NO concentration for solid (■) and supercooled liquid (□) particles with a Cl concentration of $5\text{--}20 \times 10^9 \text{ radicals cm}^{-3}$. No additional nitrate formation is observed upon addition of an equal amount of NO₂ for both the solid (▲) and the liquid (△) BA particles. The lines are added to guide the eye.

As evident from Fig3.3a-e, the organic nitrate yields from the reaction of solid BA, NA, TEA, and ELA with Cl in the presence of NO are comparable (with average nitrate yields between 4-6 percent at 0.6 ppm NO) and liquid particle reactions resulted in nitrate yields that were less than 0.5%. Erucic acid, while still exhibiting a clear phase dependence in the organic nitrate yield, shows lower nitrate yields for the reactions of solid EA particles than was observed for the other organic acid species. These results are consistent with the results reported in Chapter 2, where Cl-initiated reactions of solid and liquid EA particles in the absence of NO showed less of a difference in the 1st-4th generation oxidation product formation and oxidation kinetics than the other four organic acid particle types. Possible explanations for the small differences observed in solid versus liquid EA particles compared to the other organic acid species are discussed in Chapter 2. In short, this difference may be explained by 1) the existence of a melt layer on solid EA particles that is thicker than the melt layer in the other solid organic acid particles due to the lower melting point of EA; 2) difference in the structure of the solid formed upon freezing EA compared to the other solid particles.

If organic nitrate formation in solid particles is a surface-dominated phenomenon, changing the surface area to volume ratio of the solid particles should change the yield of organic nitrate formed from reaction 3-4b. Using methanol as a gas-phase reference to ensure chlorine radical concentration was constant, the yields of organic nitrate from the reaction of small (55-60 nm) and large (155-180 nm) BA particles were compared. These data are shown in Figure 3.4 and suggest the importance of a surface-enhanced formation pathway for organic nitrate formation.

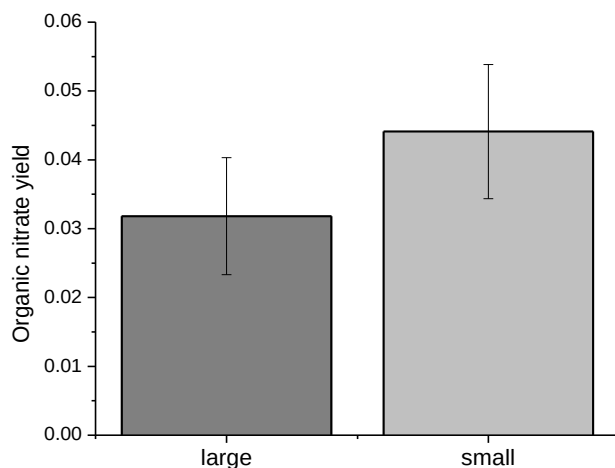


Figure 3.4. Organic nitrate yields from the reaction of small (55-60 nm) and large (155-180 nm) BA particles in the presence of NO (600 ppb) at constant Cl.

To investigate the possible formation of the nitrate through the reaction of RO with NO₂ [reaction (3-5)], an equal concentration of NO₂ was added to the flow tube along with the NO during the reaction of solid and liquid BA particles. The addition of up to 600 ppb of NO₂ leads to no measurable increase in the nitrate yield for either the solid or the liquid particles suggesting that the RO radicals do not react with NO₂ to form an organic nitrate. The NO was not removed in these experiments because doing so would have changed the Cl concentration by eliminating the NO + Cl + M → NOCl + M reaction in the gas phase; however, in separate experiments (not shown) no additional nitrate was observed when the NO was eliminated and NO₂ was added alone during the reaction of BA particles. Since NO is produced from the 355 nm photolysis of NO₂, the amount of NO that was generated from the NO₂ must be known in order to determine whether these results are consistent with those discussed above and displayed in Fig 3.3a. The rate of NO production from the photolysis of

NO₂ at 355 nm is given by $\frac{d[NO]}{dt} = j_{NO_2}[NO_2] = I_{NO_2}\sigma_{NO_2}\phi_{NO_2}[NO_2]$ where j_{NO_2} is the

photolysis rate coefficient of NO_2 , I_{NO_2} is 355 nm laser fluence, σ_{NO_2} is the absorption cross section of NO_2 , and ϕ_{NO_2} is the photolysis quantum yield at 355 nm. Integrating, $[\text{NO}] = \int j_{\text{NO}_2} [\text{NO}_2] = \int I_{\text{NO}_2} \sigma_{\text{NO}_2} \phi_{\text{NO}_2} [\text{NO}_2]$. The quantum yield is considered as unity,³⁰ the laser fluence is 100 mJ/pulse, and the absorption cross section is $4.98 \times 10^{-19} \text{ cm}^2/\text{molecule}$ ³¹. At an NO_2 concentration of 0.60 ppm, the theoretical NO concentration formed is $0.018 \times 0.60 \text{ ppm} = 0.010 \text{ ppm}$. According to the findings displayed in Fig. 3.3a, no measurable organic nitrate formation is expected at 0.010 ppm NO so the results of the NO_2 -only experiments are consistent with the NO experiments above and suggest that no organic nitrate is formed from reactions of NO_2 with alkoxy radicals. In addition to the lack of evidence for the formation of RONO_2 from the reaction of $\text{RO} + \text{NO}_2$, no evidence for the formation of RONO or RO_2NO_2 products (from $\text{R} + \text{NO}_2$ or $\text{RO}_2 + \text{NO}_2$, respectively) was observed in the mass spectrum, either, though RO_2NO_2 would likely decompose at the elevated temperatures of the vaporizer inlet.

It is possible that the rate of the $\text{RO} + \text{NO}_2$ reaction [reaction (3-5)] is not fast enough to compete with the other fates of the RO radical, such as isomerization, decomposition or reaction with O_2 , just as in analogous gas-phase reactions.³² For example, the first-order rate of RONO_2 formation from $\text{RO} + \text{NO}_2 \rightarrow \text{RONO}_2$ ($k = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, from ref. ²) in the presence of 0.6 ppm of NO_2 is 450 s^{-1} , whereas the first-order rate of reaction for $\text{RO} + \text{O}_2 \rightarrow \text{ketone} + \text{HO}_2$ ($k = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, from ref. ³³) is $4 \times 10^4 \text{ s}^{-1}$ in 20% O_2 (152 Torr). The rates of isomerization and decomposition of the RO radicals in the gas phase can be similarly fast,³² so it is not surprising that the $\text{RO} + \text{NO}_2$ reaction may not be competitive in the particles. However, we note that Gross and Bertram recently observed the formation of $-\text{ONO}_2$ groups from the NO_3 -initiated oxidation of an alkane self-assembled

monolayer in the presence of NO₂ and attributed it to this reaction.¹⁶ It is not clear why such a reaction would not be observed in the present work, but it may be related to the fact that the timescales for the experiments were very different (two seconds for these flow tube experiments vs. 0.5–2.5 h for the monolayer experiments of Gross and Bertram).

It is worth noting here that the BA-nitrate is observed in the mass spectrum despite the fact that the particles are heated to 230 °C in the vaporizer suggesting that they are thermally stable at elevated temperatures. A more systematic study of the BA-nitrate signal as a function of vaporizer temperature (Fig. 3.5) demonstrates that it is still observed at temperatures up to 380 °C. Below 200 °C, the particles are not efficiently vaporized, causing BA and the organic nitrate product to “stick” to the vaporizer. For this reason, the temperatures used in this experiment were limited to >200 °C. These experiments were conducted by performing the reaction of BA with Cl in the presence of 0.6 ppm NO and the radical exposure (1.7×10^{10} molecules/cm³ *s) and NO were held constant while the temperature was ramped up from 200 °C to 380 °C and then allowed to cool back down to 200 °C to ensure the nitrate product was being formed in the same abundance throughout the experiment and that only the vaporizer temperature was affecting the observed nitrate signal. Below 250 °C, it appears as if the organic nitrate signal reaches a plateau, where a further decrease in temperature does not lead to an increase in organic nitrate formation. Thus, it appears as if thermal decomposition in the atmosphere, where temperatures are much lower than those used in these vaporizer studies, is probably a negligible pathway for removal of such particulate organic nitrates. Consequently, these nitrates may enable long-range transport of NO_x in the atmosphere.

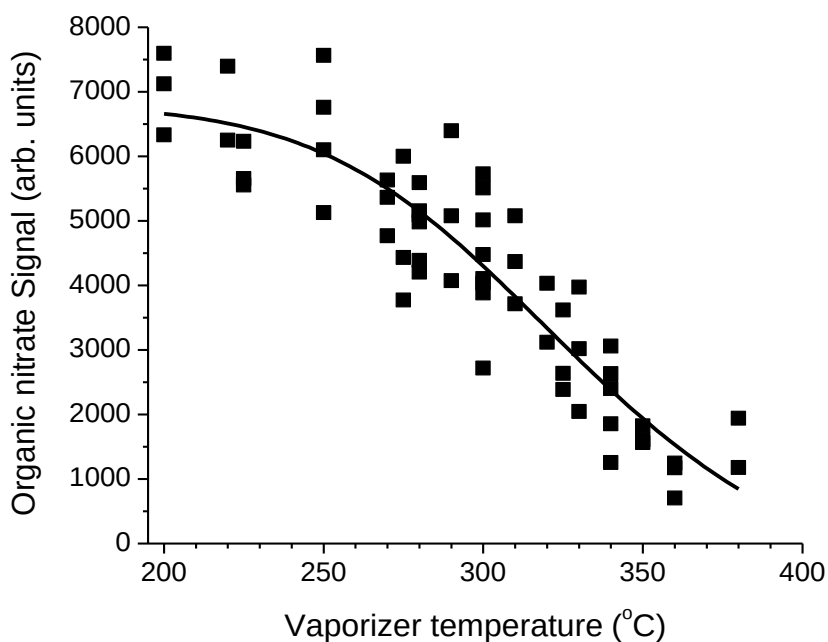


Figure 3.5. Organic nitrate signal decreases at particle vaporizer temperatures above 250 °C. Experiments are typically conducted with a temperature of 230 °C so thermal degradation of the nitrate is expected to be minimal.

3.3.2. Temperature dependence of organic nitrate yields

In order to learn more about the organic nitrate formation in the solid particles, the nitrate yields were measured as a function of flow tube temperature. In the gas phase, the $\text{RO}_2 + \text{NO}$ reaction is termolecular involving a third body for collisional stabilization of the ROONO^* intermediate. Thus, the yields of organic nitrate increase with increasing pressure and decreasing temperature.³⁴⁻³⁷ Just such a negative temperature dependence is also observed for the BA-nitrate yields in the present experiments (Fig. 3.6) in which the Cl and NO concentrations were held constant across the range of temperatures at $8\text{--}10 \times 10^9$ molecules cm^{-3} and 0.6 ppm, respectively. In the pre-cooled (*i.e.* solidified) particles the nitrate yield increases from 3% at 20 °C to 5% at -15 °C suggesting that the rate of ROONO^* dissociation is smaller at lower temperatures analogous to the gas-phase reaction of $\text{RO}_2 +$

NO. From this temperature dependence an effective activation energy of -7.5 kJ mol^{-1} ($\pm 4.4 \text{ kJ mol}^{-1}$) for the BA-nitrate channel is obtained. This estimate is in line with effective activation energies obtained for organic nitrate formation in analogous gas-phase reactions ranging from about -9 kJ mol^{-1} to -13 kJ mol^{-1} .^{20, 37-39}

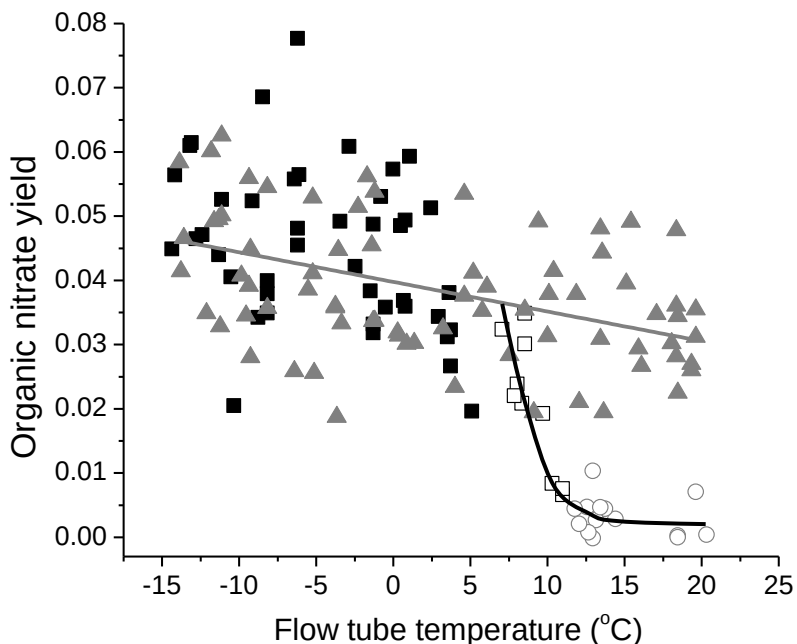


Figure 3.6. Organic nitrate yield as a function of flow tube temperature for reaction of solid (▲) and supercooled liquid (○) brassidic acid particles in the presence of NO. At $\sim 12^\circ\text{C}$, some particles begin freezing (□) and at temperatures below 8°C , yields from the liquid particles match those from the solid particles indicating that the supercooled droplets have frozen in the flow tube (■). A fit to the solid data yields an effective activation energy of $-7.5 (\pm 4.4) \text{ kJ mol}^{-1}$.

At temperatures higher than 12°C , the non-cooled particles exist as supercooled droplets (since they are not sent through the -80°C bath to force solidification), and they show negligible nitrate yields. However, as the flow tube temperature is decreased from 12°C to 8°C , the supercooled particles solidify because they are no longer stable at the lower temperature and the nitrate yield increases. At temperatures below 8°C the nitrate yields

from the non-cooled particles are equivalent to the yields from the pre-cooled particles indicating that the supercooled droplets have frozen in the flow tube; thus, on the timescale of these experiments (two seconds) the BA can be supercooled by as much as 42 °C below its melting point.

3.3.3. Photochemistry of the organic nitrate

Also important in the chemistry of gas-phase organic nitrates is their ability to absorb UV light. In fact, photolysis has been estimated to be the most important removal pathway for some gas-phase organic nitrates.⁴⁰ It is possible, therefore, that the condensed-phase organic nitrate formed in the heterogeneous oxidation of BA may also absorb UV radiation; this could have implications for the stability of such nitrates in ambient aerosol. Although it was not possible to measure the absorption spectrum of the nitrate in this study, it was possible to determine whether it absorbs UV radiation at 355 nm (which was utilized here for the photodissociation of Cl₂ to create Cl radicals) by using two separate methods for varying the Cl radical concentration. Method 1 involves using low concentrations of Cl₂ ($\sim 3 \times 10^{14}$ molecules/cm³) and increasing the laser power (up to 1000 mW) to vary the concentration of Cl, and method 2 involves using low laser power (~ 350 mW) and changing the Cl₂ concentration ($\sim 4 \times 10^{13} - 7 \times 10^{14}$ molecules/cm³) to vary the concentration of Cl. The results of these experiments are shown in Fig. 3.7 where the black squares represent the nitrate yields from method 1 and the gray triangles represent the nitrate yields obtained using method 2. With each method the Cl exposure was measured from the observed loss of gas-phase methanol. For both methods the nitrate yield is seen to decrease with increasing exposure and is presumed to result from subsequent oxidation of the nitrate product initiated by reaction with Cl radicals. It is not clear why the organic nitrate yield decreases with [Cl] at

a faster rate using method 2 than method 1, as the organic nitrate product is exposed to the same Cl concentration in each case. One explanation for the greater decrease in the nitrate yield using method 2 is the ability of Cl₂ to adsorb to the particle surface and block surface sites where NO may collide with the particle, thus decreasing the local NO concentration at the particle surface. This phenomenon cannot explain the observation of greater organic nitrate yields using method 2 compared to method 1, however, as the Cl₂ concentrations were greater using method 2 than method 1 at high at high Cl concentrations. The effect of Cl₂ adsorption on particle oxidation is explored further in Chapter3.

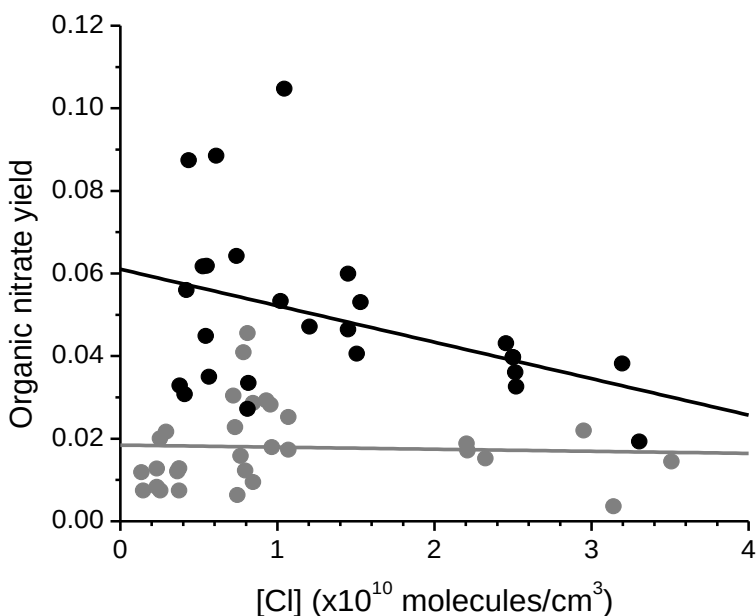


Figure 3.7. Organic nitrate yield from solid brassidic acid particles as a function of Cl concentration which was varied by changing either: (1) the photodissociation laser intensity (with low Cl₂ concentration) (●) or (2) the Cl₂ precursor concentration (with low laser intensity) (●). The difference in yields using the two methods is taken as indirect evidence of nitrate photolysis by the 355 nm laser.

It is observed that at a given Cl radical concentration the nitrate yields are higher when low laser powers are used (method 2) than when higher laser powers are used (method 1).

This observation suggests that the condensed-phase organic nitrates may absorb 355 nm light and photodissociate with some important consequences. First, these results may indicate that the absorption spectrum is red-shifted compared to the spectra of gas-phase organic nitrates which generally absorb near 190–220 nm ($\pi \rightarrow \pi^*$ transition) and 260 nm ($n \rightarrow \pi^*$ transition).^{41, 42} Such a shift could be attributed to the much larger size of the nitrates formed in the particles^{40, 43-45} compared to gas-phase nitrates or to the unique environment at the surface of the particle. Further work will be required to confirm this red-shift and to determine its origin. Second, the apparent photodissociation of the nitrates means that the yields reported above are only lower bounds, so the nitrate yields from the reaction of ambient particles may be larger.

Photolysis of the nitrates may also represent an important loss process in ambient particles. A simple time-constant analysis illustrates the potential significance of the photodissociation; assuming that the difference in the yields for the two methods in Fig. 3.6 reflects photodissociation of the nitrate, then approximately 2/3 of the nitrate dissociates over the two-second residence time in the flow tube. The corresponding time constant in the flow tube (the time required for the nitrate to dissociate to 1/e its initial concentration) is $\tau_{\text{FT}} = 1.8$ s. The time constant for dissociation in the ambient particles will be longer since the flux of 355 nm photons reaching the earth ($\sim 10^{15}$ photons $\text{cm}^{-2} \text{s}^{-1}$ at a solar zenith angle of 0°) is much smaller than the flux used from the laser ($\sim 2 \times 10^{18}$ photons $\text{cm}^{-2} \text{s}^{-1}$ for 1000 mW). Thus, $\tau_{\text{atm}} = 2000\tau_{\text{FT}} = 3600$ s, or one hour. By comparison, the lifetime of the organic nitrate with respect to reaction with OH radicals in the atmosphere can be estimated from the kinetics of oxidation of other long-carbon-chain acids with OH radicals if we assume that the presence of the nitrate group has no effect on the rate of OH reaction. Although little data

exists on OH + unsaturated fatty acid kinetics, we have measured effective reactive uptake coefficient of OH on oleic acid and 2-ODA aerosol particles to be 0.4-0.5 (see Chapters 4-5). For 75 nm particles (typical of those used here), and an effective reactive uptake coefficient of 0.5, the effective rate constant of the reaction of particulate phase organic acid + OH can be obtained from rearrangement of eqn. 2.1 (Ch. 2) and is $k \sim 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. With $10^6 \text{ radicals/cm}^3$ of OH in the troposphere, this corresponds to a reactive lifetime of ~87 hours. Thus, photodissociation may compete with reaction with OH as a significant loss mechanism for particle-bound organic nitrates in the troposphere. Of course at larger solar zenith angles the solar flux will be smaller and the photolysis time constant will be longer than what is estimated here; conversely, the nitrate will absorb UV light throughout the spectrum, not just at 355 nm, so the lifetime will end up being shorter than what is estimated. A more complete assessment of the potential importance of photodissociation will require further work to measure the rate of photodissociation more directly and to measure the UV-visible absorption spectrum.

3.4. Discussion

In the present work several observations have been made regarding the formation of organic nitrates upon radical-initiated oxidation of model aerosols: (1) intact nitrates are detected (as opposed to just fragments thereof) at temperatures up to 380 °C, (2) nitrates are observed on solid particles but not on liquid ones, (3) nitrate yields of up to 6% are measured on solid particles in the presence of NO, (4) no additional nitrate formation is observed upon addition of as much as 600 ppb of NO₂, (5) the nitrate yield is larger for small particles than large particles, (6) the nitrate yield increases with decreasing flow tube temperature, and (7) the nitrate yield is smaller when larger laser intensities are used.

Together, these observations provide some insight into how nitrates are formed and under what conditions they may be formed in ambient particles. The most striking of these is that nitrates are only formed on solid particles and not on liquid ones, and we suggest that this is the consequence of the different rates of diffusion in the two phases. After the initial attack by the Cl radical, the alkyl radical quickly adds O₂ to form the alkylperoxy radical, RO₂ [reaction (3-2)]. This RO₂ radical can then react either with other RO₂ radicals [reactions (3-3a) and (3-3b)] or with NO [reactions (3-4a) and (3-4b)]. In liquid particles the RO₂ radicals are able to diffuse into the particle quickly with a time constant of approximately 6 μs (assuming the RO₂ diffusion constant is the same as that for oleic acid, $2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, from ref. ⁴⁶). In contrast, the observed time constant for reaction is approximately two seconds, thus indicating the liquid particles are well mixed with respect to the RO₂ radicals. The dominant fate of these radicals in the liquid particles is the RO₂–RO₂ reaction, whereas in solid particles the rate of this reaction is limited by diffusion and reaction with NO near the surface becomes competitive. Evidence of a surface-dominated process exists in the size-dependent organic nitrate yield data, where the organic nitrate yield was larger for small particles than for large ones at a fixed Cl exposure.

These conclusions are consistent with our previous findings for the reaction of solid and liquid BA particles in the absence of NO_x,²⁵ in that study it was believed that slow diffusion of the oxidation products, including both the RO₂ radicals and the first-generation products, in the solid particles led them to remain near the surface where they were oxidized further to generate more-highly-functionalized (*i.e.* higher-generation) products. Likewise, in the present study RO₂ radicals at the surface of the solid may be immobilized and able to react with NO to form the organic nitrate before reacting with other species, including other RO₂

radicals. Thus, the primary effect that the particle phase has on the oxidation reactions (either with or without NO) appears to be the immobilization of species at the surface resulting in their enhanced chemical transformation relative to the rest of the particle. However, it is also possible that the nitrate is only observed in the solid particles because the branching ratio for nitrate formation from the $\text{RO}_2 + \text{NO}$ [reaction (3-4a)] is larger in the solid phase than in the liquid phase. Additional experiments are required to determine if such a difference exists.

It is difficult to estimate how significant organic nitrate formation might be in ambient aerosols from the results of the model organic acid particles studied here. However, Fig. 3.3a-e suggests that in polluted urban areas, where NO concentrations may be as high as 200 ppb, organic nitrates are formed. The maximum yield of ~6% is much smaller than nitrate yields from gas-phase reactions of RO_2 radicals with NO which increase with hydrocarbon size until they approach 30% for C15 and larger hydrocarbons.^{13, 47} Some of the discrepancy could be attributable to the continued oxidation of the nitrate by Cl radicals or photodissociation by the 355 nm laser light, as already mentioned. In addition, the reaction of RO_2 radicals with other RO_2 radicals certainly limits the formation of the nitrate in these experiments, but under ambient conditions such reactions are less important since the rate of oxidation is much smaller. More specifically, the OH concentration in the atmosphere is approximately four orders of magnitude lower than the Cl concentrations used here, so the steady-state RO_2 concentration will be much lower. This could lead to the $\text{RO}_2\text{--NO}$ reaction being competitive with the $\text{RO}_2\text{--RO}_2$ reactions even at NO concentrations significantly lower than 200 ppb. Further work is required to determine the rates of the $\text{RO}_2\text{--RO}_2$ and $\text{RO}_2\text{--NO}$ reactions in particles, and more studies with a variety of organic species are required to determine how general the conclusions of the present work may be.

The findings of the current study indicate that organic particles in the atmosphere may age differently and have different physical properties depending on whether they are liquid or solid. Solid particles may also evolve very differently depending on whether they do so in high-NO_x or low-NO_x conditions; specifically, in the presence of high concentrations of NO the addition of nitrate groups will serve to reduce the volatility of the particles, whereas oxidation with low concentrations of NO will lead to the addition of multiple carbonyl and alcohol groups and perhaps to the creation of smaller, more-volatile scission products.^{14, 27, 29, 48, 49} The mixing state of these particles may also be drastically different if the oxidation products are well mixed in the liquid droplets but reside primarily on the surface of the solid particles. Such a difference could influence subsequent reaction of the particles as well as their abilities to take up water and to scatter or absorb light.

3.5. Conclusions

The Cl-initiated oxidation of solid and supercooled liquid brassidic acid, nervonic acid, trans-11-eicosenoic acid, elaidic acid, and erucic acid particles were investigated in the presence of NO and NO₂ (BA only). For the first time, organic nitrate formation from the heterogeneous oxidation of model organic aerosols in the presence of NO was observed, but none was formed by the addition of up to 600 ppb of NO₂. Also, no organic nitrate formation was observed in liquid particles, but the nitrate yields in the solid particles were measured to be as large as 6% with a negative temperature dependence over the range 259–293 K. The corresponding effective activation energy of $-7.5 (\pm 4.4) \text{ kJ mol}^{-1}$ suggests that the mechanism of particulate organic nitrate formation is analogous to the termolecular gas-phase reaction of $\text{RO}_2 + \text{NO} \rightarrow \text{ROONO}^* \xrightarrow{\text{M}} \text{RONO}_2$. The yields are smaller than those

from analogous gas-phase reactions, but this may result from photodissociation of the nitrate by the UV (355 nm) laser for which there is indirect evidence. Additionally, enhanced rates of the $\text{RO}_2 + \text{RO}_2$ reactions in the condensed phase could lead to smaller nitrate yields. The results suggest that slower diffusion of the RO_2 radicals in the solid particles compared to the liquid particles makes the $\text{RO}_2 + \text{NO}$ reaction competitive with the $\text{RO}_2 + \text{RO}_2$ reactions and results in nitrate formation near the surface of the particle. The organic nitrates formed in these experiments are observed intact after the reacted particles have been vaporized at temperatures up to 380 °C suggesting that they are thermally stable in the troposphere and may enable long-range transport of NO_x if they photodissociate on the timescale of days. Preliminary evidence also suggests that the particulate organic nitrates formed here may absorb UV radiation, suggesting this may be an important removal pathway of particulate organic nitrates in the troposphere, although further experiments are needed in order to determine the significance of this removal pathway. The findings from these experiments are not specific to unsaturated carboxylic acids but should apply to nearly all particulate hydrocarbons, and they indicate that the particle phase could be important in determining how organic aerosols evolve chemically through radical-initiated oxidation in polluted atmospheres.

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CHAPTER 4

A “VIRTUAL INJECTOR” FLOW-TUBE APPROACH FOR MEASURING GAS-PHASE AND HETEROGENEOUS OXIDATION KINETICS

4.1. Introduction

Many different experimental approaches to measuring gas-phase rate constants are used including those which result in absolute rate constant determination and those which utilize relative rates whereby the rate constant of an “unknown” is measured *relative* to a reaction which occurs at a known rate. In either case, movable-injector apparatus are commonly used in order to vary the reaction time between oxidant and reactant. In those experiments, at least one reactant (at least two reactants for relative rates experiments) is introduced into a small, movable injector tube while the other reactant enters the flow tube apparatus through a port at the rear end of the flow tube. The reaction time between the two reactants may then be controlled by controlling the position of the injector within the flow tube. In addition to gas-phase rate constant measurements, the movable injector approach has been used to study gas-particle heterogeneous oxidation kinetics whereby the contact time between particles and gas phase oxidant such as NO_3 or O_3 is manipulated by moving the injector and the heterogeneous rates of reaction are determined.¹⁻⁷

There are several restrictions inherent to using movable injector apparatus, especially in multi-phase or heterogeneous reaction kinetics studies. In order to achieve pseudo-first order

conditions when two reactants are involved in a reaction, one reactant must be in excess of the other so that a steady-state approximation may be made. In heterogeneous oxidation kinetics measurements, it is often difficult to achieve particle concentrations high enough for the particle-phase reactant to be in excess of the gas phase reactant. Therefore, the gas phase reactant must be maintained in excess of the particle phase species. When the gas phase reactant is a radical species or other oxidative, short-lived species such as O_3 , it may be difficult to maintain high enough concentrations of gas phase oxidant to achieve pseudo first-order conditions. Another difficulty faced in movable injector studies using particle phase reactants is the susceptibility to particle loss inside the flow tube apparatus as well as incomplete gas-particle mixing. In order to accurately study heterogeneous reaction kinetics, the mixing between the two reactants must occur on timescales much shorter than the reaction time in the flow tube and there must be minimal particle loss inside the flow tube. In gas phase movable injector experiments, it is usually feasible to achieve pseudo-first order conditions by maintaining the longer lived reactant in excess of the radical or short-lived species and loss of the gas phase species in the flow tube is usually negligible.

Movable injector apparatus require very rapid mixing of reactants with respect to the reaction time and small concentration gradients in the radial dimension. The reason mixing is so critical in conventional movable injector systems stems from the design of the apparatus where one reactant is more or less filling the entire flow tube while the other reactant is being introduced through a smaller tube that enters the larger flow-tube radially centered. One can imagine with laminar flows and short distance to the flow-tube exit (corresponding to short reaction times), the flows may not be well mixed on the time scale of the reaction, or residence time in the flow tube. To overcome these limitations, manual movable injectors

often use turbulent flows in order to achieve mixing. For heterogeneous reaction kinetics studies, this can lead to increased particle loss to the flow tube walls.

As an alternative to conventional movable injector approaches, this chapter describes a “virtual injector” flow tube for measuring both gas-phase and gas-particle kinetics in which the gas flow through the flow-tube continuously varies the reaction time. The virtual injector approach overcomes many of the limitations of conventional movable injector techniques. By generating reactive gas phase species using photolysis-initiated mechanisms, a more or less uniform concentration of the gas phase reactive species is generated immediately upon introduction of the light source. The gas flow through the flow tube then moves the particles or other gas phase reactant through this flow tube containing a uniform concentration of reactive species. In this way, the gas-phase and particle species react with the photo-generated reactive species for increasingly longer time as the flow travels down the flow tube. Using the virtual injector technique, therefore, absolute rate constant determination is possible if the reactive species concentration is known and the fractional loss of the gas or particle phase species may be monitored as a function of reaction time. However, the virtual injector technique does not *require* the concentration of the reactive species be known as the technique may also be used to perform relative rates measurements. Using the reaction of a gas-phase reference species with a known rate constant to place the particle decay on an absolute scale allows the determination of rate constants or uptake coefficients to be measured. Here, gas phase and heterogeneous relative rates measurements were carried out with photo-generated tropospheric oxidants O_3 , NO_3 , OH and Cl .

4.2. Experimental details

4.2.1. Flow tube reactions

A diagram of the apparatus is shown in Figure 4.1 and consists of a 1-m long glass flow-tube (2" i.d.) in which gas-phase and particle species react with photo-generated reactive species, OH, Cl, NO₃ or O₃ at atmospheric pressure and temperature in the presence of 20% O₂. The flow tube is coupled to an Aerosol Chemical Ionization Mass Spectrometer (CIMS)⁸ which is able to detect both gas and particle phase species as they exit the virtual injector apparatus. The flow tube eluent is sampled into the ion tube region through a stainless steel orifice (0.5 mm i.d.) in a heated (230-240 °C) stainless steel vaporizer tube (1/4 inch o.d., 4 inches long). The flow containing either gas phase species and/or vaporized aerosol species then enters a heated (160 °C) stainless steel ion tube (1/2 inch o.d., 8 inches long, 40 Torr) of the CIMS instrument where it mixed with a 2 slpm flow of N₂ containing reagent ions generated from a radioactive ²¹⁰Po source (NRD).

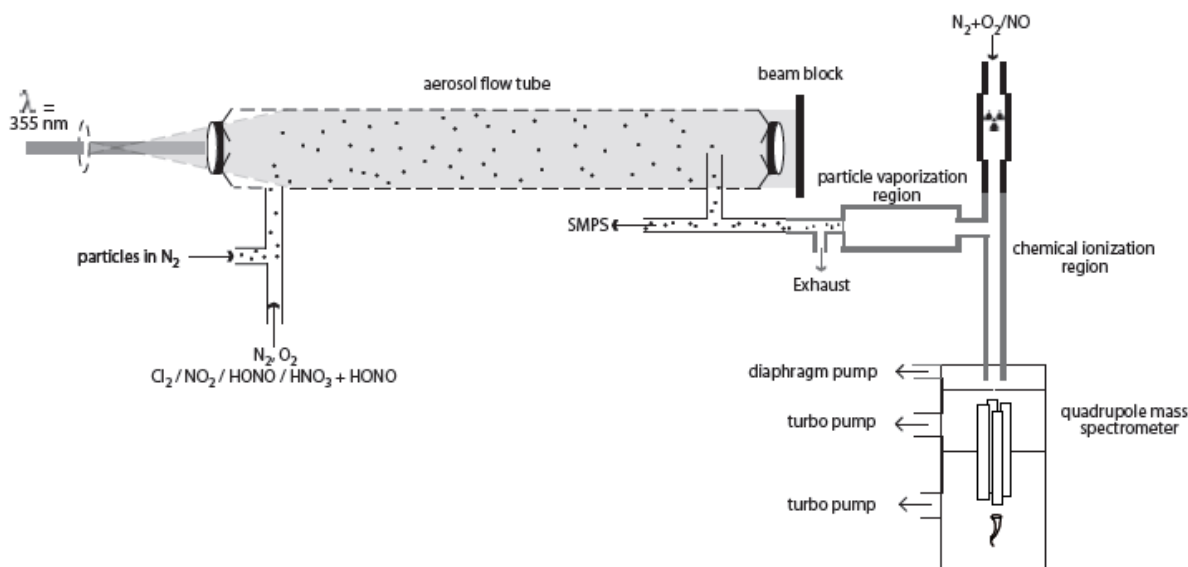


Figure 4.1. Diagram of apparatus used in these studies. Reactions are carried out in the flow-tube and gases and particles are sampled by an Aerosol CIMS as they exit the flow tube.

The Cl, NO₃, O₃, and OH were created by photolysis of a precursor species using radiation from the third-harmonic (355 nm) of a 10-Hz Nd:YAG laser (Quanta-Ray PRO-250) which is expanded to fill the 2"-inner diameter of the flow-tube using a ~6 cm focal length lens. The photodissociation reactions used to generate the different radicals and O₃ are summarized in Table 4.1.

Chlorine and NO₂ were introduced to the flow-tube from lecture bottles of the gases diluted in N₂ and HCl and HNO₃ were introduced into a trap containing free-flowing NaNO₂ through a small bubbler. The HONO that was used for the creation of OH radicals was generated by flowing HCl vapor from a 30% HCl solution through a trap containing free-flowing NaNO₂. Due to the high water content of the HCl solution, an ice bath was used to decrease the vapor pressure of water relative to HCl in order to keep the NaNO₂ as dry as possible. In order to generate NO₃ radicals from HONO, HNO₃ rather than HCl was used to generate OH. The total gas flow was typically 1.2-1.8 SLPM (standard liters per minute) and contained 20% O₂ in order to best represent atmospheric conditions. While in actuality there exists a distribution of flow velocities which vary with radial position in the flow tube, the Aerosol CIMS takes a sample of the entire flow which is representative of the average flow velocity within the flow tube. It is assumed, therefore that the reaction time is determined by the bulk flow velocity which was typically 1.0-1.5 cm/second, corresponding to a residence time of 66-100 seconds.

Table 4.1. Reactions used for the photo- generation of OH, Cl, NO₃, and O₃ in these studies where a 355 nm pulsed laser was used to photodissociate a precursor species with a given cross section.

Generated reactive species	Reaction(s)	Cross section of photo-reactive species @ 355 nm (cm ² /molecule) ^(ref)
OH	HCl + NaNO ₂ → HONO + NaCl HONO + hν → OH + NO	3 x 10 ⁻¹⁹ (9, 10)
Cl	Cl ₂ + hν → 2 Cl	1.6 x 10 ⁻¹⁹ (11)
NO ₃	HNO ₃ + NaNO ₂ → HONO + NaNO ₃ HONO + hν → OH + NO OH + HNO ₃ → NO ₃ + H ₂ O	3 x 10 ⁻¹⁹ (9, 10)
O ₃	NO ₂ + hν → O + NO O + O ₂ → O ₃	4.9 x 10 ⁻¹⁹ (12, 13)

By photo-generating the reactive gas phase species, an effectively uniform concentration of the gas phase reactive species is generated immediately upon introduction of the light source thus initiating reactions throughout the volume of the entire flow-tube. The gas flow through the flow tube then moves the particles or other gas phase reactant through this uniform concentration of reactive species. In this way, the gas-phase acts as a “virtual injector” and particle species react with the photo-generated reactive species for continuously increasing time as the flow travels down the flow tube. The gas and particle phase species which are nearest the outlet of the continuous flow flow-tube when the laser is introduced will experience the shortest reaction times while those near the inlet to the reaction flow-tube will experience the longest reaction times.

In the virtual injector approach described here, a laminar flow flow-tube with a 1” radius is used and diffusion at atmospheric pressure is too slow to allow complete mixing in the radial dimension and the laminar flow limits mixing due to turbulence. However, since the reactive species are regenerated at every pulse of the laser (every 100 msec) throughout the flow-tube in both the radial and axial dimensions, there are minimal concentration gradients

established for the photo-generated species. Reactive species precursors, gas phase reactants (including gas phase reference compounds and gas phase species whose rate constants are to be measured) and particles are well mixed prior to entering the flow-tube so when the reactive gas is generated, the gases and particles within the flow-tube are exposed to the same reactive species concentration. Although the virtual injector approach may be used to obtain absolute rate constant data, addition of a gas phase reference species for which the rate constant with the reactive species is known allows any spatial variation in the concentration of gas-phase reactive species to be accounted for.

4.2.2. Chemical ionization

Gas-phase and particle species were ionized through proton-transfer reactions using $\text{H}^+(\text{H}_2\text{O})_n$ ($n=2,3$) reagent ions generated by flowing N_2 through the ^{210}Po ionizer during Cl and O_3 initiated reactions. When HONO was present (in the generation of NO_3 and OH) the NO^+ reagent ion was predominant and resulted in hydride abstraction and NO^+ adduct formation of gas and particle phase species. In this case, a trace amount of NO with N_2 through the ^{210}Po ionizer was added to ensure that during photolysis, when $[\text{HONO}]$ changed, the ionization chemistry remained constant, with the generation of $[\text{M-H}]^+$ and $[\text{M+NO}]^+$.

4.2.3. Particle generation and characterization

Oleic acid particles were generated through homogeneous nucleation by flowing 0.9 slpm (standard liters per minute) of N_2 through a reservoir containing oleic acid and heated to $\sim 130^\circ\text{C}$ using a temperature controller. For olive oil particle generation, higher reservoir temperatures ($\sim 200^\circ\text{C}$) were used in order to obtain sufficient mass spectral signal of

multiple components. The oleic acid or olive oil aerosol was then reheated as it flowed through a heated section of 1/2 inch o.d. glass tubing to narrow the distribution of particle sizes. The reheater temperatures used for the generation of each particle type were approximately the same for each particle type and ranged from 140-150 °C. After they exited this stage the particles cooled to room temperature before entering the flow tube.

4.2.4. Chemicals

Gas-phase organic species were taken directly from the bottle with no further purification and were introduced either from a lecture bottle containing a mixture in N₂ or by placing a small drop on an o-ring at an inlet to the flow-tube. Aerosols were generated through homogeneous nucleation of heated vapors as described above. The following chemicals were purchased from Sigma-Aldrich: butanal (99%), α -pinene (99+%), β -pinene (99+%), isoprene (99%), 2-methyl-2-butene ($\geq 95\%$), 2,4-hexadienal (95%), 1-octene (98%), methacrolein (95%), cyclohexene (99%), 2,3-dimethyl-2-butene (98%), acetone ($\geq 99.5\%$), acetone-d₆ (99.9% atom D), free-flowing sodium nitrite (99.5%), acetone-¹³C (CH₃¹³COCH₃) (99% atom ¹³C) and HNO₃ (70%). Formation of the partially deuterated acetone species occurred over time in a lecture bottle or was the H-D exchange was catalyzed by addition of a small drop of HNO₃ to the acetone-d₆ liquid. D-limonene ($\geq 96\%$), and oleic acid (>99%) were purchased from Fluka. Squalene (99+%) was purchased from Acros Organics. HCl (36.5-38.0%) was purchased from J.T. Baker. Cl₂ gas (high purity) and N₂ gas (from a liquid N₂ dewar), and O₂ (industrial grade) were purchased from National Specialty Gases. Colavita extra virgin cold pressed olive oil was used for the complex particle studies.

4.3. Results

4.3.1. Measurement of gas and heterogeneous relative rates

In a typical experiment, the fractional losses of a gas-phase reference species and a gas-phase or particle species are monitored from the corresponding peak areas in the mass spectra during reaction. Example experiments are shown in Figure 4.2a-b in which isoprene ($m/z = 98$ amu) and α -pinene ($m/z = 166$ amu) react with OH generated when the 355 nm radiation is introduced in a gas-phase relative rates experiment and 3-hexanone (m/z 130) and oleic acid (m/z 312) particles react with OH generated when the 355 nm radiation is introduced in a heterogeneous relative rates experiment. The behaviors of the two corresponding signals illustrate several important aspects of the virtual injector approach.

First, the fact that the signals decrease as soon as the radiation is introduced and continue to decay for the entire 66-second residence time in the flow-tube as calculated from the bulk linear flow velocity ($100 \text{ cm}/66 \text{ sec} = 1.5 \text{ cm/sec}$) confirms that the gases or particles near the exit of the flow-tube are reacting with OH as are the gases or particles near the entrance of the flow-tube. If OH were not created near the exit of the flow-tube, for example if the radiation was attenuated significantly by the HONO precursor, a delay in the onset of the decay would be expected. Secondly, the decays are nearly exponential indicating that the reactions are practically pseudo-first order with a nearly-uniform OH concentration throughout the entire length of the flow-tube. Exponential decay fits to the time decays of isoprene and α -pinene in Figure 4.2a, for example, yield R^2 values of 0.999 and 0.993, respectively. Lastly, the recovery of the signals when the radiation is removed also provides useful kinetic data since it represents the reverse of the time decay experiment in which the

reaction time is continuously decreased. This is comparable to pushing the injector further into the flow-tube during analogous manual movable injector techniques.

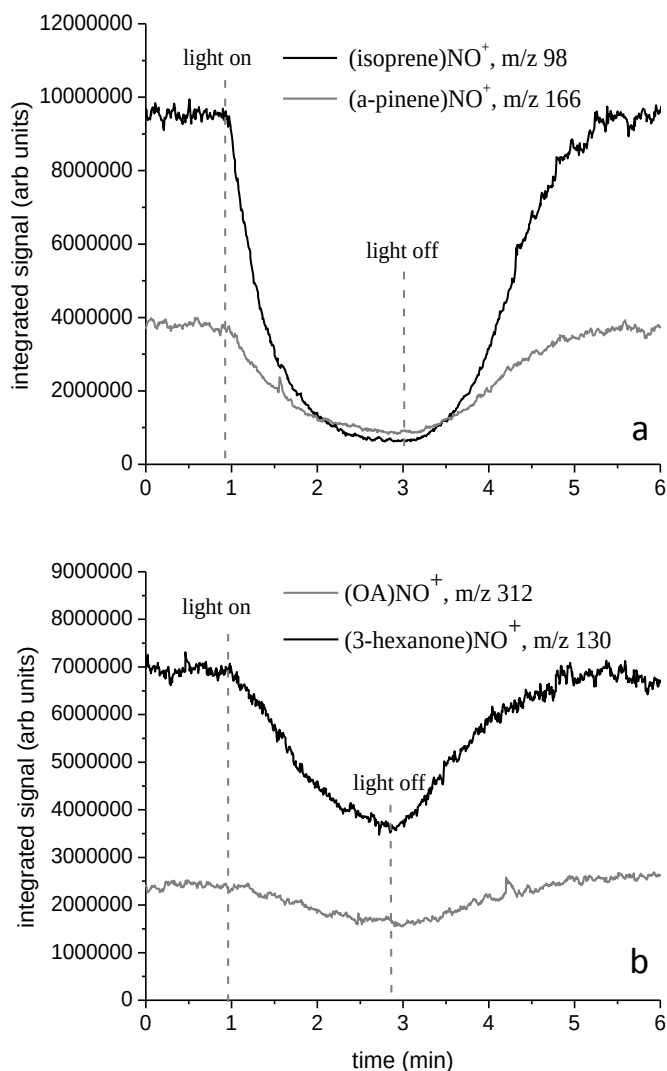


Figure 4.2 Time profile of integrated signals of **(a)** isoprene and α - pinene **(b)** 3-hexanone and oleic acid particles before, during and after reaction with OH.

4.3.2. Gas-phase relative rates measurements

In the virtual injector technique, the concentration of reactive species (radical or ozone) is more or less uniform throughout the volume of the flow-tube when the radiation is

introduced and the decay of gas and particle phase reactants occur as a function of the time that the reactant has been exposed to the reactive species. In theory, the virtual injector technique may be used to determine absolute gas-phase and heterogeneous rate coefficients by observing the time decay of the gas or particle phase reactant with a known reactive species concentration. An often simpler approach to obtaining bimolecular rate constants involves the well-established relative rates approach whereby the simultaneous decays of a reference species and the species whose rate constant is of interest are measured and the measured rate constant, k_X is determined by:¹⁴

$$-\ln\left(\frac{[X]}{[X]_o}\right) = -\frac{k_X}{k_R} \ln\left(\frac{[R]}{[R]_o}\right) \quad 4-1$$

where $[X]/[X]_o$ is the fraction of the gas-phase reactive species being measured remaining after a given amount of reaction time, $[R]/[R]_o$ is the fraction of the gas-phase reference species remaining after the same elapsed time, and k_X and k_R are the rate constants for the measured and reference reactions with the photo-generated reactive species (OH, Cl, NO₃ or O₃). Thus, from the slope of a ln-ln plot of the fraction of each species reacted, the ratio of rate constants can be obtained, and using an established gas-phase reference rate constant from the literature, k_R , k_X can be calculated. An example of this type of plot is shown in Figure 4.3 for the reaction of α -pinene and the gas-phase reference isoprene with OH where the slope of the fit and thus the ratio of the rate constants was 0.534. From repeat measurements, an average slope of 0.538 is calculated and with knowledge of the OH + isoprene rate constant determined in previous studies ($k_R = 1.00 (\pm 0.15) \times 10^{-10} \text{ cm}^3/\text{molecule}/\text{sec}$.¹⁵), the rate constant for OH + α -pinene is determined to be $5.38 (\pm 0.30) \times 10^{-11} \text{ cm}^3/\text{molecule}/\text{sec}$ where the error bars represent the uncertainty in the measurement of

the slope ($2\sigma = 0.014$) with the propagated uncertainty in the rate constant for the reference reaction. The measured rate constant for OH + α -pinene is in good agreement with the value of $5.3 \times 10^{-11} \text{ cm}^3/\text{molecule}/\text{sec.}$ recommended by the IUPAC Subcommittee on Gas Kinetic Data Evaluation at 298 K.¹⁶

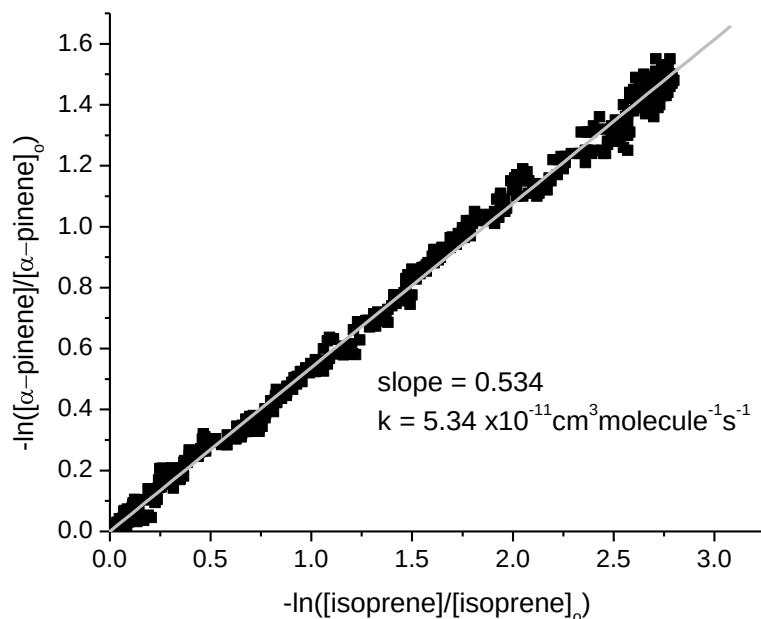


Figure 4.3. Example of ln-ln plot used to fit gas phase relative rates data. Shown are α -pinene and isoprene. The measured rate constant is determined by $k = \text{slope} \cdot (k_{\text{ref}})$

As a validation of the virtual injector approach to studying relative rates kinetics, the rate constants for reactions of several gas-phase organic species with O_3 , NO_3 , OH and Cl were measured using various reference species (see Table 4.2). The measured rate constants are shown in Figure 4.4 plotted vs. values taken from the literature demonstrating very good agreement for most species spanning a range of more than five orders of magnitude. As with any relative rates measurements, the uncertainty in the measured rate constant is limited by the accuracy of the published rate constants of the reference species. The notable exceptions

to the good agreement are the rate constants for the reactions of OH with methacrolein and 1-octene which are ~30% lower than the literature values, from the IUPAC Subcommittee on Gas Kinetic Data Evaluation¹⁶ and McGillen et al.¹⁷, respectively. The reason for the discrepancy in these measurements remains unresolved, but given the good agreement in all of the other measurements they do not appear to invalidate the virtual injector approach.

Table 4.2. Gas phase relative rates results with reference rate constants (k_{ref}), literature rate constants (k_{lit}), and measured rate constants ($k \pm 2\sigma$) as well as the absolute error of the measured rate constant including the error on the reference rate constant. References, where applicable are given as left superscripts

Reactive Species	Reactant	Reference	k_{ref} (cm ³ /molecule/sec.)	k_{lit} (cm ³ /molecule/sec.)	$k (\pm 2\sigma)$ (cm ³ /molecule/sec.)	Absolute error of relative rates measurement
OH	butanal	naphthalene	¹⁸ 2.59 (± 0.24) $\times 10^{-11}$	¹⁹ 2.38 (± 0.15) $\times 10^{-11}$	2.41(± 0.32) $\times 10^{-11}$	(± 0.39) $\times 10^{-11}$
	2,4-hexadienal	isoprene	¹⁵ 1.00 (± 0.15) $\times 10^{-10}$	N/A	5.90 (± 0.18) $\times 10^{-11}$	(± 0.90) $\times 10^{-11}$
	2,4-hexadienal	α -pinene	²⁰ 5.45 (± 0.32) $\times 10^{-11}$	N/A	5.97 (± 0.26) $\times 10^{-11}$	(± 0.44) $\times 10^{-11}$
	1-octene	α -pinene	²⁰ 5.45 (± 0.32) $\times 10^{-11}$	¹⁷ 3.62 (± 0.68) $\times 10^{-11}$	2.62 (± 0.34) $\times 10^{-11}$	(± 0.38) $\times 10^{-11}$
	2-methyl-2-butene	α -pinene	²⁰ 5.45 (± 0.32) $\times 10^{-11}$	²¹ 8.67 (± 0.35) $\times 10^{-11}$	9.08 (± 0.58) $\times 10^{-11}$	(± 0.79) $\times 10^{-11}$
	methacrolein	α -pinene	²⁰ 5.45 (± 0.32) $\times 10^{-11}$	¹⁶ 2.90 (± 0.75) $\times 10^{-11}$	1.99 (± 0.25) $\times 10^{-11}$	(± 0.28) $\times 10^{-11}$
	α -pinene	isoprene	¹⁵ 1.00 (± 0.15) $\times 10^{-10}$	²⁰ 5.45 (± 0.32) $\times 10^{-11}$	5.38 (± 0.14) $\times 10^{-11}$	(± 0.82) $\times 10^{-11}$
	β -pinene	isoprene	¹⁵ 1.00 (± 0.15) $\times 10^{-10}$	²⁰ 7.95 (± 0.52) $\times 10^{-11}$	8.01 (± 0.97) $\times 10^{-11}$	(± 1.5) $\times 10^{-11}$
	D-limonene	isoprene	¹⁵ 1.00 (± 0.15) $\times 10^{-10}$	²⁰ 1.69 (± 0.5) $\times 10^{-10}$	1.67 (± 0.05) $\times 10^{-10}$	(± 0.26) $\times 10^{-10}$
Cl	α -pinene	isoprene	²² 4.6 (± 0.5) $\times 10^{-10}$	²³ 5.3 (± 0.1) $\times 10^{-10}$	4.7 (± 0.04) $\times 10^{-10}$	(± 0.5) $\times 10^{-10}$
	β -pinene	isoprene	²² 4.6 (± 0.5) $\times 10^{-10}$	²⁴ 5.3 (± 1.5) $\times 10^{-10}$	3.8 (± 0.4) $\times 10^{-10}$	(± 0.6) $\times 10^{-10}$
	D-limonene	isoprene	²² 4.6 (± 0.5) $\times 10^{-10}$	²⁴ 6.4 (± 0.8) $\times 10^{-10}$	5.9 (± 0.1) $\times 10^{-10}$	(± 0.6) $\times 10^{-10}$
	acetone-d1	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	N/A	1.83 (± 0.04) $\times 10^{-12}$	(± 0.28) $\times 10^{-12}$
	acetone-d3	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	N/A	1.13 (± 0.04) $\times 10^{-12}$	(± 0.17) $\times 10^{-12}$
	acetone-d4	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	N/A	8.69 (± 0.38) $\times 10^{-13}$	(± 1.4) $\times 10^{-13}$
	acetone-d5	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	N/A	5.74 (± 0.54) $\times 10^{-13}$	(± 1.0) $\times 10^{-13}$
	acetone-d6	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	²⁶ 3.94 (± 0.25) $\times 10^{-13}$	3.93 (± 0.35) $\times 10^{-13}$	(± 0.71) $\times 10^{-13}$
	acetone-C13	acetone	²⁵ 2.07 (± 0.31) $\times 10^{-12}$	N/A	2.10 (± 0.04) $\times 10^{-12}$	(± 0.31) $\times 10^{-12}$
	CD ₃ OH	methanol	²⁷ 5.6 (± 0.2) $\times 10^{-11}$	N/A	3.8 (± 0.3) $\times 10^{-11}$	(± 0.3) $\times 10^{-11}$
	butyraldehyde	n-propanol	²⁸ 1.53 (± 0.13) $\times 10^{-10}$	²⁹ 1.43 (± 0.17) $\times 10^{-10}$	1.44 (± 0.04) $\times 10^{-10}$	(± 0.13) $\times 10^{-10}$
O₃	cyclopentene	2,3-dimethyl-2-butene	³⁰ 1.0 (± 0.2) $\times 10^{-15}$	³¹ 6.55 (± 0.43) $\times 10^{-16}$	6.0 (± 0.20) $\times 10^{-16}$	(± 1) $\times 10^{-16}$
	bicyclo (2.2.1)hept-2-ene	2,3-dimethyl-2-butene	³⁰ 1.0 (± 0.2) $\times 10^{-15}$	³² 1.55 (± 0.55) $\times 10^{-15}$	1.4 (± 0.08) $\times 10^{-15}$	(± 0.3) $\times 10^{-15}$
NO₃	cycloheptene	isoprene	³³ 7.3 (± 0.9) $\times 10^{-13}$	³⁴ 4.94 (± 0.20) $\times 10^{-13}$	5.3 (± 0.53) $\times 10^{-13}$	(± 0.22) $\times 10^{-13}$
	1-octene	1-hexene	³⁵ 1.85 (± 0.66) $\times 10^{-14}$	³⁶ 2.35 (± 0.15) $\times 10^{-14}$	2.25 (± 0.09) $\times 10^{-14}$	(± 0.81) $\times 10^{-14}$

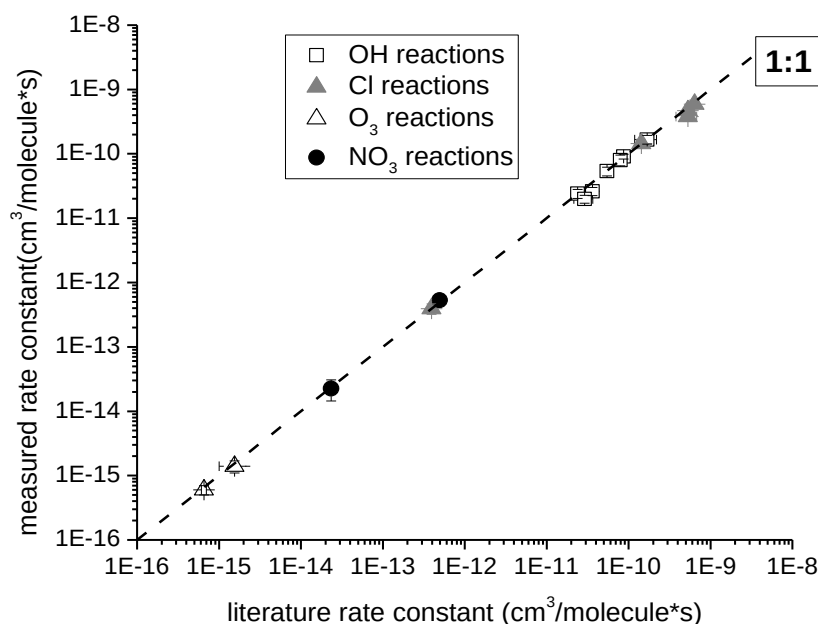


Figure 4.4. Measured versus literature rate constants for gas phase relative rates experiments performed with OH, Cl, NO₃ and O₃. Also shown is the 1:1 line.

Since the reactions are carried out under nearly-pseudo-first-order conditions where a steady-state of O₃ or radical species is maintained, the kinetics are measured by following the losses of the other gas-phase reactants, thus allowing the simultaneous measurement of the rates of reaction of multiple species with the reactive species. As a demonstration of the usefulness of this aspect of the approach, the rates of reaction of Cl radicals with a mixture of acetone and the various deuterated isotopologues of acetone, acetone-d1 – acetone-d6, were measured simultaneously. The Cl + acetone reaction was used as the reference reaction since its rate constant is well known ($k = 2.07 \times 10^{-12} \text{ cm}^3/\text{molecule}/\text{sec}^{25}$). The rate constant for the acetone-d2 + Cl reaction could not be measured because of a product of the acetone + Cl reaction appeared at the same m/z as acetone-d2 ($m/z = 90$). Figure 4.4 a-b displays the time decays and ln-ln plot for each of the deuterated isotopologues for one such measurement and

the results of repeat measurements are given in Table 4.2. For acetone d-1 through d-5, there are no values for these rate constants in the literature to which to compare, but Wine and co-workers measured the rate constant for the Cl + acetone-d6 reaction (personal communication) to be $3.94 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec}$. using an absolute method (resonance fluorescence detection of Cl radicals), in very good agreement with the value measured in this work, $k = 3.93 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec}$.

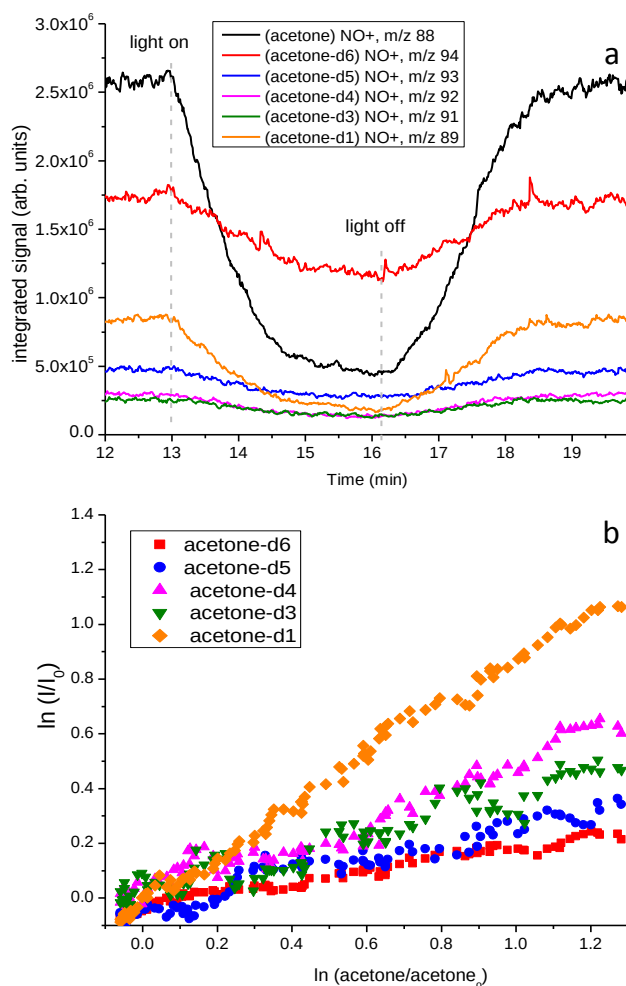


Figure 4.5. (a) Time decay and recovery of acetone and five of its six deuterium isotopologues upon introduction and removal of 355 nm radiation. (b) ln-ln plot of all acetone deuterium isotopologues.

A linear decrease in the rate constant is observed for increasing number of deuterium atoms. Because deuterium atoms are heavier than hydrogen, the vibrational frequency of the C-D bonds is lower than those of C-H bonds and the zero-point energy barrier for D abstraction is greater than H abstraction. This greater energy barrier is reflected in the kinetics of the abstraction reactions where D-abstraction is slower than H-abstraction. The measured kinetic isotope effect ($k_H/k_D = 5.4$) is also similar to values reported for the OH + acetone/acetone-d6 reaction (5.3³⁷, 5.1³⁸, 5.9³⁹, and 6.0⁴⁰ at 298 K). The fact that these acetone isotopologue rate constants span a range from $4 - 20 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec.}$ may make them useful as reference species for measuring the kinetics of slower Cl reactions including those with aerosol particles for which effective rate constants are generally $10^{-12} \text{ cm}^3/\text{molecule}/\text{sec.}$ and smaller.

4.3.3. Aerosol reactive uptake measurements

Reactive uptake by single-component particles

It was shown, above, that the virtual injector approach provides accurate gas phase relative rates data over a wide range of rate constants from relatively slow ($\sim 10^{-16} \text{ cm}^3/\text{molecule}/\text{sec.}$) reactions in the case of O_3 to fairly fast ($\sim 10^{-10} \text{ cm}^3/\text{molecule}/\text{sec.}$) reactions in the case of Cl. It is also possible to measure the rate of reaction of particle-phase species relative to a gas-phase reference reaction with the virtual injector approach using the same basic concepts as described above for gas-gas relative rates. However, the effective rate constant, k_X , obtained from the observed loss of the *particle* species depends on factors surface area to volume ratio of the particles. In heterogeneous relative rates experiments, therefore, it is often more suitable to express the efficiency of a reaction in terms of a reactive uptake coefficient, γ . This uptake coefficient is unitless and represents the fraction of gas-

particle collisions that results in reactive loss. The *effective* uptake coefficient can be calculated from the measured fractional rate of loss of the particle species, X:⁴¹

$$\gamma_{\text{part}} = \left[\frac{d([X]/[X_o])}{dt} \right] \frac{1}{[Y]} \frac{4RT}{\bar{c}} \frac{V}{S_A} [X_o] \quad 4-2$$

where [Y] is the concentration of the gas-phase reactive species, R is the gas constant, T is the temperature, $\bar{c}$ is the mean speed of the gas-phase reactant and V/S_A is the volume-to-surface-area ratio of the particles. In the virtual injector approach, the concentration of gas phase reactive species is in a steady state and [Y] may be separated from the denominator of the term in brackets. The effective reactive uptake coefficient calculated from equation 4-2 will differ from the reactive uptake coefficient calculated from the rate of loss of the gas-phase species if there are other reactions that occur in the particle phase but not the gas phase. For instance, in the case of oleic acid + O₃, the Criegee radical formed in the particle phase may react with a second oleic acid molecule, leading to a secondary loss mechanism and increasing the rate of loss of oleic acid with respect to the gas phase reference that was exposed to the same amount of O₃.

As evident from equation 4-2, in order to obtain an absolute measure of the heterogeneous kinetics, the fractional rate of loss of X needs to be measured which requires an explicit knowledge of [X]/[X]_o as a function of reaction time. Additionally, the absolute concentration of the gas-phase reactant, Y (O₃, NO₃, OH or Cl in the present experiments), must be known since the gas-particle collision rate is dependent on this concentration. Absolute rate measurements are, in theory, feasible with the virtual injector approach; however, in making mixed-phase relative rates measurements, it is not necessary to know the reaction time or the reactive gas concentration explicitly.⁴¹ The observed rate of loss of the

gas-phase reference species, R, serves as an in situ measure of the integrated product of reactive species concentration and reaction time.

To demonstrate the ability to measure reactive uptake coefficients with the virtual injector approach, the reactions of oleic acid particles with OH, Cl, NO₃ and O₃ were studied (see Table 4.3). Oleic acid is an optimal species with which to validate this approach for measuring heterogeneous kinetics because it forms spherical liquid particles such that the surface-area-to-volume ratio is well defined, it has a low vapor pressure such that the particles don't evaporate, and the heterogeneous reactions with O₃ and NO₃ have been studied previously.

Table 4.3. Oleic acid uptake coefficients. Error bars represent 2 σ .

Reactive Species	$\gamma_{\text{part}} (\pm 2\sigma)$ (measured)	γ (literature) ^(ref)	Gas-phase Reference ^(ref)
O ₃	$(8.1 \pm 0.9) \times 10^{-4}$	$1.38 (\pm 0.06) \times 10^{-3}$ ⁽⁴²⁾	Bicyclo(2,2,1)-2-heptene ^(31, 43)
NO ₃	0.14 ± 0.03	$0.18 (\pm 0.82/-0.11)$ ⁽⁴⁴⁾	Isoprene ⁽⁴³⁾
OH	0.40 ± 0.03	N/A	3-hexanone ⁽⁴⁵⁾
Cl	1.23 ± 0.16	N/A	Methanol ^(16, 43)

The effective uptake coefficient measured for reaction with O₃, $\gamma_{\text{part}} = (8.1 \pm 0.9) \times 10^{-4}$, is smaller than the value of $1.38 (\pm 0.06) \times 10^{-3}$ reported previously, indicating a slower reaction of O₃ with particle phase oleic acid in the present experiments.⁴² This difference could arise if the rate constant used for the gas-phase reference (bicyclo(2,2,1)-2-heptene) in the present experiments is incorrect. There have been only two reports of the rate constant for the reaction of bicyclo(2,2,1)-2-heptene with O₃ to my knowledge.^{32, 46} For the reference rate constant, the value recommended by an author of those papers was that measured in Ref. ³², discounting the earlier results in Ref. ⁴⁶. If the earlier rate constant value is used, the resulting effective reactive uptake coefficient is $\gamma_{\text{part}} = 1.1 \times 10^{-3}$, much closer to the

previously reported values. However, use of the virtual injector approach to measure the rate constant of bicyclo(2,2,1)-2-heptene shows very good agreement (see Table 4.2) with the value that was recommended by Atkinson and Arey⁴³ and with Ref. ⁴⁶ making the choice of rate constant an unlikely source of error. Alternatively, it is possible that either the OH scavenger (cyclohexane) or one of the OH oxidation products of the scavenger (such as cyclohexanol) was present in such quantities that considerable surface concentrations of these species existed and were able to effectively block reaction sites of O₃ on the oleic acid particles. Using proton transfer ionization, we are “blind” to cyclohexane and thus the concentration of the scavenger is unknown. We are able to observe cyclohexanol in the mass spectrum during reaction but are unaware of the detection sensitivity to this species. It is feasible, therefore that very high concentrations of OH scavenger and OH + scavenger reaction products were present and these species may partition to the particle surface. The O₃ + oleic acid uptake experiments were performed at various scavenger concentrations (varied by adjusting the flow from a mixture in a lecture bottle) and a maximum in the reactive uptake was observed before the reactive uptake began to decrease with increasing scavenger concentration. Although absolute scavenger concentrations were unknown, this provides indirect evidence for scavenger adsorption to the particle surface as there are no other known mechanisms by which the scavenger may affect the reactive uptake of O₃ onto the particle surface. The NO₃ effective uptake coefficient measured here, $\gamma_{\text{part}} = 0.14 (\pm 0.03)$, is consistent with the only other study to have measured it in which γ is reported to be 0.18 (+0.82/-0.11) at room temperature.⁴⁴

Although the uptake coefficients of OH ($\gamma_{\text{part}} = 0.40 \pm 0.03$) and Cl ($\gamma_{\text{part}} = 1.23 \pm 0.17$) with oleic acid have not been reported previously, the values measured here are consistent

with efficient uptake of these radicals on other organic particles. For example, uptake coefficients of 0.51⁴⁷ and 0.3⁴⁸ and 0.56⁴⁹ have been reported for reaction of OH with squalane particles. Likewise, very efficient reactions have been reported for the reaction of OH and Cl with dioctyl sebacate particles with reactive uptake coefficients greater than unity.^{41, 50, 51}

Reactions of complex, multicomponent particles.

Because the effective reactive uptake kinetics are derived from the observed loss of the particle species rather than the loss of the gas phase reactive species, it is also possible to measure the rates of reaction of several different particle species simultaneously. Comparison of the relative rates of reaction of individual species in homogeneously mixed particles and measurement of the reaction rate constants of these species may provide valuable information about the importance of particle complexity in heterogeneous reaction kinetics as well as information on the reaction rates of molecular markers with tropospheric oxidants.

Commonly in source apportionment studies, concentrations of molecular markers in ambient aerosol are used to trace tropospheric aerosols back to their sources. For instance, levoglucosan is commonly used as a molecular marker for biomass burning (especially wood smoke) aerosols⁵²⁻⁵⁴ and palmitoleic acid, oleic acid, and cholesterol may be used as molecular markers for food cooking emissions⁵⁵⁻⁵⁸. It is assumed in these source apportionment studies that significant reactive loss of these molecular marker species does not occur over their transport time in the troposphere. However, many studies suggest that the reactive loss of these species may be important under atmospheric conditions. For example, Hennigan et al.⁵⁹ report an effective rate constant for levoglucosan + OH of 1.1

$\times 10^{-11}$ cm³/molecule/sec., corresponding to a reactive tropospheric lifetime (with 10^6 OH radicals/cm³) of 25 hours. Likewise, using the effective reactive uptake coefficient of OH on oleic acid measured herein and reported in Table 4.3, an effective rate constant for 100 nm oleic acid particles with OH is 2.4×10^{-12} cm³/molecule/sec, corresponding to a reactive lifetime of 117 hrs. Other researchers have also demonstrated significant reactive transformation of particle phase molecular markers for motor vehicle emissions.^{60, 61} It is not clear, however, how the particle complexity may affect the effective rate constants of the particle species with different oxidants and whether effective rate constants determined from pure particle oxidation studies may be applied to complex aerosols, such as those in the troposphere.

As a demonstration of the usefulness of the virtual injector approach for measuring uptake kinetics of mixed particles, reactions of olive oil aerosol with O₃, NO₃, OH and Cl were carried out. Olive oil was chosen because it is a liquid at room temperature forming spherical particles, and though it is chemically complex it is known to contain large amounts of oleic acid and squalene⁶²⁻⁶⁴ which appear at $m/z = 283$ and $m/z = 411$, respectively, in the proton transfer mass spectrum (Figure 4.6). The rates of loss of these species as well as of an unknown component represented by peaks at $m/z = 397$ (with proton-transfer ionization) and $m/z = 426$ (with NO⁺ adduct ionization) were measured with all four reactive species. Either proton transfer or NO⁺ ionization was used depending on the reactive species being generated (see Section 4.2.1).

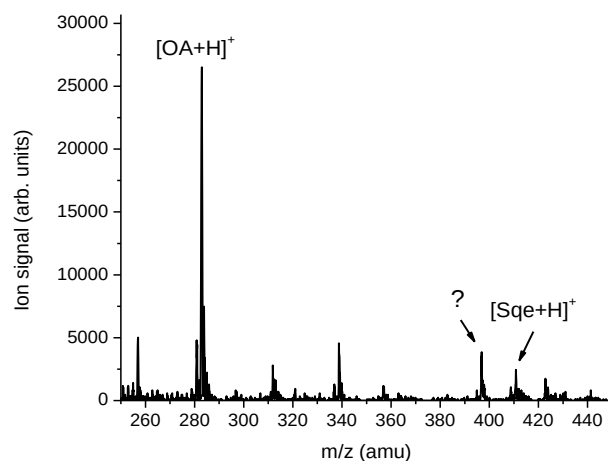


Figure 4.6. Proton transfer mass spectrum of olive oil showing oleic acid and Squalene (Sqe), as well as the peak of unknown identity, that were studied using all 4 reactive species (OH, Cl, NO₃ and O₃)

Figure 4.7 shows representative reactive decays for the three olive oil constituents with NO₃ radicals as a function of the NO₃ exposure as measured from the observed loss of the gas-phase reference, isoprene. From the initial slopes of the decays, effective bimolecular rate constants, k_X , are derived based the reference rate constant recommendation by the IUPAC Subcommittee on Gas Kinetic Data Evaluation ($k_R = 7.0 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec.}$)⁶⁵. A reactive uptake coefficient for each of the species cannot be calculated from the values of k_X using equation 4-2 because their absolute concentrations in the olive oil particles are unknown. However, the effective rate constants can be used to compare the reactivity of the different components even though the exact composition of the particle is unknown. Effective rate constants for reactions of the three constituents with all four of the reactive species, O₃, NO₃, OH and Cl, are listed in Table 4.4. Since the effective rate constants measured in this way are functions of the particle surface-area-to-volume ratio,

and therefore of particle size, the rate constants in Table 4.4. have been normalized to a particle size of 100 nm for intercomparison.

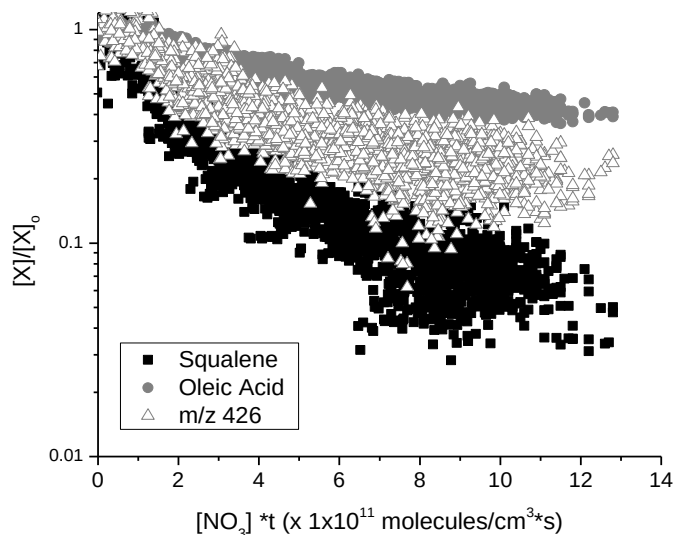


Figure 4.7. Exposure decay of three major olive oil components, Squalene, Oleic Acid and an unknown compound at m/z 426 in the NO^+ ionization mass spectrum.

Table 4.4. Effective rate constants for olive oil constituents (normalized to particle diameter =100 nm)

Reactive Species	Oleic Acid ($\text{cm}^3/\text{molec/s}$)	Squalene ($\text{cm}^3/\text{molec/s}$)	m/z = 397 or m/z = 426 ($\text{cm}^3/\text{molec/s}$)	Gas-phase Reference
O₃	2.1×10^{-15}	5.6×10^{-15}	$< 2.0 \times 10^{-17}$	Bicyclo(2,2,1)-2-heptene
NO₃	1.1×10^{-12}	4.0×10^{-12}	2.3×10^{-12}	isoprene
OH	3.5×10^{-11} (b)	1.1×10^{-10} (a)	2.3×10^{-11} (b)	(a) isoprene (b) butanal
Cl	2.6×10^{-11} (d)	1.2×10^{-10} (c)	1.7×10^{-11} (d)	(c) butanal (d) 2-butanone

From these rate constants it can be concluded that oleic acid and squalene react at similar rates for all of the reactant species with squalene reacting approximately 3-5 times faster than oleic acid. This is not surprising in the case of O_3 reaction where a double bond is required

for reaction to occur since squalene is a polyunsaturated molecule with six double bonds whereas oleic acid contains only one. Although reaction of OH, Cl and NO₃ may occur with species lacking double bonds, the presence of a double bond, in most cases, leads to a faster reaction.⁴³ What is more surprising than the relative reactivity of squalene and oleic acid is that the reactivity of oleic acid in the olive oil particles cannot be predicted from the rates of reaction in the pure oleic acid (Table 4.3). The effective rate constants measured for oleic acid reacting with OH in pure particles is $k_X = 1.9 \times 10^{-12} \text{ cm}^3/\text{molecule}/\text{sec}$. (derived from an uptake coefficient of $\gamma_{\text{part}} = 0.40$ and assuming a 100 nm particle), and in olive oil particles $k_X = 2.4 \times 10^{-11} \text{ cm}^3/\text{molecule}/\text{sec}$., an increase of more than a factor of 12. The effective reactive uptake coefficient of OH on pure squalene particles has been measured and although the results were widely varied (ranging from $\gamma_{\text{part}} = 2.1$ to $\gamma_{\text{part}} = 4.9$), the average reactive uptake coefficient from many reactions ($\gamma_{\text{part}} = 3.5 \pm 0.9$) corresponds to an effective rate constant of $2.7 \times 10^{-11} \text{ cm}^3/\text{molecule}/\text{sec}$. The effective rate constant of squalene + OH in an olive oil particle, on the other hand, was determined to be $1.1 \times 10^{-10} \text{ cm}^3/\text{molecule}/\text{sec}$, an enhancement of a factor of 4 compared to pure particles. The reason for the enhancements of effective rate constants in complex mixtures compared to pure particles is unknown. Perhaps it is due to the morphology of the complex particles or it may be due to secondary loss mechanisms that occur in complex particles and not pure particles. Similar evidence of enhancement of reactive loss in complex compared to pure particles is found in the literature. In fact, Kessler et al.⁶⁶ determine the reactive lifetime of levoglucosan in pure particles to be 10.6 days in the troposphere with $3 \times 10^6 \text{ OH radicals}/\text{cm}^3$ or 31.8 days with an OH concentration of $1 \times 10^6 \text{ radicals}/\text{cm}^3$. Hennigan et al.⁵⁹ predict the reactive lifetime of levoglucosan in complex biomass burning aerosols to be 0.7-2.2 days in the troposphere with

1×10^6 OH radicals/cm³. Thus, levoglucosan appears to react 14.5 to 45 times faster in complex particles made from biomass burning than levoglucosan in pure particles.

The effective rate constants calculated above for oleic acid and squalene in the olive oil particles were used to predict atmospheric lifetimes of each of the constituents with respect to each of the reactive species. For example, the lifetimes of oleic acid and squalene with respect to O₃ are estimated to be on the order of minutes ([O₃] = 30-200 ppb)⁶⁷. The lifetimes of oleic acid and squalene with respect to NO₃ in a “clean” atmosphere ([NO₃] = 10 ppt)⁶⁷ are on the order of 10 hours and 3 hours, respectively, but may be as short as 5 and 2 minutes in areas of high NO₃ concentrations ([NO₃] = 100 ppt)⁶⁷. These lifetimes suggest that NO₃ and O₃ are important oxidants of these unsaturated hydrocarbons and may suggest that in some cases, NO₃ reactions may out-compete O₃ reactions especially at nighttime when NO₃ concentrations increase and O₃ concentrations diminish. The extent to which NO₃ will be important, however, depends on the relative concentrations of NO₃ and O₃. Consequently, the relative importance of these two oxidants will depend on the atmospheric composition. Nonetheless, to the extent that olive oil is a good surrogate for ambient organic aerosols, these measurements demonstrate that reactions by both O₃ and NO₃ can be important in determining lifetimes of some particle constituents and that these lifetimes may not be accurately described by using the rates of reactions of pure particles.

Finally, an interesting observation was made in the NO₃ + olive oil experiments which could not be predicted from the reactions of pure particles: the reactive decays of all three species (Figure 4.6) deviate from an exponential decay like those observed in all other experiments with both pure particles and olive oil. More specifically, the decay of the particle-phase species slow down at the largest NO₃ exposures which correspond to the

longest reaction times using the virtual injector approach as the radical concentrations are more or less uniform along the length of the flow-tube. The gas-phase reference signal continues to decay exponentially, suggesting that the slowing of the particle-phase species decays at long reaction times is not due to a drop in the NO_3 concentrations. There is some phenomenon, therefore, that is unique to the particle-phase species that occurs when the particles have reacted for longer amounts of time. It is possible that the state of the particles change in some way as to result in a slowing of the reaction of all three species. It is not clear what this change in state is, but it could be that the particles form some sort of glassy solid or highly viscous liquid in which diffusion of NO_3 into the particle or diffusion of “fresh” (unreacted) olive oil components to the surface may be hindered. It is also possible that particles which reacted for the longest times in the flow-tube may have some sort of build-up of products on the particle surface which prevent the NO_3 from diffusing far enough into the particle to react with another oleic acid or squalene molecule. Such an effect has been observed previously in the ozonolysis of mixed oleic acid and n-docosane particles where the slowing of reaction was attributed to the formation of a solid shell near the surface of the particle.⁶⁸ Further experiments will be required to elucidate the nature of this effect and to determine why it is not observed in the reactions of olive oil components with OH and Cl radicals or with O_3 nor in the reactions of any of the reactive species with model, single-component, organic aerosols.

4.4. Discussion

4.4.1. Requirements for virtual injector approach

The virtual injector approach may be used, in theory, to study gas and heterogeneous reaction kinetics in an absolute manner. The time decays of the reactants are nearly perfectly

exponential, with $R^2 > 0.99$, suggesting the reactive species (OH, Cl, NO₃, O₃) concentration is nearly essentially uniform throughout the flow-tube volume. If the steady-state reactive species concentration were known, the exponential time decays of the reactant(s) could be used to obtain absolute rate constant measurements. Thus, measurement of absolute rate constants using the virtual injector technique requires instrumentation capable of detecting the gas or particle phase species of interest as well as instrumentation capable of measuring the absolute concentration of the reactive species. The relative rates approach to the virtual injector experiments eliminates the need for extra instrumentation to measure the reactive species concentration and in doing so also accounts for any small spatial variation in the concentration of reactive species. The relative rates measurements demonstrated here used a pulsed high frequency (10 Hz) laser to initiate reaction and a chemical ionization mass spectrometer to detect gas-phase and particle species. However, other radiation sources and methods of detection could be used and depend on the experimental goals. The basic requirements of the virtual injector approach are discussed below.

Radiation source

It is necessary that the reactive species be generated throughout the entire flow-tube rapidly, on a timescale much shorter than the residence time in the flow-tube. This may be achieved using radiation, as described here with a pulsed high frequency laser. The essential consideration is that the volume of the flow-tube be rapidly filled with radiation so that immediately upon introduction of the radiation, the reactive species may be generated throughout with minimal concentration gradients. Some sort of shutter or manual beam block is needed to allow the light to be introduced to or removed from the flow-tube, and the source fluence must be stable during the reaction time in the flow-tube which is determined,

ultimately, by the bulk flow velocity. The importance of a stable source fluence is to minimize temporal variability in the reactive species concentration. While shot-to-shot variability in the laser fluence may not affect the outcome of the experiments, fluctuations in the fluence on the time scale of even a few seconds may cause temporal fluctuations in the reactive species. The laser intensity from the Nd:YAG laser used herein varies by less than 1% over the course of a few minutes, or the timescale of these experiments. Finally, the source must have sufficient intensity at the wavelength(s) used to photodissociate the precursor efficiently. The intensity required will depend on the specific details of the experiment, including the precursor concentration and cross section, residence time and magnitude of concentration of reactive species required to observe desired reaction(s).

Residence time in reactor

As the contact time is continuously changing in the virtual injector technique, the sampling rate must be faster than the decay rate in order to collect multiple data points as the decay is occurring. The ratio of the contact time to the sampling time will determine how many different contact times can be obtained in a kinetic decay. As a rule of thumb, a minimum of 20 is required to obtain a good fit to the decay function. In the experiments described here, the mass spectrometer software is collecting 2 samples per second, so a residence time of at least 10 seconds is needed. In practice, much longer times are used (60-100 seconds) providing many more data points (120-200) along the time decays of the reactants. Besides the possibility for wall loss of reactants, there is no real limitation to the lowest flows, and thus the longest reaction time which may be used. Although the detector will require some minimal flow, the flow-tube flow can still be lower than this as long as the

flow the detector requires is made up before the sample stream reaches the detector. Thus, the virtual injector technique may be used to study long reaction times.

Detector(s)

For either gas phase or heterogeneous relative rates measurements, an analytical instrument or set of instruments capable of detecting relative changes in concentrations of the gas-phase reference species and the gas-phase or particle reactant(s) is required. When relative rates are measured it is not necessary to be able to detect absolute concentrations of these species. In the present experiments where relative rates measurements are made, one instrument, a chemical ionization mass spectrometer, is used to detect simultaneously all relevant gas-phase and particle species. The use of more than one instrument requires synchronization of the instruments and the slowest sampling rate will determine the minimum flow-tube residence time that is required, to collect multiple data points in the decay. The use of a FTIR, for example, might necessitate a 30 second sampling time which would require a flow-tube residence time of at least 600 seconds for 20 data points along the decay.

For absolute rate constant measurements, an instrument is required that is capable of detecting the gas phase or particle-phase species of interest (more than one instrument may be required if multiple reactants are being measured simultaneously) as well as an instrument for detecting the absolute concentration of reactive species is required. In situ measurements of the reactive species concentration or measurements of reactive species concentrations at very short times after exiting the flow-tube is required because the constant photolysis of the precursor is what is maintaining the constant concentration of reactive species. When the radiation is no longer able to reach the precursor upon exiting the flow-tube, concentrations

of reactive species will drop rapidly. There are very few techniques that may allow in situ reactive species concentrations to be determined. For OH quantification, laser-induced fluorescence (LIF)^{69, 70} may be used in situ if the excitation and fluorescence wavelengths do not coincide with the photolysis wavelength. Ozone concentrations may be determined nearly in situ by positioning a UV absorption cell at the flow-tube output. Likely a negligible concentration drop in ozone would occur in the short time the sample flow would travel upon exiting the flow-tube and entering the absorption cell. As one can see, although it is feasible to perform absolute rate constant measurements with the virtual injector, the relative ease of the relative rates approach overcomes many of the limitations of absolute measurements by not requiring the reactive species concentration to be known.

Minimal radiation and precursor depletion

As discussed above, the virtual injector approach is dependent on being able to generate a uniform concentration of reactive species throughout the flow-tube, both radially, and length-wise thus ensuring the kinetics are measured as a function of the continuously changing reaction time and not confounded by a changing concentration of the reactive species. This uniformity requires that neither the precursor concentration nor the radiation source intensity is depleted significantly along the length of the flow-tube. As a rule of thumb, the precursor concentration should be low enough that the radiation intensity is reduced by no more than 10% at the exit of the flow-tube. For the 1-m long flow-tube (pathlength) used in the present experiments, a simple Beer's Law calculation indicates that the product of the precursor concentration and its absorption cross section must be no more than $-\ln(0.9)/100\text{cm}$ or $1.05 \times 10^{-3} \text{ cm}^{-1}$; for example, in the generation of O_3 from NO_2 photolysis, the NO_2 absorption cross section at 355 nm is $4.9 \times 10^{-19} \text{ cm}^2/\text{molecule}$ no more than $2.1 \times 10^{15} \text{ molecules/cm}^3$ of

NO₂ should be used. Likewise, if the radiation intensity is too large the precursor concentration could be diminished. To deplete no more than 10% of the precursor, the photolysis frequency, j , which is the product of the radiation fluence, precursor absorption cross section and photodissociation quantum yield, should be kept below $1.05 \times 10^{-3} \text{ sec}^{-1}$. In the generation of O₃ from NO₂ photolysis, the quantum yield is unity⁷¹ and this requirement means that the laser fluence should be kept below $2.2 \times 10^{15} \text{ photons/cm}^2/\text{sec}$. (= 2.5 mJ/pulse). However, NO₂ is continually regenerated through the reactions of NO with O₃ and O, so laser fluences higher than this can be and are used. Significant depletion of either the precursor or the radiation intensity can be observed experimentally as a deviation from an exponential function that starts at the time the light is introduced and approaches an asymptote at the maximum retention time in the flow tube, determined by the bulk flow velocities.

4.4.2 Advantages of virtual injector approach

There are several benefits to using the virtual injector approach for measuring kinetics, especially gas-particle uptake kinetics. First of all, it is possible to study reactions of all four major tropospheric oxidants (OH, Cl, NO₃, O₃) of organic species using photolysis of suitable precursors. We have shown it is possible to generate these species using a single wavelength (355 nm) which makes it easier to study the kinetics of the different reactive species with a given particle source or gas phase compound. However it is possible to use the virtual injector approach with any photogenerated source of reactive species and does not require 355 nm laser light.

Another advantage of this approach is that the reactions can be carried out under nearly-pseudo-first-order conditions since the reactive species are continually regenerated down the

entire length of the flow-tube. This ability makes it possible to study reactions under pseudo-first order conditions even when the radical or O_3 concentrations are smaller than those of the other gas-phase or particle reactants as the continuous regeneration causes an effective steady state of the reactive species. The steady state of reactive species, makes it possible to monitor the loss of multiple reactant species simultaneously as displayed for acetone and its isotopologues and in the reactions of complex, multi-component aerosol particles as demonstrated with the reactions of olive oil particles.

The use of the gas flow as a virtual injector also makes it possible to follow the progress of the reaction as a function of reaction time instead of reactant concentration as is often done especially in studying gas-particle kinetics. This allows the virtual injector approach to be used in either absolute or relative rates studies. Also, the distinction between following reactions as a function of time and as a function of reactive species concentration can be important since the rates of a reaction derived in these two ways may not be comparable.⁷² For example, the rate of a reaction may be a function of reactive species concentration if mass transport in the particles is limiting or if secondary chemistry involving radical intermediate species leads to an additional loss channel of particle phase species.

Another advantage of the virtual injector approach is that the experiments can be carried out in a relatively short amount of time as determined by the residence time of the flow in the flow-tube. While brevity is not the goal of these experiments, as reactions are being monitored as a function of reaction time, it is possible to effectively carry out two reactive decays in two minutes. In the experiments presented here, the residence time in the flow-tube apparatus is as short as one minute. Thus when the light is introduced, it takes one minute for the decay to occur and when the laser is blocked the recovery of the signal is analogous to

continuously shortening the reaction time and this data can also be used to derive rate constant data.

4.4.3. Potential limitations of virtual injector approach

A major limitation of the virtual injector approach is that the reactive species must be generated from dissociation of a precursor. While we have been able accomplish this for O_3 , NO_3 , OH and Cl , there are other reactive species that may prove more difficult, if not impossible, to generate in this way. It is also not possible to accurately determine rate constants in this manner if more than one oxidant is present. While in absolute rate constant determination methods where the gas or particle phase species is in a steady state, the relative change in reactive species during reaction can be used to determine bimolecular rate constants even when more than one reactive species is present. Because, in the virtual injector approach, it is the reactive species that is being held in a steady state while the change in the other reactant is monitored, only one reactive species may be present during a given experiment.

Although the virtual injector technique is not solely a relative rates technique, relative rates measurements in the virtual injector are susceptible to the same disadvantages of any relative rates measurements, namely that the uncertainty in the results are often governed by the uncertainty in the reference rate constant (as apparent in Table 4.2). Also, it may prove to be difficult to find an appropriate gas-phase species to use as a reference since it must meet several criteria. The selected gas phase reference must: 1) react with the radical or O_3 at a similar rate as the species to be measured, 2) not absorb strongly the light that is being used to initiate the reaction (355 nm in the present experiments), 3) not react with the precursor

species used to photo-generate the radical or O₃, 4) be able to be detected at the same time that the other reactant(s) is (are) detected but as a different signal response.

4.5. Conclusions

A novel technique for studying gas phase and heterogeneous oxidation kinetics has been developed whereby photogenerated reactive species (O₃, NO₃, OH and Cl) are generated at more or less constant concentrations that are uniform throughout the length of the flow tube. The gas flow, itself, acts as a virtual injector, pushing the reactants through the flow-tube containing a steady state of reactive species. In this manner, the decay of gas and particle phase species may be observed as a function of reaction time. This means that with a known reactive species concentration, absolute rate measurements could be performed. Relative rates measurements simplify the rate constant measurement by eliminating the need to know the absolute concentration of any species. Because it is the reactive species that is held in a steady state, various species for which rate constants are desired can be added to the flow-tube and their rate constants can be determined simultaneously. The utility of the virtual injector approach in measuring gas phase rate constants that range from slow (10^{-16} cm³/molecule/s) to fast (10^{-10} cm³/molecule/s) has been presented. Also, heterogeneous reaction kinetics have been explored using the virtual injector approach whereby simple, single component aerosols composed of oleic acid and complex, multicomponent olive oil particles underwent reactions with OH, Cl, O₃ and NO₃.

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CHAPTER 5

ARTIFACTS IN MEASURING AEROSOL UPTAKE KINETICS: THE ROLES OF TIME, CONCENTRATION AND ADSORPTION

5.1. Introduction

The rates at which heterogeneous oxidation processes proceed and the products formed as a result of these reactions has become a topic of recent research interest as they can influence the fate and properties of aerosols in the troposphere. Organic aerosol oxidation by gas phase oxidants is of particular importance as organic matter in tropospheric aerosols comprises 10-90% of the fine particulate mass.²⁻⁴ Heterogeneous aging of organic aerosols by atmospheric oxidants such as hydroxyl radicals, nitrate radicals and ozone may modify aerosol properties such as the ability to directly scatter and absorb solar radiation⁵⁻⁷ and the ability to act as nuclei for cloud condensation^{7, 8} which may indirectly influence the Earth's radiation balance.

Among the most important oxidants responsible for atmospheric radical-initiated oxidation of organic particles in the troposphere are hydroxyl radicals (OH). Chlorine radicals (Cl) are also commonly used as a proxy for OH radicals in the laboratory because they generally react by a similar mechanism and can be generated in higher concentrations, though their significance in the atmosphere is limited. Multiple experiments have shown that both OH and Cl reactions with organic aerosols are very efficient with reactive uptake

coefficients (the probability that radical-particle collision will result in reaction) between 0.1 and 0.9⁹⁻¹³.

Numerous experiments have suggested that secondary chemistry may play an important role in the rapid reactive uptake of radical species into organic aerosol. The reactive uptake coefficient of Cl¹⁴ and OH^{15, 16} on dioctyl sebacate (DOS) particles has been reported to be greater than unity, and the authors have suggested secondary radical chemistry to explain the rapid loss rate of DOS in these particles. Smith et al.¹⁷ and Che et al.¹⁸ have recently published results in which the reactive uptake of OH on squalane particles was studied in two separate reaction chambers that differed in the amount of reaction time and found that at shorter times (~37 seconds) and average OH concentrations of 1×10^{10} molecules/cm³, the reactive uptake of OH on Sq particles was 0.3 ± 0.07 ¹⁷ whereas at longer times (1.5-3 hours) and lower OH concentrations ($1-7 \times 10^8$ molecules/cm³) the reactive uptake was 0.51 ± 0.10 ¹⁸. As a possible explanation of the different reactive uptakes measured in these two experiments, Che et al.¹⁸ have suggested the importance of a secondary loss mechanism at low OH concentrations whereby a radical intermediate, such as RO or RO₂, may abstract a hydrogen from squalane.

Secondary radical chemistry and surface renewal processes may result in decay kinetics for which time and concentration are not interchangeable variables according to a kinetic model, devised by McNeill et al.¹⁹ This model suggests that laboratory studies employing high radical concentrations (10^{10} - 10^{12} molecules/cm³) and short times (seconds to minutes) may not be representative of reactions which occur in the troposphere with much smaller concentrations ($\sim 10^6$ molecules/cm³) and long interaction times (days to weeks). Whether

time and concentration are equivalent variables in organic aerosol oxidation kinetics, therefore, remains an open question.

In the present work, whether radical concentration and time are interchangeable variables during the OH- and Cl-initiated oxidation reactions of squalane (Sq), 2-oxylododecanoic acid (2-ODA) and brassidic acid (BA) particles is explored. Two different reactor flow tubes, varying in the internal volume and in the reactant interaction time by a factor of 33, were used to measure the kinetics in two ways: by changing reaction time and by changing radical concentration. To achieve the same radical exposure ($[\text{OH}] \cdot t$ or $[\text{Cl}] \cdot t$) in the two flow tube systems, the radical concentration was varied by the same factor. Further, the influences that the radical precursors (O_3 and Cl_2) have on the measured rates of these reactions are investigated through a systematic study of 2-ODA oxidation as a function of the precursor concentration. Squalane and 2-ODA were chosen for these experiments because they are both branched species which may form liquid particles at room temperature and are representatives of branched, saturated organic molecules found in ambient aerosols. Brassidic acid is an unbranched, unsaturated fatty acid that is able to be supercooled at room temperature^{20, 21} and is representative of unsaturated fatty acids in ambient aerosols. Also, all three species have low vapor pressures at room temperature thus making them amenable to studying the heterogeneous reactions between gas-phase oxidants and condensed phase organics.

5.2. Materials and methods

5.2.1. Particle generation

Particles of Sq, 2-ODA and BA were generated through homogeneous nucleation by flowing 0.9 slpm (standard liters per minute) of N_2 through a reservoir containing either Sq,

2-ODA or BA heated to 135-145 °C. The aerosol was then reheated as it flowed through ½-inch o.d. glass tubing (4 inches long, 250 °C). Typically, reheating of the aerosol results in narrowing of the particle size distribution from a geometric standard deviation (gsd) of ~1.4 to a gsd of ~1.2. As both 2-ODA and BA are solids at room temperature with melting points of 34 - 36 °C²² and 58-59 °C²³, respectively, their vapor nucleated and formed supercooled liquid droplets as they cooled to room temperature. After they exited this stage, the squalane, 2-ODA, and BA particles cooled to room temperature and were typically 180-220 nm (gsd= 1.20-1.24), 45-120 nm (gsd= 1.2-1.3), and 90-100 nm (gsd= 1.2-1.3), respectively. The particle size distributions were measured using a scanning mobility particle sizer (SMPS) consisting of a DMA (TSI, Inc. model 3081) and CPC (model 3785, TSI, Inc.).

5.2.2. Flow tube reactions

A schematic of the experimental setup is shown in Fig. 5.1. After particle generation, the particles entered one of two flow tube reactors along with N₂, O₂, O₃ or Cl₂ and a gas-phase reference species. Hydroxyl radicals were generated by photodissociation of O₃ using the fourth harmonic (266 nm) from a 10-Hz pulsed Nd:YAG laser (QuantaRay PRO-250, Spectra-Physics), and residual water vapor in the apparatus was sufficient to react with O(¹D) to generate OH radicals:



Chlorine radicals were generated by photodissociation of Cl₂ using the third harmonic (355 nm) of the same laser. In each case, the laser fluence was varied to adjust the radical concentration, but it was not measured. For the small flow tube, the laser beam from the Nd:YAG (beam diameter = ~1 cm) was directed down the axis of the flow tube so that the

volume of the flow tube was filled with light during the experiments. For the large flow tube, a convex quartz lens with a focal length of 6 cm was positioned so that the beam would expand to approximately one inch in diameter as it passed through the one-inch window and then continue to expand to fill the flow tube within ~4 cm of entering the flow tube.

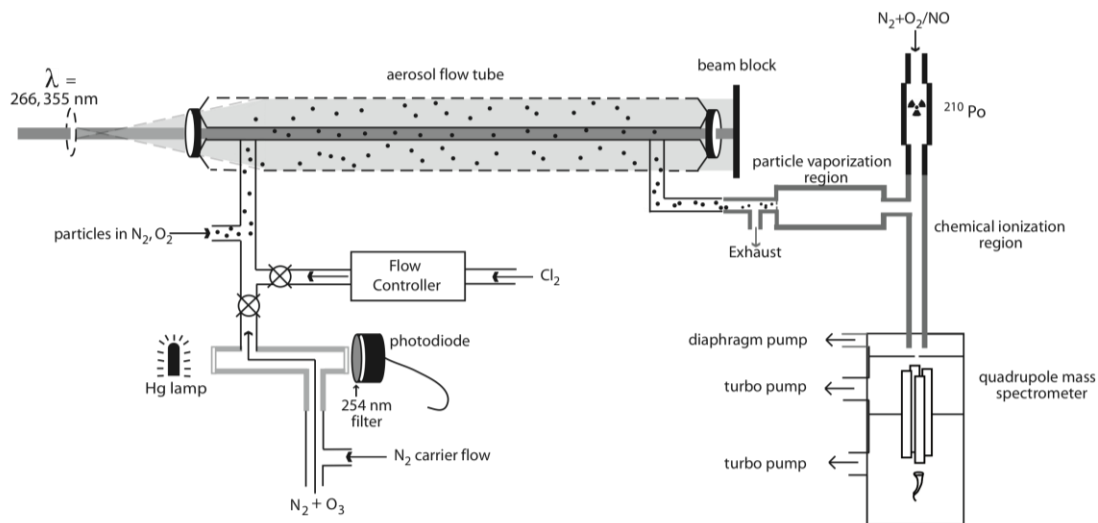


Figure 5.1. Schematic diagram of the experimental setup to collect particle kinetic decays with: 1) fixed reaction time of 2 seconds (small flow tube) or 2) variable reaction time up to 66 seconds (large flow tube). The chemical ionization schemes used for particle and gas-phase reference detection are described in the text.

Reactions were carried out at atmospheric pressure and 293 K in two separate glass flow tubes with the dimensions 1.1 cm i.d. x 90.0 cm length and 5.1 cm i.d. x 91.4 cm length, and will be referred to from this point forward as the “small” and “large” flow tubes, respectively. Upon exiting the flow tube, gas and particle phase species were analyzed by an Aerosol Chemical Ionization Mass Spectrometer. For the OH experiments, Sq or 2-ODA aerosols (0.9 slpm N₂ flow), O₂ (0.125 slpm for the small flow tube and 0.100 slpm for the large flow tube) and gas-phase reference (≤ 1 sccm, standard cubic centimeter per minute) were introduced into one inlet port of the flow tube reactor. Ozone, the OH precursor, was generated using a commercial ozone generator (Model L11, Pacific Ozone Technology) and

stored on silica gel at -80 °C. By passing a small flow (5-10 sccm) of N₂ over the trapped O₃ and then diluting the O₃ in a N₂ carrier flow (1.48 slpm for the small flow tube and 0.7 slpm for the large flow tube), O₃ was introduced into the second inlet port of the flow tube reactor. The total flow of 1.7 slpm for the large flow tube and 2.5 slpm for the small flow tube thus contained 5-6% O₂. For the Cl experiments, Sq, BA or 2-ODA particles, N₂ carrier flow and O₂ were added as described above, but Cl₂ was added as the radical precursor instead of O₃, and the 1.7 slpm and 2.5 slpm flows for the large and small flow tubes contained 20% O₂. Based on the total flow velocity and the volumes of the two flow tubes, the total reactant interaction times were 2 seconds and 66 seconds for the small and large flow tubes, respectively.

The concentrations of OH or Cl radicals generated were varied by changing either the concentration of O₃ or Cl₂ or the Nd:YAG laser fluence. The concentration of O₃ in the carrier flow was determined by Beer's Law in a UV absorption cell equipped with a UV pen lamp (254 nm) and a photodiode detector with a 254 nm filter and corrected for dilution upon meeting the particle and O₂ flows. For the Cl₂ concentration dependence experiments, the concentration of Cl₂ in the flow tube was calculated from the flow of Cl₂ from a lecture bottle of known concentration.

The integrated OH exposure, [OH]_{avg} • t, was determined using mixed-phase relative rates^{15, 24} with gas-phase references of methanol ($k_{OH} = 9.0 (\pm 0.8) \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec.}$)²⁵ and 2-hexanol ($k_{OH} = 1.21 (\pm 0.07) \times 10^{-11} \text{ cm}^3/\text{molecule}/\text{sec.}$)²⁶ for the reactions of squalane and 2-ODA particle reactions, respectively. Acetone-d₁ was used as the gas-phase reference for Sq + Cl, and its rate constant was measured previously in this lab ($k_{Cl} = 1.83 (\pm 0.28) \times 10^{-12} \text{ cm}^3/\text{molecule}/\text{sec.}$) (unpublished). Acetone-d₁ was chosen as a gas phase

reference because a product of Sq oxidation appeared at the same m/z as acetone but the rates of reaction of both species with Cl are comparable. Acetone ($k_{Cl} = 2.07 (\pm 0.31) \times 10^{-12}$ cm³/molecule/sec.)²⁷ was used as the gas-phase reference for the 2-ODA + Cl and BA + Cl reactions.

5.2.3. Collection of particle decay data in the two flow tubes

Use of the small flow tube for studying heterogeneous reactions between gas-phase radicals and organic aerosols has been described in detail elsewhere^{14, 20, 21}. In summary, the reaction time (~2 sec.) is too short to enable the collection of many data points as the aerosol species concentration decays as a function of time. For this reason, in order collect particle decay data, the radical concentration must be changed either continuously or in discrete steps by adjusting the power of the photodissociation laser or the concentration of the radical precursor. In doing so, it is assumed that changing the radical concentration is equivalent to changing the reaction time in reaching a given radical exposure. The large flow tube used here, however, allows the observation of particle and gas-phase reference decays as a function of time at nearly-constant radical concentration as the particles and gas-phase species exit the flow tube. This “virtual injector” flow-tube has been described in detail in Chapter 4. In short, upon introduction of the photodissociation laser either OH or Cl is produced throughout the flow tube and the reaction begins; particles nearest the end of the flow tube exit first with the least amount of time to react with the radical species, while those furthest from the exit of the flow tube have the longest time (66 seconds) to react. Thus, particle decay data were collected:

- 1) As a function of radical concentration at fixed time in the small flow tube
- 2) As a function of time at a fixed radical concentration in the large flow tube.

The goals of these experiments are to determine if the two methods of measuring kinetics yield the same result in both gas-phase and heterogeneous relative rates experiments and to infer from these results whether radical concentration and time are interchangeable variables in studying particle oxidation kinetics. In order to best compare the particle decay data obtained with each flow tube, the OH or Cl concentration in each flow tube was adjusted so that ~20% of the particle-phase species reacted away over the course of each experiment. Reactions in the small flow tube were performed by discrete measurements where the O₃ or Cl₂ concentration and laser power were set so that upon introducing the laser light into the flow tube, the particle phase species would react by ~20%. By alternately turning on and off the laser source into the flow tube, the particle phase and gas-phase reference signal were obtained before, during, and after each reaction.

Because the particles have much more time to react with the OH or Cl radicals in the large flow tube it was necessary to use smaller radical concentrations so that after the 66 second residence time only ~20% of the particle phase species had reacted. This was achieved by adjusting the amount of O₃ or Cl₂ entering the flow tube and the laser power was maintained at the same laser power used in the reactions in the small flow tube above. For the O₃ and Cl₂ concentration dependence experiments, the O₃ and Cl₂ concentrations were fixed and the laser fluence was adjusted in order to reach equivalent radical concentrations in each flow tube.

5.2.4. Chemical ionization and detection

The flow tube eluent containing aerosol and gas-phase references was sampled into the mass spectrometer through a stainless steel orifice (0.5 mm i.d.) in a heated (180 °C) stainless steel vaporizer tube (1/4 inch o.d., 4 inches long). The vaporized aerosol flow then entered

the heated (150 °C) stainless steel ion tube (1/2 inch o.d., 8 inches long, 40 Torr) of the CIMS instrument where it mixed with a 2 slpm flow of N₂ containing H⁺(H₂O)_n (where n=2,3) or NO⁺ reagent ions generated from a radioactive ²¹⁰Po source (NRD). When H⁺(H₂O)_n ions were used for ionization, small amounts of O₂ were added to the flow through the ²¹⁰Po source in order to increase the H⁺(H₂O)_n ion signal by approximately a factor of two.

For the reactions of 2-ODA and 2-hexanol with OH and for the reactions of 2-ODA, BA and acetone with Cl, proton transfer from H⁺(H₂O)_n was used to generate protonated molecular ions. Squalane particles were detected through hydride abstraction and the acetone-d₁ gas-phase reference (for the reaction with Cl) was detected via NO⁺-adduct formation, both using NO⁺ ions. Methanol, the gas-phase reference used for the OH + Sq reaction, is not efficiently ionized by NO⁺ and thus in order to determine the OH exposure after a Sq particle reaction, ionization was rapidly changed to proton transfer via H⁺(H₂O)_n by replacing the NO through the ²¹⁰Po with O₂ and the decay was repeated at the same laser fluence and O₃ flow. This method was repeated approximately ten times and the time between recording respective squalane and methanol decays (the time required to change ionization schemes) was typically 0.5-1 minute.

The ions generated as described above were then sampled into the high vacuum region through a 200-μm orifice by means of a small potential gradient (2–5 V) and differential pumping. Ions were filtered using a quadrupole mass spectrometer (ABB Extrel) and detected using a Channeltron electron multiplier (model 4816, Burle).

5.2.5. Gases and chemicals

Gases used were: N₂ (99.99%, National Welders), O₂ (industrial grade, National Welders), and NO (CP grade, National Welders). Flows were measured and maintained using

mass flow controllers (MKS). 2-hexanol, methanol and acetone were purchased from Sigma Aldrich and had purities greater than 99%. Squalane (>99%) and brassidic acid (~99%) were purchased from Sigma Aldrich and MP Biomedicals, respectively, and 2-octyldodecanoic acid (2-ODA) was provided by JarChem Industries, Inc. (Newark, NJ).

5.3. Results and discussion

5.3.1. Reactive uptake experiments in the small and large flow tubes

Reactions between OH and Sq and 2-ODA aerosols and between Cl and Sq, 2-ODA and BA aerosols were studied in each flow tube. The concentration of the O₃ or Cl₂ radical precursor was adjusted in order to reach the same extent of reaction in each flow tube while maintaining a constant laser fluence. The effective reactive uptake coefficients for the gas-particle reactions were calculated using the following equation:¹⁴

$$\gamma_{part} = \left[\frac{d([X]/[X]_0)}{d([Y] \bullet t)} \right] \frac{4RT}{\bar{c}} \frac{V}{S_A} [X]_0. \quad 5-3$$

Here, γ_{part} is the effective reactive uptake coefficient of OH or Cl in the aerosol particle as measured from the rate of loss of the aerosol species, $[Y]$ is the concentration of OH or Cl, V/S_a ($= d/6$) is the volume to surface area ratio of the particles determined using the particle size data from the SMPS, R is the gas constant, T is the temperature, $\bar{c}$ is the mean speed of OH or Cl, and $[X]_0$ is the initial concentration of Sq, 2-ODA, or BA in the unreacted particles. The term in brackets represents the slope of the initial decay of the particle-phase species with respect to radical exposure ($= [Y] \bullet t$) which is determined from the measured fractional loss of the gas-phase reference species, $[R]/[R]_0$:

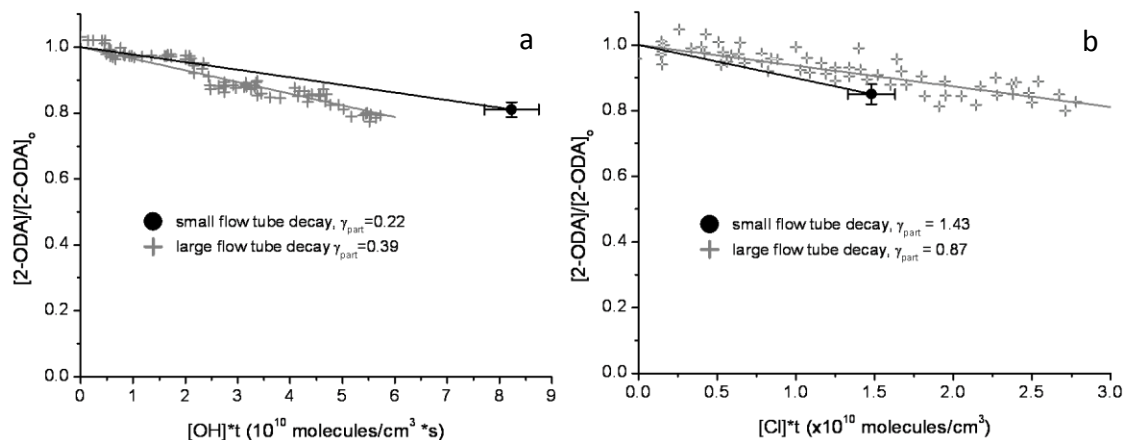
$$([Y] \bullet t) = -\frac{1}{k} \ln \left(\frac{[R]}{[R]_0} \right), \quad 5-4$$

where k is the rate constant of the reaction of the reference species with OH or Cl. For the small flow tube measurements, the slope of the initial decay in Eq. 3 is approximated by the discrete change:

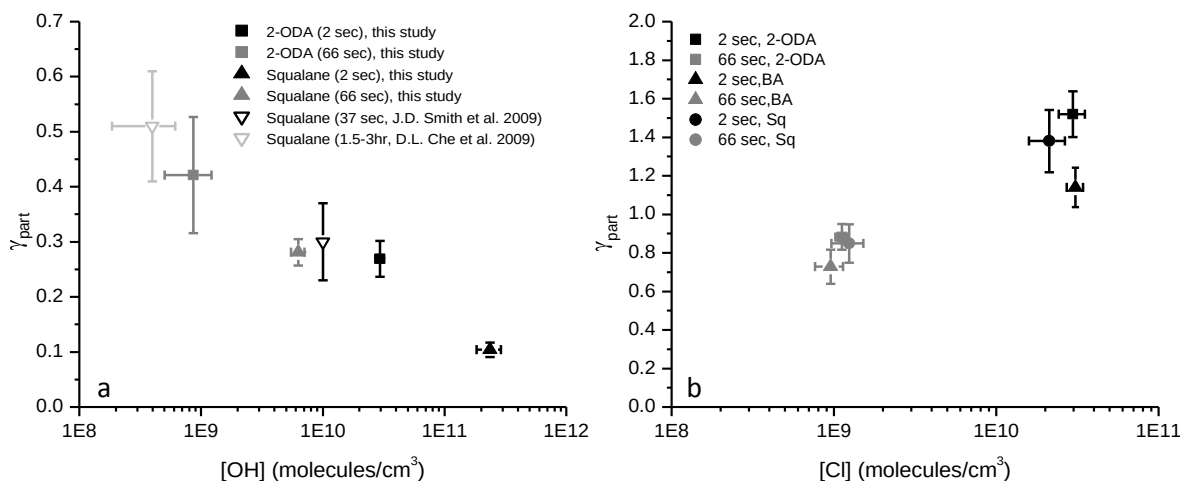
$$\frac{d\left(\frac{[X]}{[X]_0}\right)}{d([Y] \bullet t)} \approx \frac{\Delta\left(\frac{[X]}{[X]_0}\right)}{\Delta([Y] \bullet t)}. \quad 5-5$$

Sample decays of 2-ODA aerosol particles as a function of OH and Cl exposure in the two reactor flow tubes are shown in Figures 5.2a and 5.2b, respectively. From repeated measurements, the average γ_{part} for reactive uptake of OH with 2-ODA and Sq particles and the reactive uptake of Cl with 2-ODA, squalane and BA particles were determined and are displayed in Figures 5.3a and 5.3b as a function of the average radical concentration, respectively.

The data in Fig. 5.3a show that in the two flow tube experiments, where different OH concentrations were needed to reach the same nominal exposure, the effective reactive uptake coefficient, γ_{part} , increases with decreasing OH concentration. This trend is consistent with the results of Che et al.¹⁸ and Smith et al.¹⁷ for OH + Sq aerosols, also shown in Fig. 5.3a, in which the effective uptake coefficient was larger for the longer-residence-time (1.5-3 hours) experiments relative to the shorter-residence-time (37 seconds) experiments. The data in Fig. 5.3b, on the other hand, show that for the reaction with Cl radicals the effective reactive uptake coefficient increases with decreasing Cl concentration. At first glance, then, it appears as if the rates of reaction are somehow related to the radical concentration implying that experiments conducted by varying reaction time are not equivalent to those conducted by changing the radical concentration.



Figures 5.2 a-b. a) Sample 2-ODA particle decays from small and large flow tubes showing the slope of the line used to determine the effective reactive uptake coefficient of OH in each case. b) Sample 2-ODA particle decays from small and large flow tubes showing the slope of the line used to determine the reactive uptake coefficient of Cl in each case.



Figures 5.3 a-b. a) effective reactive uptake coefficient of OH on 2-ODA particles and Sq particles in the large and small flow tubes as a function of OH concentration. The data of Che et al.¹⁸ and Smith et al.¹⁷ are shown for comparison. b) effective reactive uptake coefficient of Cl on 2-ODA, Sq, and BA particles as measured by the rate of loss of particle phase species in the large and small flow tubes as a function of Cl concentration.

To investigate this effect further, several measurements of the relative rates of just gas-phase species with OH and Cl were made as well, and it was found that no such discrepancy was observed between the small and large flow tubes. For example, for the OH reactions the

rate of 1-butanol relative to that of 2-hexanol was measured to be 0.63 ($\pm$ 0.07) and 0.61 ($\pm$ 0.04) in the small and large flow tubes, respectively, compared to a ratio of 0.72 ($\pm$ 0.07) calculated from published rate constants of these reactions (1-butanol: $k_{OH} = 8.66 \times 10^{-12}$ cm³/molecule/sec.²⁸; 2-hexanol: $k_{OH} = 1.21 \times 10^{-11}$ cm³/molecule/sec.²⁶). Thus, it appears as if only the rates of the gas-particle reactions are influenced by the radical concentrations. Consequently, it might not be possible to use the rates of reactions measured in flow tube experiments to represent accurately the rates of reactions in the atmosphere where radical concentrations are orders of magnitude smaller and reaction times are orders of magnitude larger. However, it must be noted that in these experiments the concentration of the precursor (O₃ for OH and Cl₂ for Cl) was not the same in the small and large flow tubes; a higher concentration of precursor was used in the small flow tube to generate a higher concentration of the radical. What effect, if any, does the precursor concentration have on the radical uptake kinetics?

5.3.2. Rate of reaction of 2-ODA with OH with a fixed [O₃]

To explore the effects of O₃ and Cl₂ concentrations on the reactive uptake of OH and Cl, respectively, systematic experiments were carried out using 2-ODA particles. Brassidic acid particles were not chosen for this study since BA contains a double bond and thus undergoes reactions with O₃, the OH precursor. Squalane particles were not used because the squalane + OH experiments are relatively time-consuming since different chemical ionization schemes are used to observe the reaction of the squalane (using NO⁺) and methanol, the gas-phase reference species (using H⁺(H₂O)_n) (see section 5.2.4). For these reasons, 2-ODA particles were chosen to investigate the effects of precursor species on the reactive uptake of OH and Cl.

The reaction of 2-ODA with OH was performed in the small and large flow tubes using the fluence of the photodissociation laser to control the amount of OH production at fixed O₃ concentrations. Generally, the laser fluence was adjusted such that the 2-ODA reacted by approximately 20% over the length of each flow tube. As before, 2-hexanol was used as the gas-phase reference. The results of one such experiment, where the concentration of O₃ was 3-4 x 10¹⁵ molecules/cm³ are shown in Fig. 5.4. Now, when O₃ concentration is the same in the two flow tubes, γ_{part} is nearly the same despite the fact that the reaction times and [OH] differed by a factor of 33: $\gamma_{part} = 0.31$ and 0.32 for the small and large flow tubes, respectively. In other words, [OH] and time are truly interchangeable parameters in these gas-particle kinetics experiments as long as the O₃ concentration is fixed. These results suggest that O₃ is affecting the particle reaction kinetics in some way warranting a systematic study as a function of O₃ concentration.

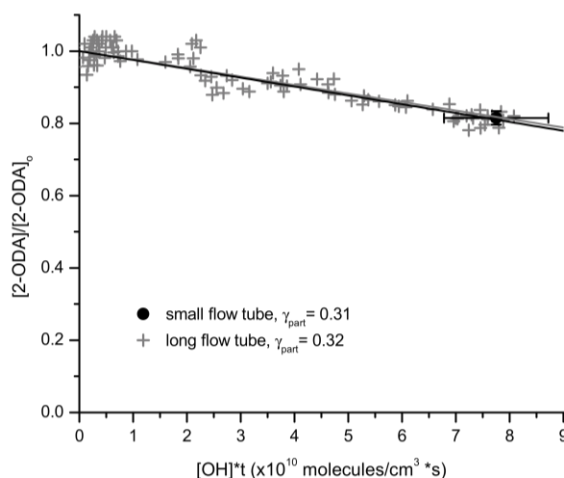


Figure 5.4. 2-ODA decay from reaction with OH in the small and large flow tubes with [O₃] = 3-4 x 10¹⁵ molecules/cm³.

5.3.3. Rate of reaction of 2-ODA with OH as a function of [O₃]

To better understand the effect that O₃ has on the rate of reaction of 2-ODA particles with OH, γ_{part} was measured as a function of O₃ concentration in the small and large flow tubes (Fig. 5.5). In these experiments, the laser fluence was used to control [OH] at a fixed O₃ concentration which ranged from 2.7×10^{14} molecules/cm³ to 8.3×10^{15} molecules/cm³. The reactive uptake coefficient initially decreases with increasing [O₃] and then reaches a plateau where a further increase in [O₃] has no effect on the reactive uptake of OH. In order to ensure that this trend was not due to a change in the reactivity of the gas-phase reference species, a gas-phase relative rates experiment using the reactions of 1-butanol + OH and 2-hexanol + OH was performed as a function of O₃ concentration (grey triangles in Fig. 5.5). No variation in the ratio of the rate constants was observed across the range of ozone concentrations used indicating that the trend observed in the 2-ODA uptake coefficient is, indeed, specific to the particles.

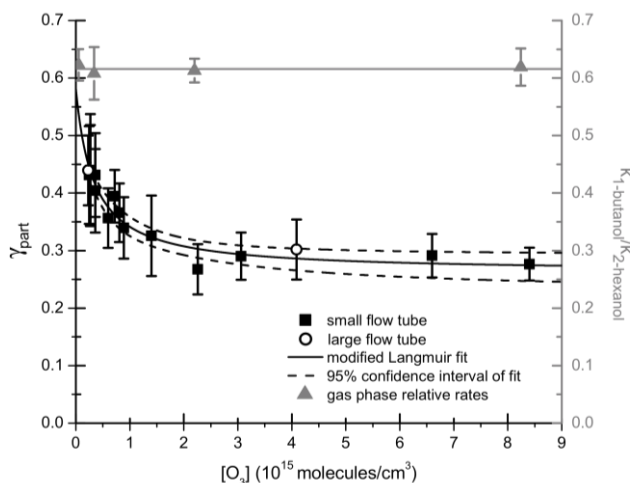


Figure 5.5: Effective reactive uptake coefficient, γ_{part} , of OH on 2-ODA particles as a function of O₃ concentration. The Langmuir-type adsorption isotherm used to fit the data is also shown with 95% confidence intervals. The best fit parameters are: $\gamma_o = 0.56 (\pm 0.07)$, $K = 2.60 (\pm 1.40) \times 10^{-15}$ cm³/molecule, and $f = 1.86 (\pm 0.16)$. Also shown are the results of a gas-phase relative rates experiment where the ratio of the rate constants of 1-butanol and 2-hexanol + OH was determined as a function of [O₃].

The uptake coefficient data in Fig. 5.5 are fit well by a Langmuir-type isotherm with the form:

$$\gamma = \gamma_0 \left(1 - \frac{\theta}{f} \right). \quad 5-6$$

where γ_0 corresponds to the uptake coefficient in the absence of O_3 , f is an adjustable parameter which accounts for the incomplete inhibition of the rate of reaction even at the highest values of $[O_3]$, and θ is the fractional surface coverage of O_3 :

$$\theta = \frac{K[O_3]}{1 + K[O_3]}, \quad 5-7$$

where K is the O_3 adsorption/desorption equilibrium constant. The fact that this modified Langmuir function fits the data in Fig. 5.5 well suggests that O_3 is adsorbing to the particle surface where it affects the observed rate of reaction of 2-ODA with OH. The best fit parameters are: $\gamma_0 = 0.56 (\pm 0.07)$, $K = 2.60 (\pm 1.40) \times 10^{-15} \text{ cm}^3/\text{molecule}$, $f = 1.86 (\pm 0.16)$.

The value of $\gamma_0 = 0.56$ represents the predicted effective uptake coefficient in the absence of any inhibition by adsorbed O_3 . Very few experiments exist in which the reactive uptake coefficient of OH on organic films or particles has been measured in the absence of O_3 to which γ_0 can be compared. In one such study, Bagot et al.⁹ have determined the reactive uptake of OH on squalane films using 355-nm laser photolysis of a low pressure of HONO to generate OH above the squalane surface. In that study, the reactive uptake coefficient of OH on squalane films was 0.49 ± 0.04 which is comparable to the value of $\gamma_0 = 0.56 (\pm 0.07)$ reported here for 2-ODA aerosols. Likewise, these values are similar to the results of Che et al.¹⁸ in which $\gamma = 0.51$ was measured for reaction of squalane particles with OH over a

timescale of 1.5-3 hours using a presumably low concentration of O₃ to generate OH, though this concentration was not measured.

The adsorption/desorption equilibrium constant of O₃ on the 2-ODA particle surface deduced from the Langmuir fit in Fig. 5.5 is $K = 2.6 (\pm 1.4) \times 10^{-15} \text{ cm}^3/\text{molecule}$ and is comparable to the adsorption/desorption equilibrium constant obtained from experiments of O₃ adsorption on other organic surfaces²⁹⁻³². In particular, Kwamena et al.³⁰ describe the Langmuir-Hinshelwood adsorption of O₃ on various liquid organic aerosols, and for supercooled liquid azelaic acid aerosols they report a value of $K = 2.2 \times 10^{-15} \text{ cm}^3/\text{molecule}$. This good agreement is not surprising, as both the azelaic acid particles used in that study and the 2-ODA aerosols used here are supercooled liquid organic carboxylic acid particles.

The parameter f in the modified Langmuir function used to fit the data is a measure of the degree to which the reactive uptake coefficient is affected by the presence of O₃ at the particle surface. A value of $f = 1$ would represent a Langmuir adsorption isotherm for which the reaction is completely inhibited at saturation (when $\theta = 1$), whereas a value of $f > 1$ represents incomplete inhibition even at saturation. In the fit to the data in Fig. 5.5, the value of f is $1.86 (\pm 0.16)$ indicating that when O₃ has reached its surface saturation concentration, the reaction between OH and 2-ODA still proceeds at 54% ($= 1 / 1.86$) of the rate if O₃ were absent (γ_0). This partial hindrance of the reaction could be due to: 1) the existence of a layer of O₃ that acts as a barrier between OH and the 2-ODA particle surface which slows but does not inhibit the reaction, or 2) the incomplete coverage of the surface by O₃ islands or other such phenomena whereby OH can still react with 2-ODA that is not covered by O₃. An O₃ layer may act as either a physical barrier, where only OH that is able to diffuse through the O₃ layer may react with 2-ODA, or a chemical barrier which reacts with OH to form HO₂.

From gas-phase rate constants of OH and HO₂ reactions with analogous organic species,³³⁻³⁶ it is expected that the conversion of OH to HO₂ would slow considerably, if not halt entirely, the reactive loss of 2-ODA. The formation of island-like structures of O₃ would be feasible if O₃ self-adsorption is favored relative to O₃ adsorption to the 2-ODA surface once a critical concentration of O₃ exists at the surface.

5.3.4. Rate of reaction of 2-ODA with Cl as a function of [Cl₂]

Unlike the reaction of OH with 2-ODA, for which the rate of reaction decreased at higher OH concentration, it was found that the apparent uptake coefficient for the Cl reaction with 2-ODA increased with Cl concentration (Fig. 5.3b). Is it possible that this trend is related to the concentrations of Cl₂ used in those experiments in a similar way that the rate of OH reaction was influenced by the concentration of O₃? To investigate this possibility, γ_{part} was measured as a function of Cl₂ concentration (shown in Fig. 5.6) with the laser fluence adjusted in each experiment to achieve approximately 20% reaction of the 2-ODA. Experiments were conducted in both the small flow tube and in the large flow tube, and it was found that the effective reactive uptake coefficients are equal at a given Cl₂ concentration even though [Cl] and reaction time differed by a factor of 33 in the two flow tubes. Thus, [Cl] and time are equivalent and interchangeable variables in measuring the reactive uptake of Cl on 2-ODA particles for a given Cl₂ concentration.

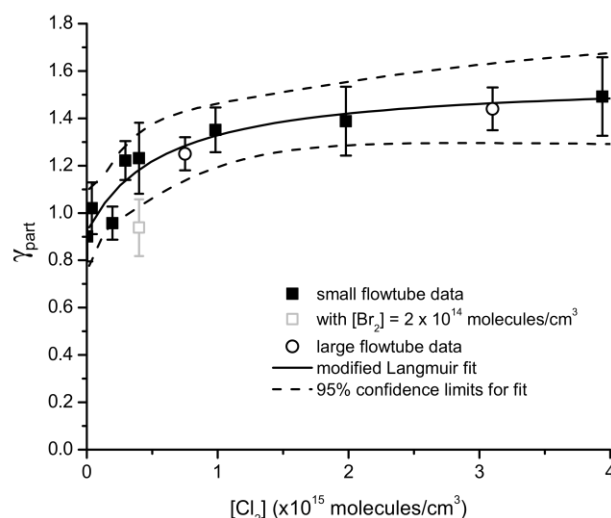


Figure 5.6: Effective reactive uptake coefficient, γ_{part} , for Cl on 2-ODA particles as a function of Cl_2 concentration. The Langmuir-type adsorption isotherm used to fit the data is also shown with 95% confidence intervals. The best fit parameters are: $\gamma_o = 0.92 (\pm 0.07)$, $K = 1.72 (\pm 1.23) \times 10^{-15} \text{ cm}^3/\text{molecule}$, and $f = -1.42 (\pm 0.30)$.

As seen in Fig. 5.6, the reactive uptake coefficient increases with increasing $[\text{Cl}_2]$ and then reaches a plateau where a further increase in $[\text{Cl}_2]$ has little to no effect on the observed rate of reaction. As with the OH uptake dependence experiments, these data are well represented by a Langmuir-type isotherm (Eq. 4-6) with: $\gamma_o = 0.92 (\pm 0.07)$, $K = 1.72 (\pm 1.23) \times 10^{-15} \text{ cm}^3/\text{molecule}$, and $f = -1.42 (\pm 0.30)$. To ensure that the observed change in the rate of 2-ODA reaction was not due to a change in the reactivity of the gas-phase reference species, a gas-phase relative rates experiment of Cl + methanol and Cl + n-propanol was performed. The ratio of the rate constants was measured to be $2.62 (\pm 0.16)$, in good agreement with the ratio of $2.91 \left({}^{+0.74}_{-0.59} \right)$ calculated from the values recommended in the IUPAC Gas Kinetic Data Evaluation³⁷. The fact that the ratio is independent of $[\text{Cl}_2]$ indicates that the trend observed in the 2-ODA uptake coefficient is, indeed, specific to the particles.

The observed Langmuir-type dependence indicates that Cl₂ is adsorbing to the surface of the particle with a concurrent enhancement in the rate of loss of 2-ODA. The value of the uptake coefficient in the absence of the enhancement from the adsorbed Cl₂ can be estimated from the γ_o parameter obtained from the Langmuir isotherm fit: $\gamma_o = 0.92 (\pm 0.07)$. Thus, the reaction between Cl radicals from the gas phase and the 2-ODA occurs at nearly the gas-particle collision rate, consistent with analogous reactions in the gas phase which typically occur near the gas-kinetic collision rate³⁷. The parameter f in the Langmuir fit represents the degree to which the rate of 2-ODA reaction increases or decreases because of the adsorbed Cl₂. The best fit value for f is -1.42 (± 0.30) indicating that the adsorbed Cl₂ enhances the rate of 2-ODA loss by a factor of 70% ($= 1 / 1.42$), which is effectively a measure of the radical chain length.

The adsorption/desorption equilibrium constant of Cl₂ on the 2-ODA particle surface deduced from the Langmuir fit in Fig. 5.6 is $K = 1.72 (\pm 1.23) \times 10^{-15} \text{ cm}^3/\text{molecule}$. There is currently a lack of adsorption/desorption coefficients in the literature for Cl₂ on organic surfaces, but as there are no chemical reactions (and thus no chemisorption) between Cl₂ and 2-ODA, adsorption is due to physisorption. Physisorption is expected even for nonpolar adsorbents on nonpolar surfaces because of the attraction of the *instantaneous* dipole moments in the surface species and adsorbent arising from the instantaneous positions of the nuclei and electrons. For adsorbent species with near-zero *permanent* dipole moments, such as Cl₂ and O₃, the attraction to a mostly non-polar surface such as 2-ODA (although 2-ODA is slightly polar due to the presence of a carboxylic acid moiety, the long carbon chains are essentially nonpolar) is expected to result in physisorption of Cl₂ and/or O₃ to the particle surface. Because the permanent dipole moments of O₃ and Cl₂ are on the same order of

magnitude, it is expected that the Cl_2 adsorption/desorption coefficient would be similar to that of O_3 , which was measured in the OH experiments to be $K = 2.60 (\pm 1.40) \times 10^{-15} \text{ cm}^3/\text{molecule}$. Thus, the adsorption/desorption equilibrium constant obtained from the modified Langmuir isotherm for Cl_2 on 2-ODA, $K = 1.72 (\pm 1.23) \times 10^{-15} \text{ cm}^3/\text{molecule}$, is reasonable.

The most likely cause of this enhancement is from a radical chain mechanism in which the alkyl radicals ($\text{R}\cdot$) formed from the initial reaction of $\text{Cl} + 2\text{-ODA}$ react with Cl_2 to reform a Cl radical and an alkylchloride product, RCl . In fact, evidence for the formation of the RCl product is observed by the appearance of a peak at $m/z = 347 \text{ amu}$ ($[(2\text{-ODA-H+Cl})\text{H}^+]$) during the reaction of 2-ODA, even with 20% O_2 present if high Cl_2 concentrations are used. The Cl radical that is formed from the $\text{R}\cdot + \text{Cl}_2$ reaction can then react with another 2-ODA molecule thereby enhancing its rate of loss. In essence, there is a higher Cl concentration at the surface than is calculated based on the gas-particle collision rate derived from the measured rate of loss of the gas-phase reference, and this increases the effective uptake coefficient. This secondary loss of 2-ODA also explains why effective uptake coefficients greater than one are measured at high Cl_2 . Further evidence for this radical chain mechanism was observed in reactions carried out in the absence of O_2 in which the effective uptake coefficient was measured to be as high as 10 when high ($1.20 \times 10^{15} \text{ molecules/cm}^3$) concentrations of Cl_2 were used and less than unity when low ($1.97 \times 10^{15} \text{ molecules/cm}^3$) of Cl_2 were used to generate Cl (Figure 5.7).

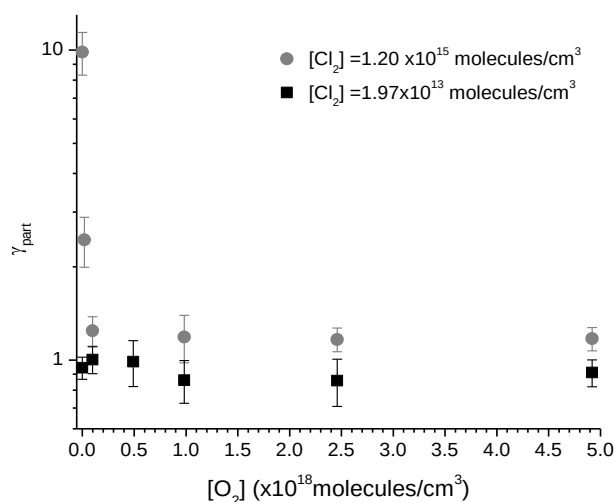


Figure 5.7. O₂ dependence of γ_{part} for “high” (1.20×10^{15} molecules/cm³) and “low” (1.97×10^{13} molecules/cm³) showing γ_{part} with high Cl₂ is consistently larger than γ_{part} with low Cl₂ until low [O₂] concentrations are reached, at which point γ_{part} increases drastically with decreasing O₂ with high Cl₂ but remains less than unity with low Cl₂.

In the presence of high Cl₂ concentrations, γ_{part} increases drastically at low [O₂] presumably because the competitive $\text{R}\cdot + \text{O}_2$ reaction is eliminated allowing the chain to propagate to a larger extent. The elimination of $\text{R}\cdot + \text{O}_2$ is apparent during reactions in the absence of added O₂, whereby the $\text{RCl}\cdot$ product is formed while the ketone and alcohol products (formed from $\text{RO}_2\cdot + \text{RO}_2\cdot$) chemistry are not formed (Figure 5.8a). At low Cl₂ concentrations and low O₂ concentrations, there is no significant rise in γ_{part} and the fate of the alkyl radicals is not clear. While it is possible that at low Cl₂ concentrations and low O₂ concentrations $\text{R}\cdot + \text{O}_2$ may still be the primary fate of the alkyl radicals, with zero added O₂ this cannot be the case as no evidence of ketone and alcohol products is observed (Figure 5.8b). Conversely, the alkyl radicals may react with other 2-ODA molecules and result in the regeneration of 2-ODA and another alkyl radical, explaining why at low [Cl₂], no significant

increase in γ_{part} from $\text{R}\cdot + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}\cdot$ is apparent although the reaction of $\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2$ is not competing (as evidenced by the lack of $\text{RO}_2\cdot$ reaction products).

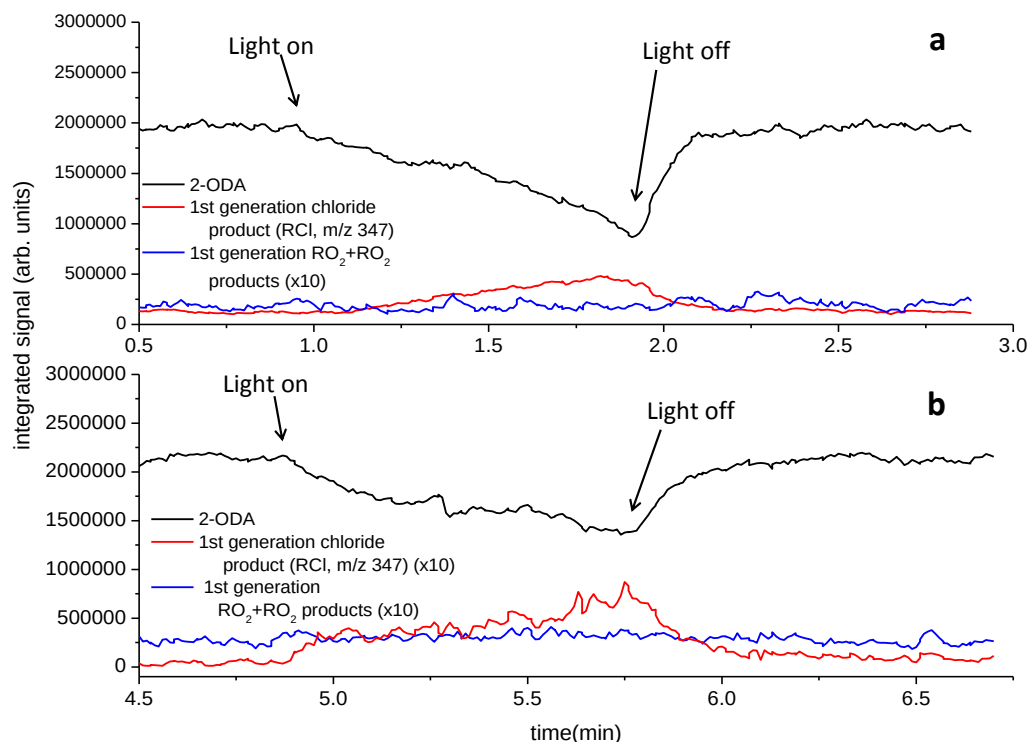


Figure 5.8. time trace of 2-ODA, 1st generation RCl product (from $\text{R}\cdot + \text{Cl}_2$) and 1st generation RO and ROH (ketone and alcohol from $\text{RO}_2 + \text{RO}_2$) in the absence of O_2 with (a) “high” (1.20×10^{15} molecules/ cm^3) and (b) “low” (1.97×10^{13} molecules/ cm^3) concentrations of Cl_2 . Note, in (a) 1st generation $\text{RO}_2 + \text{RO}_2$ scaled by 10x and in (b) 1st generation $\text{RO}_2 + \text{RO}_2$ and RCl scaled by 10x.

It may seem counterintuitive that a lightweight, volatile halogen, Cl_2 , would adsorb to the surface of a liquid 2-ODA particle instead of dissolving in it. To further investigate the plausibility of this, experiments were performed in which Br_2 was added to the flow tube along with Cl_2 to determine whether Br_2 would adsorb and affect the rate of 2-ODA loss. Br_2 was used to decouple the effect of adsorption from the radical reactions since the Br radicals generated by photolysis of Br_2 should not react with the gas-phase reference, acetone, or the particles; for example, the $\text{Br} + \text{acetone}$ rate constant is estimated to be only 1.0×10^{-20}

cm³/molecule/sec. at 298 K ³⁸, and reactions between Br and gas-phase organic compounds are typically orders of magnitude slower than analogous reactions with Cl ³⁹⁻⁴¹. However, the Br₂ is expected to interact with the surface in a similar way as Cl₂ does thereby providing a probe of surface adsorption. The effective uptake coefficient measured from the 2-ODA loss decreased from $\gamma_{\text{part}} = 1.23$ in the absence of Br₂ to $\gamma_{\text{part}} = 0.94$ in the presence of 2×10^{14} molecules/cm³ of Br₂ (Fig. 5.6 open square), a statistically-significant difference at the 99% confidence level. This decrease could have resulted from either or both of two possibilities:

- 1) Br₂ at the surface “deactivates” the Cl radicals by reacting with them:



- or 2) Cl₂ is displaced by Br₂ at the surface thereby reducing the significance of the R + Cl₂ reaction in the radical chain mechanism. Either way, the decrease observed in the 2-ODA reactivity indicates that Br₂ has adsorbed to the particle surface, and by extension implies that the Cl₂ adsorption inferred from the Langmuir-type plot (Fig. 5.6) is reasonable. While it would have been interesting to study this effect as a function of [Br₂] to see if Br₂ also saturates the surface, it was not possible to increase it without adversely influencing the H⁺(H₂O)_n reagent ion signal.

5.4. Implications and conclusions

No difference is observed in the reaction kinetics of 2-ODA aerosols with OH or Cl when the decay profiles are constructed by changing the radical concentration (small flow tube) or the reaction time (large flow tube) as long as the precursor (O₃ or Cl₂) concentration is the same in both cases. Thus, it is appropriate to consider the radical concentration and reaction time as interchangeable parameters with the product of the two, the exposure (= [OH] • t or [Cl] • t), being conserved. Consequently, it seems reasonable to extrapolate results from

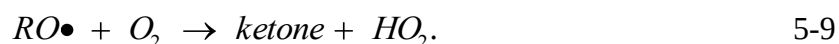
laboratory aerosol flow tube studies, in which reactions are studied with high radical concentrations on the timescales of seconds to minutes, to atmospheric processes, which involve much lower radical concentrations and occur over several days to a few weeks.

However, it has also been observed that the rates of reaction are functions of the concentrations of the precursor species, O_3 or Cl_2 . It was inferred from these dependencies that these species affect the reactivity of the radicals by adsorbing to the surface of the liquid particles. This finding has implications for many gas-particle uptake experiments since high concentrations of precursors are almost always required to carry out the reactions on the seconds-minutes timescale. For example, in the case of OH reaction with 2-ODA particles, extrapolation of the high- $[O_3]$ uptake coefficients to the atmosphere, where O_3 concentrations rarely exceed 250 ppbv⁴² (still 50 times smaller than the smallest concentration used here) would underestimate the rate by 50%. The only way to determine the magnitude of this artifact is to carry out a systematic study as a function of O_3 concentration.

The adsorption of O_3 is also believed to be responsible for the slower rate of reaction observed for squalane in the small flow tube ($\gamma_{part} = 0.10$) compared to the large flow tube ($\gamma = 0.28$) (Fig. 5.3a) where higher $[O_3]$ was used in the small flow tube. Interestingly, O_3 adsorption may also explain the range of values reported by Wilson and co-workers^{17, 18} for the reaction of OH + squalane in which they also used O_3 photolysis to generate OH (shown for comparison in Fig. 4-3a); in an aerosol flow tube study (with a residence time of 37 seconds), they report a value of $\gamma = 0.30$, and in a continuous flow stirred tank reactor (residence time of 1.5-3 hours), they report a higher value of $\gamma = 0.51$. It seems reasonable that they probably used a larger O_3 concentration in the shorter flow tube study and that O_3

adsorption resulted in a smaller uptake coefficient, but O₃ concentrations were not reported in either study.

In the atmosphere, O₃ concentrations are orders of magnitude smaller than those for which adsorption effects were observed to be significant in this study. However, if volatile species such as O₃ and Cl₂ exhibit a Langmuir-type adsorption on the surfaces of organic particles, it seems reasonable that other inert gas-phase species present at much higher concentrations in the troposphere may demonstrate similar behavior. Perhaps N₂, O₂, Ar, H₂O or CO₂, for example, adsorb to the surface of particles and influence rates of gas-particle reactions. In fact, indirect evidence for the adsorption of O₂ to liquid dioctyl sebacate (DOS) particles was observed previously in this lab ¹⁴. In that study, Cl radicals reacted with DOS particles, and the yield of the ketone product initially increased with increasing [O₂] and then approached an asymptote at higher [O₂] (Fig. 7 in that paper ¹⁴). The dependence on [O₂] was described well by a Langmuir-type functional form, and it was inferred that a reaction to create the ketone product was occurring at the surface of the particles:



However, the effect that O₂ had on the rate of reaction was not measured, and further work is required to determine whether species such as O₂, N₂ and H₂O might influence rates of gas-particle reactions under tropospheric conditions.

This work has shown that radical concentration and time can be considered interchangeable parameters in laboratory studies of gas-particle kinetics. However, it has also demonstrated that rates of gas-particle reactions can be influenced dramatically by the adsorption of inert species such as O₃ and Cl₂. This effect may not be specific to O₃ and Cl₂, and the high concentrations of other precursors that are often used in laboratory studies may

also alter the gas-particle kinetics. For example, HONO photolysis can also be used to generate OH radicals, but it is not clear to what extent HONO adsorbs to particle surfaces and how it modifies the uptake kinetics. Clearly, careful consideration of the high concentrations of precursor species used to create radical species in the laboratory must be made in order to accurately extrapolate laboratory results to the troposphere. Finally, this study has examined only single-component, model liquid particles. Likely, the extent and importance of adsorption is dependent on the chemical and physical properties of the particles, but more work is needed to explore this.

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CHAPTER 6

DEVELOPMENT OF AN ULTRA-VIOLET CAVITY RING-DOWN SPECTROMETER FOR AEROSOL EXTINCTION MEASUREMENT

6.1. Introduction

6.1.1 Aerosols and climate

Aerosols in the atmosphere, through their ability to scatter and absorb solar radiation, may influence the earth's radiative balance as well as cause visibility impairment. The ability of aerosols in the atmosphere to directly influence the radiation budget is known as the "aerosol direct effect" and is dependent on particle size, shape, and chemical composition. Whether the aerosol contains primarily absorbing or scattering components will strongly influence the net effect of the aerosol in the troposphere. The direct effect of aerosols on radiative balance and climate may be similar in magnitude to the effects of greenhouse gases and, depending on chemical composition, can range from cooling to warming.¹ Radiative forcing is a term commonly used to describe the effect of tropospheric components on radiative balance and is defined as the change in net radiative flux at the tropopause due to a specific atmospheric component.² Positive radiative forcing values are associated with light-absorbing materials such as soot (i.e. "black carbon, BC") and are linked to atmospheric heating while negative radiative forcing values are associated with primarily light scattering components such as aerosol-associated water, inorganic salts, and organic carbon (OC) and are linked to atmospheric cooling. While radiative forcing values of gases are fairly well restrained, a recent report by the Intergovernmental Panel on Climate Change (IPCC)¹

emphasizes a large uncertainty in aerosol direct effect on radiative forcing. The current lack of understanding in the role of organic aerosols in light absorption is one contributor to the large uncertainty in the climate effect of aerosols, in general.

Although it is conventionally assumed that BC is the only light absorbing species in ambient aerosol and that OC is solely light scattering, growing evidence suggests that some OC species in ambient aerosol absorb UV and visible light. Pöchl suggests a continuum where, at one end, is the strongly light absorbing BC while at the other end are colorless organic substances such as most hydrocarbons and their derivatives.³ In the middle of this continuum are absorbing, organic carbon compounds termed “brown carbon” (BrC) and include polycyclic aromatics, humic-like substances, biopolymers, and highly oxygenated hydrocarbon derivatives.³ Recently, there has been a surge of interest in BrC species due to their high abundance in continental aerosol.⁴⁻⁶ Although the mass absorption efficiencies of BrC species at visible wavelengths are much less than that of BC, their absorbance increases sharply towards lower wavelengths, making their absorption in the UV potentially significant. However, the scientific community is only beginning to understand formation processes of BrC species in ambient aerosol and how the chemical composition of organic aerosol may affect aerosol optical properties such as the absorption and scattering cross sections and the particle refractive index. Laboratory measurements of UV extinction, absorption, and scattering cross sections of organic aerosols as well as a better understanding of the chemical processes which lead to the formation of BrC species is of great importance in understanding the relationship between BrC aerosol chemical composition and UV light scattering and absorption.

6.1.2. Interaction of particles with light

The interaction between aerosols and light is complex and depends on particle size, refractive indices of the particle components, particle morphology, and wavelength of incident light. The solar radiation that reaches the Earth's surface ranges in energy from the ultra-violet (UV, ~300 nm) to the infra-red (IR, ~2500 nm). A dimensionless size parameter, x , is often used to describe the relationship between particle size and incident light and is defined by

$$x = \frac{2\pi r}{\lambda} \quad 6-1$$

where r is the particle radius and λ is the wavelength of light incident on the particle. When $x \ll 1$, the interaction between the small particles and incident radiation may be described by elastic, or Rayleigh, scattering. When the wavelength of light and particle size are on or about the same order of magnitude, the interaction between the particles and incident radiation is well described by Mie theory and is dependent on particle refractive index (RI).

$$RI = n + ik \quad 6-2$$

where n is the real component of the refractive index and k is the imaginary component of the refractive index. Mie theory describes how particle size and refractive index influence the re-radiation pattern from oscillating electrons in the molecules of spherical particles that have been exposed to a certain wavelength of light. Due to constructive and destructive interference in the re-radiation of electrons, the particles scatter light in various directions with varying efficiency and the resulting pattern is unique to particles of a given size parameter and refractive index.

The fraction of light attenuated through scattering and absorption of a single particle is given by the extinction cross section and is the sum of scattering and absorption cross sections.

$$\sigma_{ext} = \sigma_{scat} + \sigma_{abs} \quad 6-3$$

When electromagnetic radiation travels through a medium or atmospheric layer in which it gets absorbed or scattered, the light undergoes exponential decay as described by the Beer-Lambert law:

$$dI = I_o \exp(-\alpha_{ext} dz) \quad 6-4$$

where dI is the change in intensity of light as it passes through the depth of the layer, dz , and α_{ext} is the extinction coefficient in units of m^{-1} . The extinction, scattering, and absorption coefficients are related to the particle-size-dependent extinction, scattering, and absorption cross sections through

$$\frac{\alpha_{ext}}{N} = \sigma_{ext}; \quad \frac{\alpha_{scat}}{N} = \sigma_{scat}; \quad \frac{\alpha_{abs}}{N} = \sigma_{abs} \quad 6-5$$

where N is the number concentration of particles of a given particle size.

6.1.3. Cavity ring-down spectroscopy

Cavity ring-down spectroscopy (CRDS) is an optical measurement technique that allows the highly sensitive measurement of absolute optical extinction by samples that extinguish light through scattering and absorption. In CRDS, light from either a pulsed or continuous-wave laser is stored in an optical cavity with two highly reflective mirrors on axis with the laser light. The high reflectivity of the mirrors allows for pathlengths that exceed a thousand times the sample length in a way that is insensitive to variations in the intensity of the light source. As the mirrors are not 100% reflective, a minute amount of light is transmitted

during each pass and the transmitted light is measured using a detector that measures or is directly proportional to the intensity of light which was transmitted. The signal decay is then analyzed using an oscilloscope. The intensity of the pulse inside the ring-down cavity decreases exponentially in time with a rate determined by the reflectivity of the mirrors and the length of the cavity. The time constant for the exponential decay of the intensity of light stored in the CRDS cavity is referred to as the ring-down time, τ .

$$\frac{I}{I_o} = \exp(t / \tau) \quad 6-6$$

where I_o is the intensity of the incident light, I is the measured intensity at a given time, t . In an empty cavity, the rate of the intensity decay depends only on the reflectivity of the mirrors and the length of the cavity and the ring-down time is referred to as τ_o . When the ring-down cavity contains an absorbing or scattering species such as aerosol particles, additional optical loss occurs which causes a decrease in the ring-down time, τ . Because it is the rate of decay in intensity that is measured in CRDS, and not the absolute intensity, fluctuations in the intensity of incident light do not affect analysis. A wide variety of CRDS systems exist which vary in the wavelength of light, cavity dimensions, and whether pulsed or continuous-wave lasers are used. While the most common CRDS systems utilize visible wavelengths, wavelengths ranging in energy from the UV to the infrared are used.

Although cavity ring-down spectroscopy has been used to study gas scattering and absorption since 1988,^{7, 8} it has only recently been established as a useful analytical technique for obtaining aerosol optical properties such as extinction, scattering, and absorption cross sections and efficiencies, complex refractive indices, and single scattering albedo.⁹⁻¹³ As discussed in Section 6.1.2., Mie theory may be used to determine theoretical extinction cross sections of spherical particles if the particle size and refractive index are known. Likewise, a

reverse Mie fitting algorithm may be used to retrieve the refractive index of the particle species if the extinction cross sections and particle sizes are known. The extinction cross section (σ_{ext}) for a given particle size is related to the extinction coefficient α_{ext} by the number concentration of particles, N :

$$\sigma_{\text{ext}} = \frac{\alpha_{\text{ext}}}{N} \quad 6-7$$

Measurement of extinction cross section at various particle sizes allows for the determination of the complex refractive index, which offers information about particle optical properties such as absorption, as the imaginary component of the refractive index is related to light absorption.

The recent interest in BrC species has led our lab to develop a CRDS system which operates at UV wavelengths. In the CRDS experiments discussed herein, 355 nm light from the third harmonic of an Nd:YAG laser was used. Sensitive measurements of the extinction cross section of organic aerosols of known composition at various particle sizes (and thus at various size parameters) were made allowing for the retrieval of complex refractive indices using a reverse Mie-fitting algorithm. For non-absorbing aerosols, these measurements were compared to refractive index measurements which were made with a Snell's Law cell.

6.2. Materials and methods

6.2.1 Ring-down cavity specifics

The cavity is constructed of a ¾ inch outer diameter (o.d.) stainless steel tube, mounted on an optical breadboard table. Highly reflective mirrors (model number 901-0008-0365, Los Gatos Research, Inc., quoted reflectivity 99.97%, 0.8" diameter, 6" radius of curvature) are mounted on each end of the cavity and the length between the two mirrors is 1.0 m. At a

length of 3" from each end of the cavity, an inlet and outlet port (3/4" o.d., 3" length) are situated at an angle of 45°. A 10-15 sccm purge flow was placed on each mirror in order to prevent particle deposition. At the junction of the inlet and outlet ports with the cavity, two Teflon plugs were placed in order to prevent particle deposition on the high-reflectivity mirrors and in order to confine the main flow to the sample volume (the volume between the sample inlet and outlet ports). A diagram of the CRD cavity is shown in Figure 6.1.

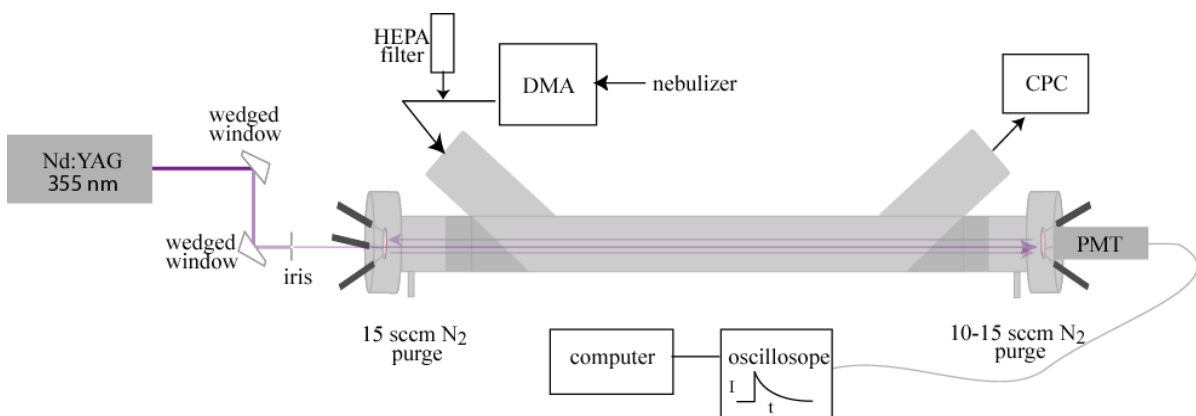


Figure 6.1. Diagram of cavity ring-down experiment.

The maximum obtainable fluence (~ 350 mJ/pulse) of the third harmonic (355 nm) of an Nd:YAG laser (QuantaRay PRO-250, Spectra-Physics) exited the laser head and proceeded through a series of optics to decrease the light intensity. After exiting the laser, the 355 nm light was reflected by a series of two wedged windows in order to reject $\sim 95\%$ of the light at the front face of each window. After the wedged windows, only ~ 9 mJ /pulse remained. This light was passed through a visible filter in order eliminate more of the 532 nm light that may not have been rejected by the dichroics in the laser or at the wedged windows. Some additional loss of 355 nm light also likely occurs at the visible filter. Lastly, an iris was used to select only the highest quality section of the beam to enter the cavity. The power of 355

nm light that is directed into the cavity is thus estimated to be ~5-8 mJ/pulse. The light that enters the ring-down cell is a small fraction of this power, as the light must pass through the back of one of the highly reflective mirrors to enter the cavity. After entering the cavity, the light is reflected within the cavity and the small amount of light that passes the mirror at the end of the cavity passes through a diffuser and 355 nm filter before being detected by the photomultiplier tube. The calculated reflectivity of the mirrors is 99.84%, comparable to the specification by the manufacturers (99.97%). This reflectivity was determined by the following equation:¹⁴

$$1 - R = \frac{L}{c \tau_o} . \quad 6-8$$

where R is the mirror reflectivity, L is the cavity length (1 m) and c is the speed of light and τ_o is the empty cell ring-down time where only N_2 and filtered air were present in the cavity ($\sim 2.10 \times 10^{-6}$ μ s). The effective pathlength of the empty ring-down cavity is approximated by:

$$l_{eff} = \tau_o c . \quad 6-9$$

With $\tau_o = 2.10 \times 10^{-6}$ seconds, the effective pathlength is 630 meters.

6.2.2. Cavity ring-down measurements of aerosol extinction

For studies of model organic aerosols, a differential mobility analyzer (DMA) was used to select particle sizes from a nebulizer output where the organic species of interest was directly nebulized without dilution. The DMA, which uses electrical mobility diameter to size select particles, allows only selected particle sizes to exit into the CRD. In order to eliminate doubly charged particles, an impactor is used to impact large particles and the 50% cut-point of the impactor is easily changed by adjusting the flow through it. To obtain an

empty cavity reading, the voltage on the DMA was dialed down to 0V so that no aerosol would enter the CRD cavity but the flows would remain the same.

The width of the particle size distribution exiting the size-selecting DMA was determined using two DMAs connected in series and the outlet of the second DMA was coupled to a condensation particle counter (CPC). As the voltages (and thus electrical mobilities) were adjusted on the second DMA, the CPC was used to count the particles as they exited. The distribution width was determined by first setting both DMAs to the same voltage and then observing the decrease in particle counts when one or the other DMA was adjusted away from that value. The geometric standard deviation of the particles exiting the size-selecting DMA was determined to be 1.05 using this method. Although size distribution widths from DMAs which are similar or equivalent in design to the TSI model 3081 used here range from 1.03 and 1.07, ¹⁵⁻¹⁸ typical distribution widths are most commonly 1.05 or greater.¹⁹

To determine particle concentrations, a CPC was used. For the model organic aerosol experiments discussed below, either a butanol-based CPC (bCPC, TSI, Inc. model 3775) or water-based CPC was connected to the CRD cavity outlet flow. The total flow through the ring-down cavity was controlled by 1) pumping 1.0 SLPM through the cavity with the wCPC, 2) pumping 1.0 SLPM through the cavity with either the wCPC or a diaphragm pump and 0.3 SLPM with the bCPC.

In order to determine the extinction coefficient (in units of m^{-1}) in the presence of an aerosol, the following relationship is used:⁹

$$\alpha_{ext} = \frac{R_L}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_o} \right) \quad 6-10$$

where R_L is the ratio of the cavity length (from mirror to mirror) to the length between the inlet and outlet ports (the length of the cavity which contains the particulate sample), c is the

speed of light, and τ and τ_0 are the ring-down times with and without particles, respectively. Example ring-down decays showing a change in the time constant when particles are added are shown in Figure 6.2. The extinction coefficient (equation 6-10) is measured over a range of particle concentrations and the extinction cross sections are determined by the slope of the linear fit of α_{ext} vs. N . For species of known refractive index, Mie theory may be used to predict σ_{ext} and components of the cavity ring-down system may be adjusted to minimize the error in the σ_{ext} measurements with respect to predicted values.

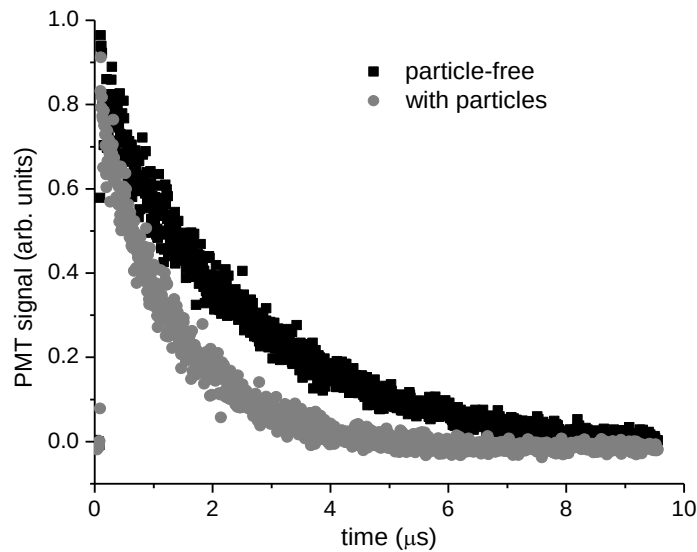


Figure 6.2. Example exponential decays for an empty cell (particle-free) and for a cell containing particles. The change in the time constant of the exponential decay is used to determine the extinction cross section.

6.2.3. Mie algorithms

Prediction of theoretical extinction cross sections

The theoretical extinction cross sections for monodisperse particles were calculated using a Mie code for each combination of real and imaginary indices of refraction values $1.400 < n < 1.700$ and $0.000 < k < 0.200$ where the complex refractive index is $RI = n + ik$. The

Mathematica Mie code used herein was written by Art Lompado at the University of Alabama at Huntsville from references therein and is available online for public use.²⁰ To account for the width of the particle size distribution on the predicted cross sections, the fractional contribution of each particle size in the log-normal distribution was accounted for.

Fitting measured extinction cross sections to complex refractive index

The best fit complex refractive index is found by minimizing the merit function, χ^2 :

$$\chi^2 = \sum_{i=1}^N \frac{(\sigma_{meas} - \sigma_{calc})^2}{\epsilon_{i\ meas}^2} \quad 6-11$$

where N is the number of particle sizes and ϵ is a measure of the error of each measured cross section. In these experiments, ϵ was treated as unity for each particle size thus the merit function was used to minimize the difference between the extinction cross section measurements only without accounting for other sources of error. The best fit refractive index is then the set of real and imaginary components, n and k, for which χ^2 is at a minimum. Doubtless, the error in the cross section measurement will affect the uncertainty associated with the best fit. However, as the purposes of these experiments are to develop the UV cavity ring-down experiments and minimize the large sources of error in the ring-down experiments, these other sources are ignored. Currently, we are working toward a better understanding of the sources of error in these experiments and what parameters in the ring-down measurements are the largest sources of uncertainty.

6.3. Results and discussion

6.3.1. Ring-down time flow dependence

The 30 second averaged particle-free cell ring-down time and standard deviation were observed as a function of total cavity flow. These results are shown in Figure 6.3. When the

total flow is increased from 1.0 slpm to 2.0 slpm, there is no effect on the particle-free ring-down time. However, if the total flow is increased past this point, the ring-down time decreases and the uncertainty in the ring-down time increases. One explanation for this behavior is that when the flow is increased past 2.0 slpm, the mirrors go slightly out of alignment. However, when the flow is decreased again, the ring-down time recovers completely suggesting misalignment may not explain this phenomenon as the alignment would not be expected to return to the exact configuration each time the flow was decreased.

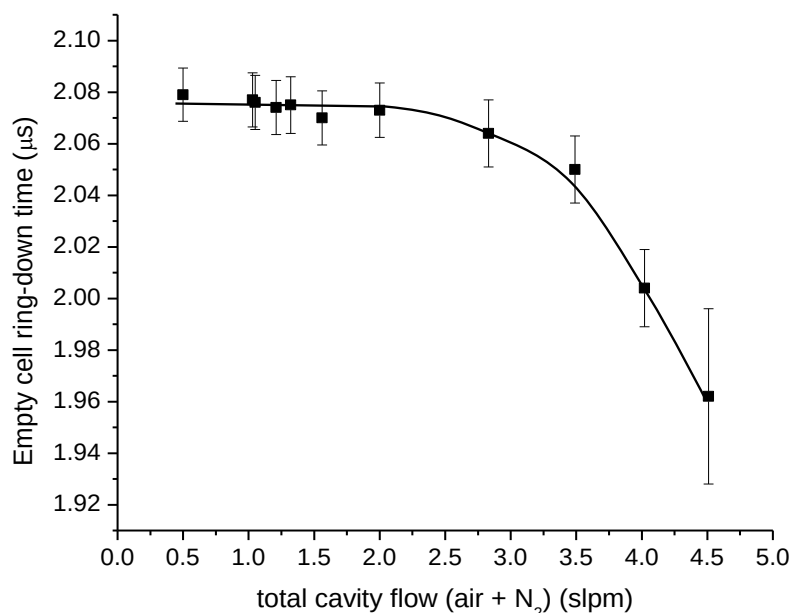


Figure 6.3. Dependence of empty cell (particle-free) ringdown time on the flow of gases (N₂+ air) through the cavity.

6.3.2. CO₂ Rayleigh scattering measurements

In order to confirm the CRD cell was able to be used to obtain the expected Rayleigh scattering cross section for CO₂ at 355 nm, either pure CO₂ or N₂ was introduced taking care that the flow always remained constant (1-1.2 slpm) throughout the ring-down cell as to not cause the mirrors to misalign. Approximately 20 ft. of tubing were used between the gas

cylinder and the ring-down cavity in order to ensure that the gas was at room temperature before entering the cavity. The gases were alternated 5 times, obtaining 5 different measurements of the change in ring-down time upon introduction of CO₂. The average measured cross section was 7.15×10^{-26} cm²/molecule. This compares very well to the literature value of $\sim 7 \times 10^{-26}$ cm²/molecule (from Fig. 1, therein).²¹

6.3.3. Standardization of cavity ring-down measurements

Because cavity ring-down measurements are absolute, calibration is not required. In fact, it has been established that the CRD may be used for the accurate determination of Rayleigh scattering cross sections of CO₂. However, if particle and air flows are not well mixed, if the CPC is not counting the particles efficiently, if the DMA is not size-selecting properly, or if there are other unforeseen experimental problems which may lead to faulty particle extinction cross section measurements, comparing the measured extinction cross sections to known values is essential. As discussed above, if the refractive index of a particle is known, and the particle is spherical (a good assumption for liquid droplets), Mie theory may be used to predict the extinction cross sections. While the refractive indices of many chemicals have been determined at visible wavelengths (most commonly, 589 nm), very little literature exists on refractive indices of organic species in the UV. While some UV refractive index data exists for small organic species²²⁻²⁴ the refractive indices of large (>200 g/mol), low vapor pressure, organic liquids at UV wavelengths are scarce in the literature. Since the refractive index varies with wavelength and this dependence is different depending on the material, extrapolation of measurements into the UV is insufficient for these purposes as the Mie-predicted cross sections vary greatly with refractive index. Therefore, precise measurement of the refractive indices at 355 nm was required.

In order to measure the refractive index of some large organic species that are amenable to liquid particle formation (low vapor pressure, low melting point), an apparatus was used that utilizes the law of refraction, or Snell's Law:

$$\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_2}{n_1} \quad 6-12$$

where θ_1 and θ_2 are the angles, measured from the normal, of the incident and refracted beams through materials 1 and 2, and n_1 and n_2 are the refractive indices of materials 1 and 2. In this case, material 1 was always air ($n=1.000$) and material 2 was the organic species of interest. A diagram of this apparatus is shown in Figure 6.4.

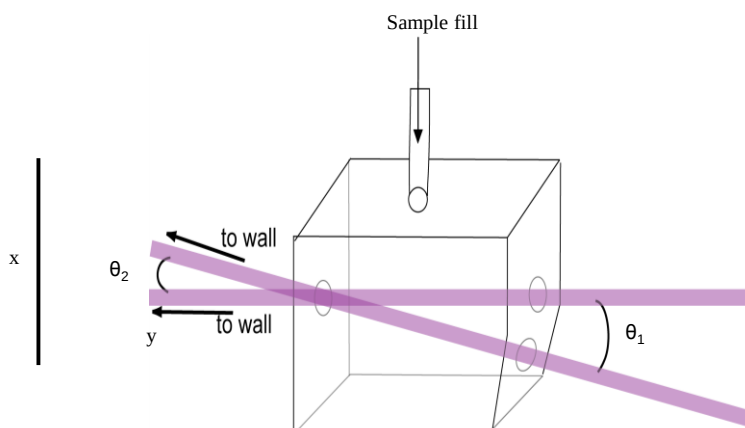


Figure 6.4. Diagram of the Snell's Law apparatus used to measure the real component of the refractive index of the various solvents and non-volatile organic compounds listed in Table 6.1.

The angle of the incident beam, measured from the normal, as the light traveled through air was determined by performing an empty cell measurement and the x and y coordinates were used to determine $\theta_{air} = \tan^{-1}(x/y) = 15.26^\circ$. The cell was then filled with the organic species of interest and the angle of light as it passed from the sample to air was measured. A table of measurements which were made with the Snell's Law cell are shown in Table 6.1. In order to ensure that the cell was aligned correctly and that accurate refractive indices could

be measured, measurements of a variety of solvents that have published refractive indices were made and are included in the same table.

Table 6.1. Summary of Snell's Law measurements of the real component of the complex refractive index, n , of solvents and large molecular weight, low volatility liquids.

	Isopropanol	Methanol	Acetonitrile	Ethanol	Water
Measured	1.393(± 0.002)	1.342(± 0.002)	1.359(± 0.002)	1.378(± 0.002)	1.347(± 0.002)
Literature²⁴	1.393	1.342	1.358	1.377	1.348
	DOS	Sq	OA	2-ODA	
Measured	1.469(± 0.002)	1.472(± 0.002)	1.483(± 0.002)	1.471(± 0.002)	

The Snell's Law cell data for common solvents shows that for every organic species studied, the measured refractive index is in good agreement with the published refractive indices to the third decimal place. For the large molecular weight, low volatility species which are amenable to liquid particle formation, the data here represent the first refractive index measurements made of these species at 355 nm to the best of my knowledge.

6.3.4. Calculation of predicted extinction cross sections.

For those species measured in the Snell's law setup (Section 6.3.3) that are able to form pure, low-volatility particles through nebulization and which show very little to no absorption at 355 nm in the UV-Vis spectra (not shown), direct comparisons between the cross sections obtained on the cavity ring-down instrument and those calculated from the Snell's Law refractive indices may be made. For instance, squalane, a large molecular weight, branched, saturated hydrocarbon which exhibits no absorption at 355 nm was measured using the Snell's Law setup to have a real refractive index of $n_{Sq} = 1.472$. Because

the absorbance of squalane is zero at 355 (confirmed by UV-Vis), the complex refractive index may be written as $RI_{Sq} = 1.472 + 0.000i$ and the Mie algorithm may be used to calculate the cross sections of various sized particles. The relative error may then be used as a metric for what experimental conditions may affect the cavity ring-down instruments such as the effect of the mirror purge flows, DMA sheath and samples flows, and the total gas flow through the ring-down cavity. The predicted extinction cross sections as a function of particle diameter for a particle size distribution with a geometric standard deviation of 1.05 are shown in Figure 6.5.

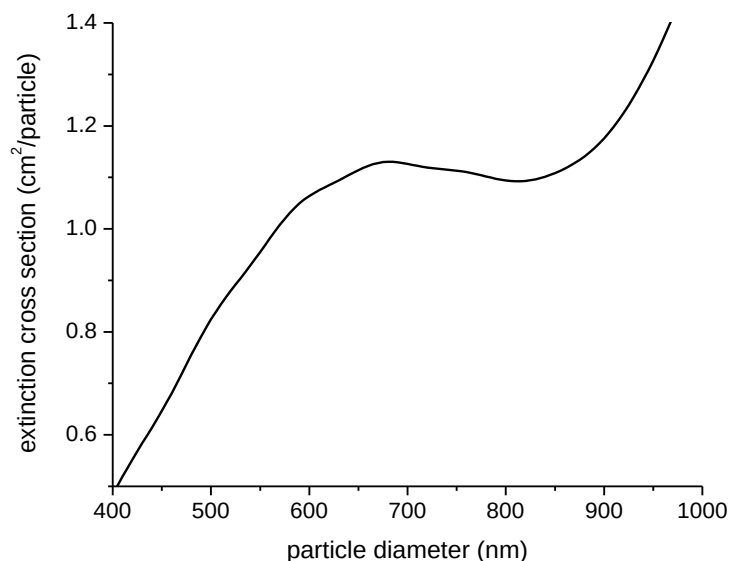


Figure 6.5. Predicted extinction cross sections for particles with a refractive index $RI = 1.472 + 0.000i$.

6.3.5. Initial cavity ring-down results

When these experiments were first being developed, a water-based CPC (wCPC) was used to count the particles at the outlet of the ring-down cavity. Regardless of the combination of mirror purge and cavity flow rates, the relative error was always positive by more than 20% and was dependent on particle type (OA, DOS, or Sq). This problem was

attributed to the undercounting of the organic aerosol particles by the wCPC and a butanol-based CPC (bCPC) confirmed this hypothesis. In short, the wCPC, which like the butanol CPC relies on growing the aerosol to a size of 1-2 μm in order to scatter light at the detector and be counted, is not able to grow the model organic aerosol compounds studied here due to the hydrophobicity of the aerosol components. A comparison between the counting efficiencies of different organic species using a bCPC and wCPC is presented in Appendix A.

6.3.6. Mirror purge flow dependence

Using a bCPC for counting the particles, the effect of the mirror purge flow on the relative errors of extinction cross section measurements for 500 nm (OA), squalane (Sq) and diocyl sebacate (DOS) particles were measured and are shown in Figure 6.6. At low purge flows, the relative error is independent of purge flow. However, above 20 standard cubic centimeters per minute (sccm), the relative error drops off rapidly with increasing flow. It is not clear what causes this purge dependence. One explanation is that as the purge flow is increased, the flow enters the cavity at the exact radial position as the light path. The sample volume is thus diluted although the entire volume is not diluted to the same degree so that the light extinction per particle is a smaller value than expected.

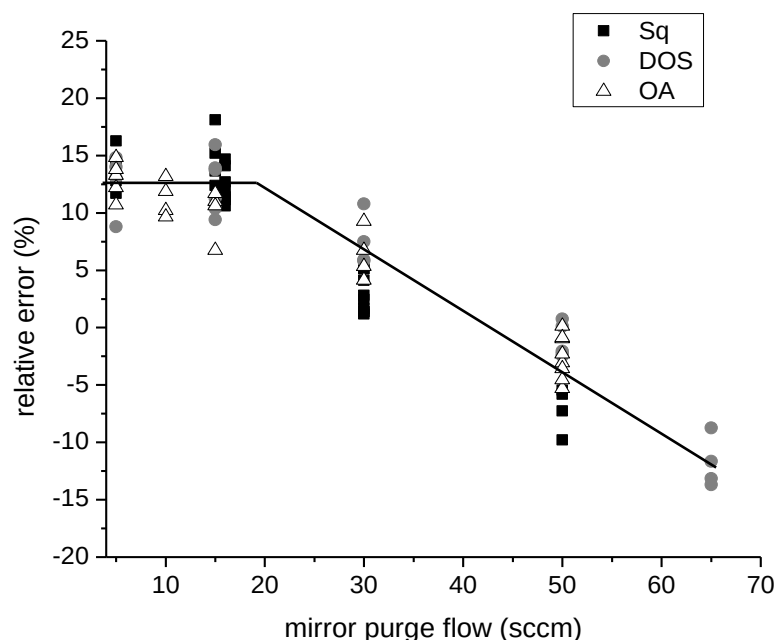


Figure 6.6. Effect of the mirror purge flow on the relative error of the extinction cross section for 500 nm Sq, DOS, and OA particles. The relative error is large at low flows due to the undercounting of 500 nm particles by the CPC.

From the purge flow dependence plot, it is clear that the relative errors in extinction cross sections for 500 nm OA, DOS, and Sq particles are all positive by the same magnitude. From repeat extinction cross section measurements of 500, 550, 600, 700, 750, and 800 nm Sq particles at 15 sccm mirror purge flows, the relative error appeared to display a size dependence where the relative errors were 10.3%, 9.0%, and 6.5% for 500, 550, and 600 nm particles and less than 1% error between 700 and 900 nm for particles with a geometric standard deviation of 1.05. The positive relative error between 500 and 600 nm was attributed to a slight size dependence of the bCPC counting efficiency. Doubly charged particle contribution was considered negligible due to the constancy of the relative error when the 50% cut-point of the DMA was changed so that sizes correlating to doubly charged particles could pass through the DMA and enter the ring-down cavity.

6.3.7. Offset correction and reverse Mie fitting algorithm

The relative errors calculated for 500, 550, and 600 nm Sq particles were used to apply correction factors to the extinction cross sections of OA and DOS at these sizes. Since the relative error of the measured extinction cross sections of 700, 800 and 900 nm Sq particles was found to be less than 1%, the extinction cross sections for OA, DOS, and Sq at these sizes were uncorrected. The resulting cross sections for each species were entered into the reverse Mie fitting algorithm in order to extract the best fit refractive indices from the measured extinction cross sections. The results of the reverse Mie fit to the measured extinction cross sections of OA and DOS and Sq are shown in Figure 6.7a-c. Also shown are the results for the Snell's Law measurement, described in Section 6.3.3.

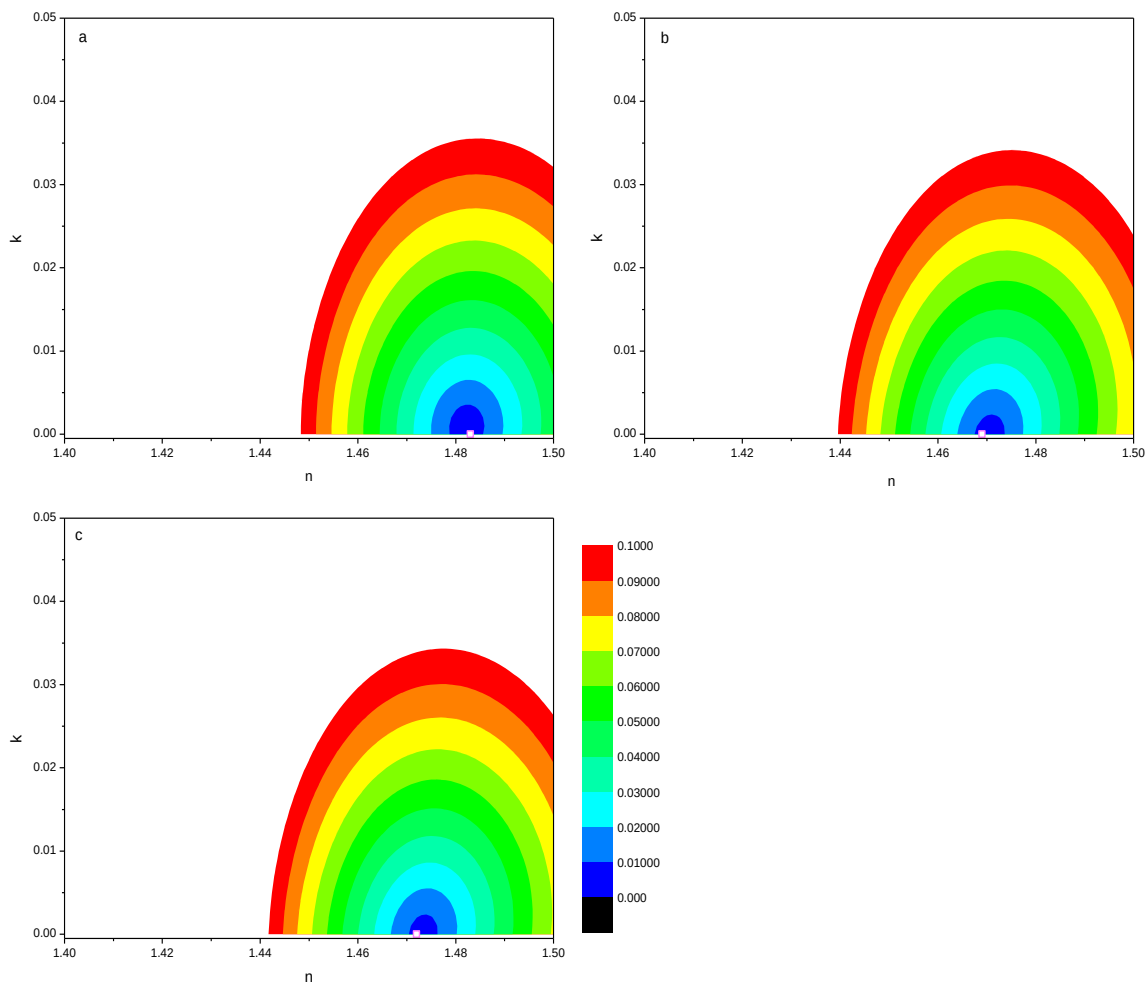


Figure 6.7. Real and imaginary components of the complex refractive index, n and k , for **a)** OA, **b)** DOS, and **c)** Sq where the contour lines represent the error of the reverse Mie fit (in μm^2). The measurements of n using the Snell's Law apparatus are shown as pink squares.

Although using the extinction cross sections of all six particle sizes to fit to a refractive index results in good agreement with the refractive index measured using Snell's Law, use of the extinction cross sections at any three of the sizes results in comparable uncertainty in the resulting refractive index and are also in good agreement with the Snell's Law measurements. As an example, the best fit refractive index from the extinction cross sections of smaller (500-600 nm) and larger (700-900 nm) oleic acid particles are shown in Figure 6.8a-b. and a summary of the best fit refractive indices for all three species are shown in Table 6.2.

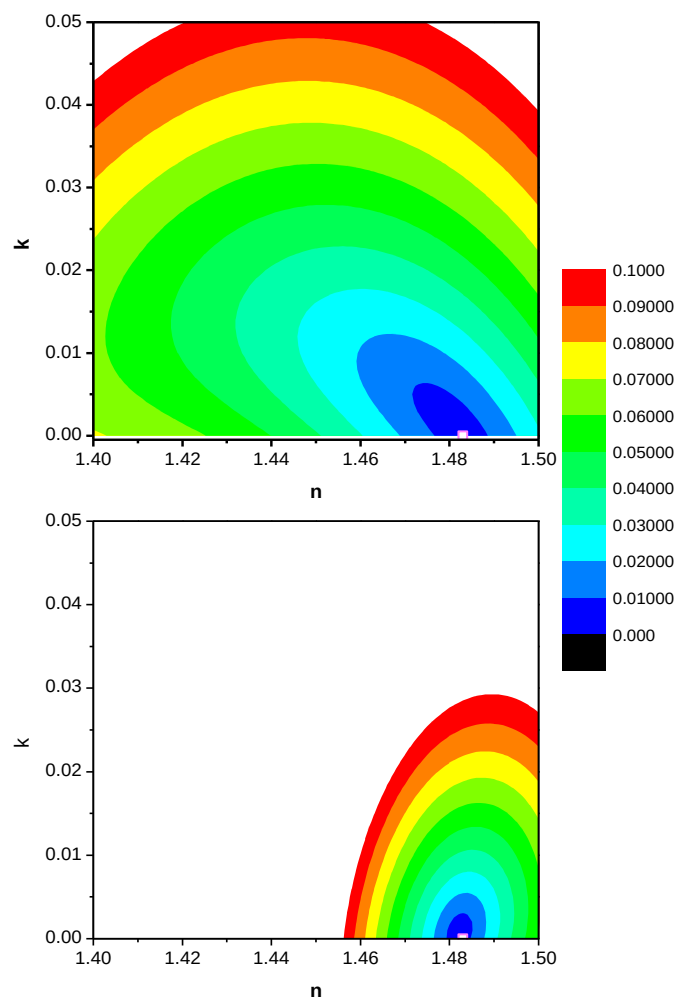


Figure 6.8. Real and imaginary components of the complex refractive index, n and k , from the reverse Mie fit in which the extinction cross sections of **a)** 500, 550, and 600 nm and **b)** 700, 800 and 900 nm oleic acid particles were used in the reverse Mie fitting algorithm. The measurements of n using the Snell's Law apparatus are shown as pink squares.

Table 6.2. Best fit refractive indices for OA, DOS, and Sq using 500, 550, and 600 nm data, 700, 800, and 900 nm data and all six sizes. Also shown are the Snell's Law measurements of the real component of the refractive index, n .

	500, 550, 600 nm ($n+ki$)	700, 800, 900 nm ($n+ki$)	All six sizes ($n+ki$)	Snell's Law measurement (n)
DOS	1.469+ 0.002i	1.470+ 0.000i	1.470+ 0.000i	1.469
OA	1.482+ 0.001i	1.482+ 0.001i	1.482+ 0.001i	1.483
Squalane	1.472+ 0.003i	1.472+ 0.000i	1.473+ 0.000i	1.472

As evident from Figure 6.8, only half of the data generated above is needed to obtain a refractive index fit that is in good agreement with the Snell's Law measurement; however, the choice of sizes have advantages and disadvantages. While using extinction cross section data from 500-600 nm particles requires a correction factor to be used in order to account for the undercounting of the CPC, the predicted extinction cross sections used in obtaining the best fit refractive index is more or less independent of the particle size distribution width (Figure 6.9). Conversely, using extinction cross section data from 700-900 nm particles does not require correction factors be applied and the uncertainty in the real and imaginary component of the refractive index is less than when smaller sizes are used. However, measurements at larger particle sizes are more sensitive to changes in the width of the particle size distribution which may be sensitive to changes in DMA parameters such as sample and sheath flow rates.

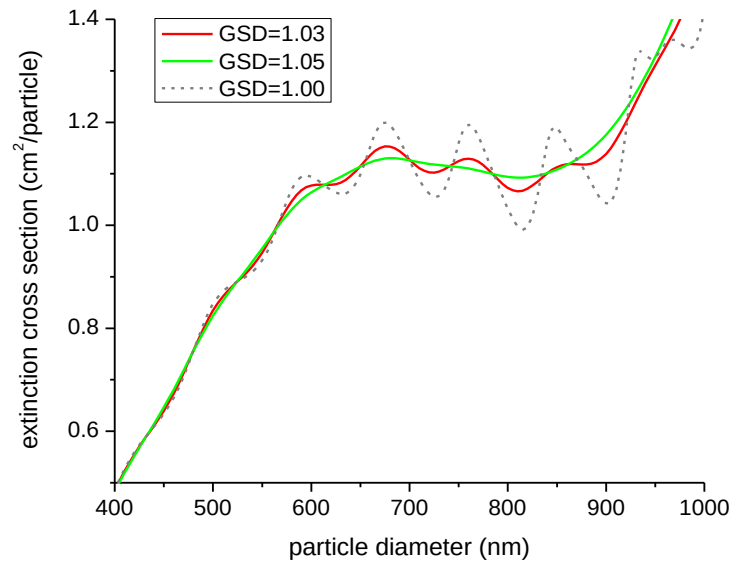


Figure 6.9. Theoretical extinction cross sections for $RI = 1.472 + 0.000i$ showing the effect of the geometric standard deviation of the particle size distribution on the predicted cross sections. The dashed line represents perfectly monodisperse particles.

While the extinction cross sections measured and used in the calculation of the complex refractive indices displayed in Figures 6.7 and 6.8 for 700- 900 nm particles are consistent with a particle size distribution with a geometric standard deviation of 1.05, the width of the distribution that exits the DMA may be sensitive to many factors including the sheath and sample flow rates through the DMA.¹⁹ Recent evidence from these experiments has suggested that the particle size distribution width may not always be consistent and thus may need to be determined in real-time during these experiments.

6.3.8. Evidence of absorption following oxidation

Yellow oleic acid

The ultimate goal of the UV cavity ring-down experiments is to observe changes in particle optical properties during BrC-forming reactions and to relate those changes to changes in the chemical composition of the aerosol. Although we have not come as far as simultaneously analyzing the chemical composition of oxidized aerosol, we have observed an increase in the 355 nm absorption of oxidized oleic acid (Figure 6.10) compared to pure oleic acid (Figure 6.8) in the best fit refractive indices obtained from the extinction cross sections of these particles. The best fit refractive index for the oxidized oleic acid was $1.482 + 0.007i$ compared to $1.482 + 0.001i$ for pure oleic acid. For these experiments, 500-600 nm particles were selected in order to determine the best fit refractive index in order to negate any changes in the width of the particle size distribution. Oleic acid was oxidized by heating in the sunlight for ~6 hours at 50-75°C and purged with nitrogen for ~2 hours to remove some semi-volatile impurities.

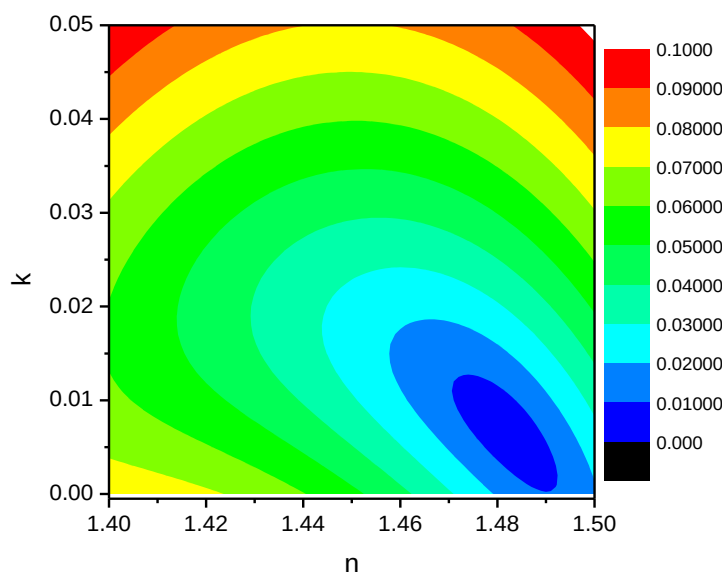


Figure 6.10. Results of the reverse Mie fit to the complex index of refraction for yellow oleic acid for which the extinction cross sections measured for 500, 550 and 600 nm particles were used. The best fit refractive index is $1.482 + 0.007i$.

The increase in absorption upon oxidation has important consequences for radiation balance in the troposphere. As the absorptive, or imaginary, component of the refractive index increases, the relative contributions of scattering and absorption to the total light extinction change. For instance the single scattering albedo (SSA), defined as the ratio of scattering cross section to total extinction (scattering + absorption) cross section, decreases drastically with increasing imaginary refractive index. For instance, a change in the imaginary component of the refractive index from $k = 0.00$ to $k = 0.01$ may change the SSA of 900 nm oleic acid particles by 20%. Shown in Figure 6.11 is a plot of SSA versus k for 900 nm particles with $n=1.483$.

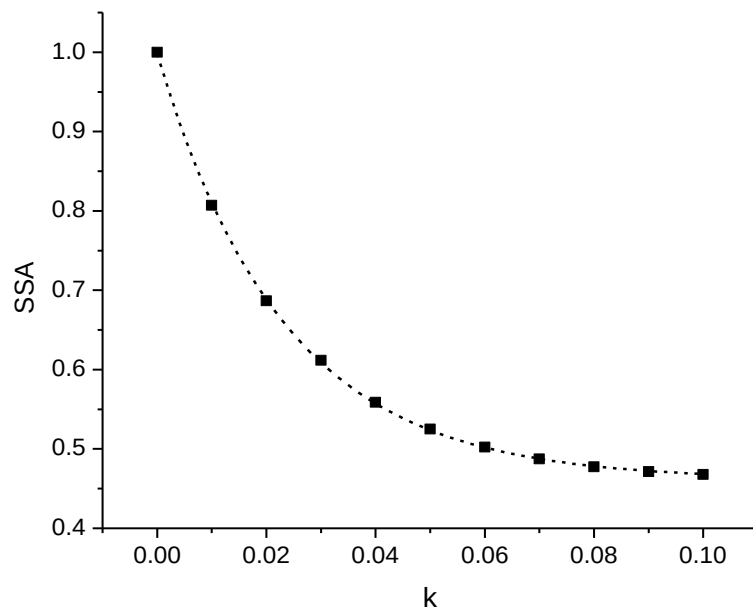


Figure 6.11. Single scattering albedo, SSA, as a function of k , the imaginary component of the refractive index, for 900 nm particles with $RI = 1.483 + ki$.

6.4. Conclusions and future direction

Although cavity ring-down spectroscopy is inherently an absolute measurement technique, many considerations must be made in using this technique for the analysis of aerosols. First, the gas flows may affect the movement and dilution of particles as they traverse the ring-down cavity. Secondly, sensitive and accurate detection of the particle concentration are needed in order to quantify particle extinction cross sections and accurate particle size information is needed in order to compare measured extinction cross sections with theoretical extinction cross sections. In addition, depending on the size parameter, the width of the size distribution may be required in order to accurately predict theoretical cross sections. With these considerations, best fit refractive indices from the reverse Mie algorithm match those measured with a Snell's Law apparatus. In addition, evidence for increased

absorption upon oxidation has been observed and these results have important implications for the aerosol direct effect in the troposphere.

As of yet, there are many practical issues which must be addressed in order to quantify changes in particle optical properties. A better understanding of the sources of error in the extinction cross section measurements are needed in order to determine the minimum detectable change in the refractive index we can measure. In order to reduce the uncertainty in the extinction measurements, a real-time measure of the particle size distribution is needed. This will allow extinction cross section measurements to be made in the particle size regime where the extinction cross section is most sensitive to changes in the refractive index. Also, in order to verify the reverse Mie fit gives an accurate description of absorption, comparisons with UV-Vis absorption coefficients should be made and differences should be reconciled. While those species which show evidence of absorption in the UV-Vis spectra also show increased imaginary refractive indices, currently a major discrepancy exists between absorption coefficients determined by UV-Vis measurements on bulk samples and the molar absorption coefficients according to:

$$\alpha = \frac{4\pi k}{\lambda} \quad 6-13$$

where α is the absorption coefficient in cm^{-1} , k is the imaginary refractive index and λ is the wavelength. For instance in the case of yellow oleic acid, $k = 0.007$ yields an absorption coefficient of $2.48 \times 10^3 \text{ cm}^{-1}$ compared to an absorption coefficient of 1.44 cm^{-1} from the UV-Vis measurement, a difference of a factor of more than three orders of magnitude. The source of this discrepancy is currently unresolved and may be associated with the unique interaction of light with these particles.

While this technique is still in the developmental stages, it holds much promise for providing valuable information on the optical properties of organic aerosols and how those properties change upon reacting. There are multiple browning reactions that would be worth exploring. In particular, the formation of HULIS from ammonium sulfate/glyoxal reactions would be interesting and have been shown to form highly absorbing species in the UV ²⁵(also Appendix B). Also, the formation of highly conjugated, UV-absorbing, nitrogen containing species from the chemical aging of secondary organic aerosol from terpene ozonolysis would be interesting to explore.²⁶⁻²⁸ Although Mie theory is restricted to spherical particles, changes in light extinction during organic nitrate forming reactions on solid particles would be worth exploring and would enable us to tie together the cavity ring-down and Aerosol-CIMS experiments performed previously.²⁹ While many other browning reactions exist, these systems may serve as a starting point in measuring optical property changes during potentially atmospherically relevant brown carbon forming reactions.

Much valuable information may be gained by coupling the cavity ring-down instrument to the aerosol flow tube/ Aerosol CIMS instruments in order to observe changes in particle optical properties as a function of oxidant exposure. In this way, it may be possible to observe changes in the scattering and absorption of particles as they are chemically aged while simultaneously gaining chemical information about the particles which may contribute to those optical changes (i.e. increased functionalization, polymerization, etc). Additionally, coupling the cavity ring-down instrument to other instruments capable of measuring particle scattering and/or absorption would provide additional information on the optical behavior of particles in the troposphere and thus their role in the direct radiative forcing effect. For example, integrating nephelometry may be used to quantify scattering cross sections from

particles in the visible (550, 650, 700 nm) region of the solar spectrum, and photoacoustic spectroscopy may be used to provide absorption measurements simultaneously with the cavity ring-down experiments in the UV. Also, additional cavity ring-down instruments may be constructed which operate at other wavelengths in order to simultaneously measure extinction cross sections at two or more size parameters, allowing for more optical information to be gained in the same amount of time. These wavelengths would only have to be ~ 30 nm apart in order to simultaneously measure cross sections at maxima and minima in the extinction vs. size parameter plot. With only a 30 nm change in wavelength, the change in refractive index would be negligible and these data may be used to extract the complex refractive index with twice as many data per time than using one ring-down cavity alone.

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CHAPTER 7

CONCLUSIONS AND FUTURE DIRECTION

7.1 Aerosol flow-tube/ Aerosol CIMS experiments

The Aerosol CIMS instrument was used in conjunction an aerosol flow tube to study the heterogeneous kinetics of solid and liquid particles with Cl radicals.^{1, 2} Solid and liquid particles of the same chemical composition were studied at room temperature so that the only variable was particle phase. Heterogeneous reaction kinetics and product formation from the reaction of Cl with particles various unsaturated fatty acids including 9 different solid particle types and 6 different liquid particle types were studied. Although little difference was observed in the reaction kinetics of solid and liquid particles, clear differences in the product distributions were observed in both the presence and absence of NO_x. In the absence of NO_x, evidence for higher oxidative turnover in solid vs. liquid particles was observed.¹ This is consistent with decreased product diffusion in solid particles where products are confined to the surface and undergo further reaction with Cl. The product formation observed in the presence of NO_x was consistent with this picture of decreased product diffusion in solid compared to liquid particles where it was evident that the peroxy radicals, too, were confined to the solid particle surface where reaction with NO was more likely.²

Development of a new tool for both gas and heterogeneous reaction kinetics experiments was developed whereby a steady-state of reactive species was generated and the time decay of gas phase and particle phase species was observed as a function of reaction time. This technique offers many advantages over other flow-tube techniques. The utility of the “virtual

injector” for studying gas phase and heterogeneous relative rates experiments was established. Bimolecular rate constants were determined for various gas phase organic reactants with Cl, OH, NO₃ and O₃, some being reported for the first time, to my knowledge. Effective reactive uptake coefficients of OH, Cl, NO₃ and O₃ were determined for a common proxy for unsaturated organic species in ambient aerosols and molecular marker for meat cooking aerosol, oleic acid. Lastly, the effective rate constants for olive oil components were determined with all four oxidants.

Using a combination of the “virtual injector” flow tube and an earlier flow-tube design, the interchangeability of reaction time and reactant concentration in heterogeneous oxidation processes was explored.³ It was found that at a constant OH or Cl radical precursor concentration, the kinetics were the same whether time or radical concentration were used to reach the same radical exposure. The precursor species, however, is able to adsorb to the particle surface and affect the reactive uptake of the radical species. Ozone, used as a radical precursor to OH, was found to adsorb to the particle surface and inhibit the reaction of OH with the underlying organic. Molecular chlorine, on the other hand, adsorbs to the particle surface and reacts with alkyl radicals which are formed during the reaction with Cl to regenerate another Cl radical at the particle surface, which increases the rate of loss of the particle phase species. These findings have important consequences for laboratory experiments of heterogeneous kinetics.

7.2. Cavity ring-down experiments

Development of the UV cavity ring-down spectrometer for organic aerosol analysis has been a challenging quest. First, design of the ring-down cavity, itself, has gone through a few iterations and it has become clear that the total flow of gases through the cavity, as well as

the purge flows on the mirrors can affect the accuracy of results. The most important change in the cavity ring-down setup was the replacement of a water based particle counter with a butanol based particle counter in order to efficiently detect organic aerosols. When the experiments were reproducible day to day, some valuable data was collected that show how well the light extinction cross sections match predicted cross sections for purely scattering particles with a real refractive index which was measured using Snell's Law. An increase in the imaginary part of the refractive index is observed when oleic acid is oxidized. The UV cavity ring-down setup may prove to be a useful tool for studying the change in aerosol optical properties during reactions which may occur in the troposphere and which may lead to the formation of brown carbon (organic, light absorbing) species.

7.3. Future direction

Aerosol CIMS experiments

The Aerosol CIMS instrument holds a lot of promise for future experiments. Using this soft ionization approach, we have the ability to explore reaction mechanisms in a way that is not convoluted by overlapping fragment ions from other products. Using CIMS, usually only one peak corresponding to each aerosol parent species is observed. Thus, while identification of unknown peaks in the mass spectrum is difficult due to the lack of fragmentation, the quantification of yields is very simple if the relative ionization efficiencies of the parent species and product can be determined. The dependence of product yields on particle phase, chemical composition, morphology, mixing state, and reaction conditions such as relative humidity and temperature are worth exploring. These data will help elucidate the important factors in determining whether functionalization or fragmentation mechanisms dominate reactions in the troposphere.

As ambient particles are complex mixtures of organic and inorganic species, performing kinetics experiments on more complex, multi-component particles would bring the experiments closer to resembling tropospheric particles. Although observing the changes to single component aerosols help us elucidate the important mechanisms at play during reactions with tropospheric oxidants, the kinetics experiments on single-component particles don't seem to represent the kinetics experiments on complex aerosols. This has important consequences for source apportionment studies which don't account for the reactive loss of molecular marker species.

Aerosol optical property measurements

The UV cavity ring-down experiments hold a lot of promise for future experiments on the optical properties of organic aerosols. Of particular interest is how the imaginary component of the refractive index changes during “brown carbon” forming reactions. It would be really interesting to couple the outlet of an aerosol flow tube apparatus to both the cavity ring-down cell and the Aerosol CIMS simultaneously in order to observe how the refractive index of particles change as they undergo oxidation reactions. There is some evidence of nitro-PAH formation from NO_3 reactions with particle-bound PAHs using UV cavity ring-down.⁴ In those experiments, there large uncertainties and large concentrations of NO_2 present (200 ± 50 ppm) which may absorb at 355 nm. It would be interesting to repeat this experiment with much lower NO_2 concentrations using photolysis of HONO in the presence of HNO_3 as described in Chapter 4. Other “browning” reactions may also be explored such as the formation of oligomeric HULIS from glyoxal (and/or methylglyoxal)- ammonium sulfate solutions,^{5, 6} and conjugated nitrogen containing species formation from limonene + O_3 secondary organic aerosol in the presence of ammonia,^{7, 8} among others.

In addition to the experiments described above, it would also be of benefit to couple the cavity ring-down experiment to other optical instruments such as the nephelometer, which gives a fairly sensitive measure of light scattering. One drawback to the nephelometer is that it requires large sampling volumes so the sample must be diluted by about a factor of 20 before entering the nephelometer. It would be difficult to obtain size selected particle concentrations out of the DMA that would be sufficient for these measurements. High particle concentrations may be generated with homogeneous nucleation. However, these particles are small and do not efficiently scatter the red, green, and blue light of the nephelometer. Preliminary experiments of differences in light scattering between liquid and solid elaidic acid particles are available in Appendix C.

It would be interesting, too, to set up a second ring-down cavity with a different wavelength of light where the refractive index is more or less the same but the size parameter is different enough that the predicted extinction cross section is different. For instance, the peaks and troughs in the predicted Mie plot of cross section vs. size parameter for OA, DOS, and Sq are all separated by ~ 0.5 size parameters. Thus, for particles with a diameter of 600-900 nm, the wavelength of light must only differ by ~ 30 nm in order to simultaneously acquire cross section data in a peak and trough, thus doubling the amount of extinction cross section data that may be acquired in a given time. Since the refractive index change of organic species is very small between 355 ± 30 nm,⁹ the acquired cross section data should be able to be used for the retrieval of the refractive index.

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APPENDIX A

COMPARISON OF THE COUNTING EFFICIENCIES OF BUTANOL AND WATER-BASED CONDENSATION PARTICLE COUNTERS

A.1. Methods

Particles of squalane (Sq), dioctyl sebacate (DOS), or oleic acid (OA) were generated by nebulization. Particle sizes were selected with a DMA and a butanol CPC (bCPC, TSI model 3775) and a water CPC (wCPC, TSI model 3785) were used to count the particles exiting the DMA simultaneously. A three way tee connector was used to split the particle flow going to each CPC and the same length of tubing was used from the tee to each CPC so that the particle loss was the same in each case. Make up air was pulled in through a HEPA filter and a stirred mixing flask was used to make sure the particle and makeup air were well mixed. In order to test whether humidifying the makeup air made a difference in the relative counting efficiency of the wCPC, a saturated paper towel was used to line a heated glass tube before entering the HEPA filter.

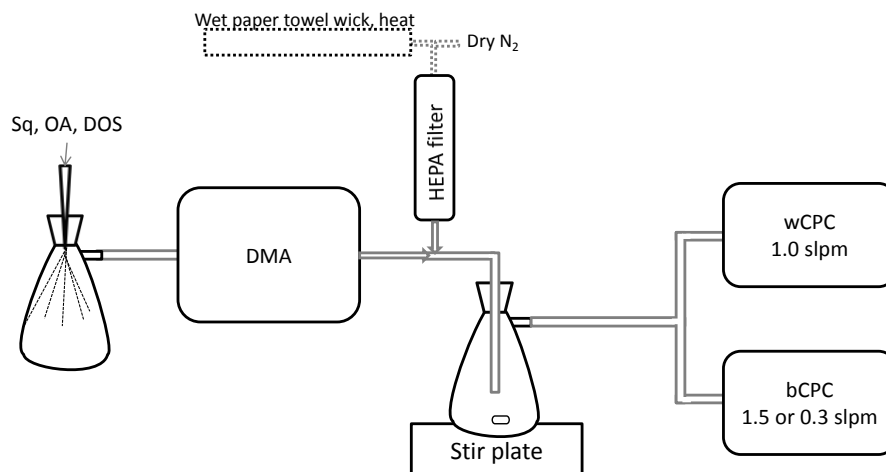


Figure A.1. Schematic diagram of CPC comparison experiment

A.2. Results and discussion

All three species studied here (squalane, diocyl sebacate and oleic acid) are considered insoluble in water; however, small differences in their affinity for water exist depending on the functional groups present. Depending on the particle type, the water CPC was up to a factor of 20 less efficient at counting 400-600 nm particles. Squalane, which is the most hydrophobic of the three species displayed the biggest discrepancy between CPCs. Humidifying the flow led to a factor of 7, 2, and 1.04 improvement in the relative counting efficiency of the wCPC for Sq, DOS, and OA, respectively for 400 nm particles suggesting that the wCPC is better able to grow the particles to the size the critical detection size (1-2 μm) after some water is already on the particle surface.

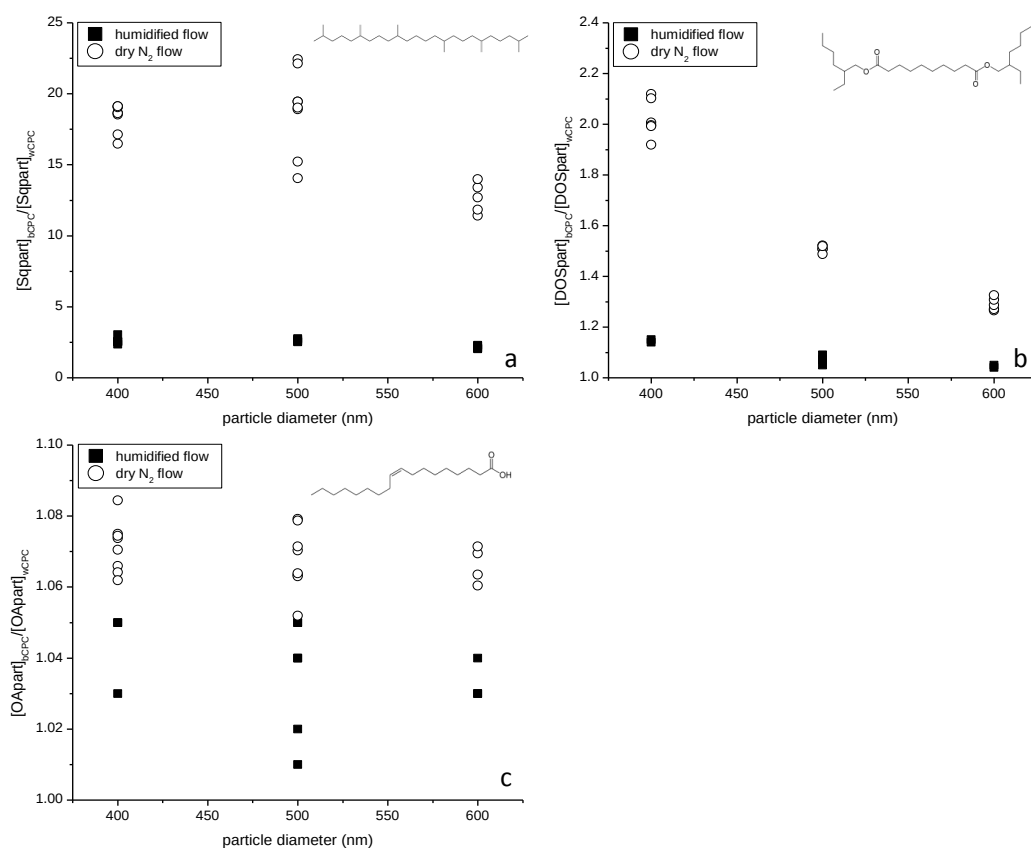


Figure A.2. Counting efficiency of wCPC relative to bCPC for a) Sq, b) DOS, and c) OA for dry N₂ and humidified flows.

APPENDIX B

TIME EVOLUTION OF A GLYOXAL-AMMONIUM SULFATE SOLUTION

B.1. Methods:

An aqueous solution containing 3 M ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and 2 M glyoxal was prepared and the change in the UV-Vis spectrum of the solution was monitored as a function of time after the solution was made.

B.2. Results and discussion:

Shown in Figure B.1a are the UV-Vis spectra collected after the glyoxal- $(\text{NH}_4)_2\text{SO}_4$ solution was made. The absorbance of the glyoxal solution at 355 nm was subtracted from the other spectra and the time evolution of the 355 nm absorbance is shown in Figure B.1b. Although the spectra collected at 43 and 48 hours are off scale at 355 nm, the change in absorbance over the first 26 hours are in very good agreement with Shapiro et al. who used almost identical concentrations of glyoxal and $(\text{NH}_4)_2\text{SO}_4$ and measured an absorbance of ~ 3.2 after accounting for the glyoxal absorbance.¹ Here, the absorbance after accounting for glyoxal absorption was ~ 3.1 .

Shapiro et al. identified four potential organic molecules resulting from the reaction of glyoxal and ammonium sulfate which may absorb strongly in the 300-450 nm region of the UV spectrum suggesting this reaction may produce a) large quantities of brown carbon or b) brown carbon species with large absorption cross sections. Either way, this reaction may be useful in measuring the change in the imaginary component of the refractive using extinction

cross section measurements on the UV cavity ring- down instrument. The challenge will be to dry the particles sufficiently before they enter the differential mobility analyzer (DMA) so that no particle size change occurs in the DMA or in the ring-down cavity.

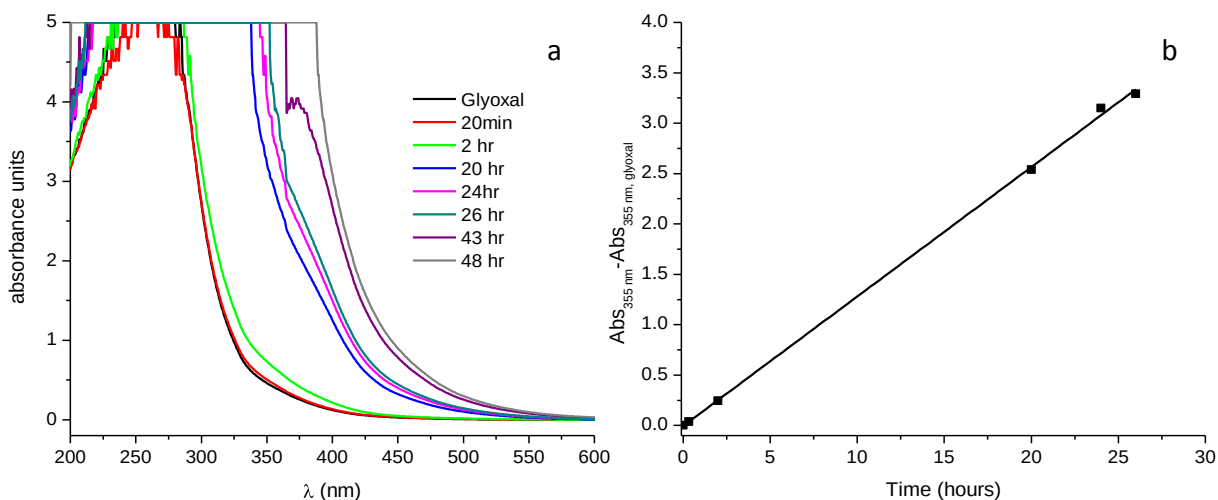


Figure B.1. a) UV-Vis spectrum of glyoxal-ammonium sulfate solution after different reaction times. b) Absorbance of solution at 355 nm as a function of reaction time minus the absorbance of the glyoxal solution.

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APPENDIX C:
SOLID AND LIQUID PARTICLE SCATTERING AND SUPERCOOLING LIFETIMES
AS MEASURED WITH NEPHELOMETRY

C.1. Methods

A schematic of the setup is shown in Figure C.1. In short, supercooled elaidic acid particles were generated by homogeneous nucleation, and were introduced into the nephelometer either as liquid (non-cooled) particles or were frozen in a -80 °C dry ice-isopropanol bath before warming back to room temperature. Alternately, the time that the non-cooled particles spent before entering the nephelometer where they may scatter light was varied by introducing additional tubing and flasks. With a known volume flow rate of the gas flow containing the particles and a knowledge of the volume the particles traverse before entering the nephelometer, the time the particles spent before entering the nephelometer was determined. A water based CPC was used to count the particles exiting the nephelometer and the scattering coefficients were normalized to the particle mass. The particle size was unknown during these experiments. The time at which the supercooled particles freeze (the supercooling lifetime) was determined by measuring the mass scattering coefficients and comparing them to the mass scattering coefficients measured in the experimental set up in Figure C.1a where the particles were directly introduced into the nephelometer from the particle source with or without a cold trap to freeze the particles.

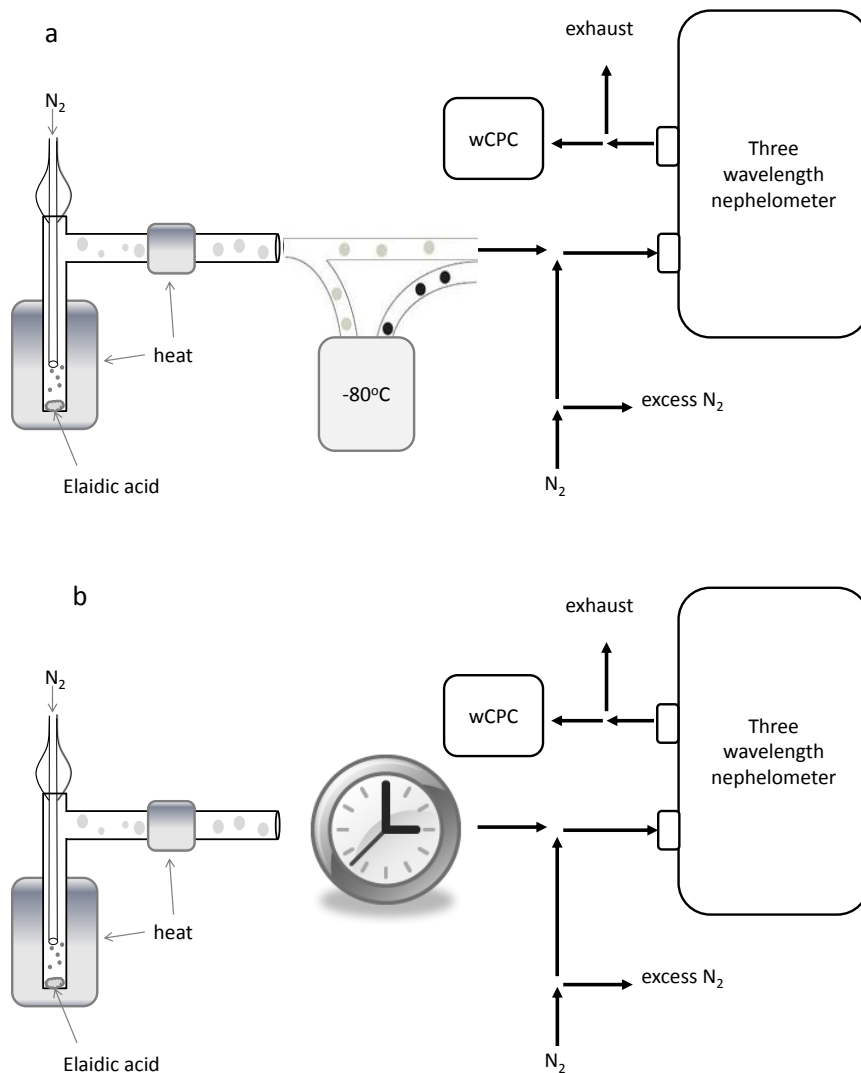


Figure C.1. a) schematic of the experimental design for measuring the mass scattering coefficients of supercooled and solid elaidic acid particles. b) schematic of the experimental design for determining supercooling lifetimes.

C.2. Results and discussion

The results of the direct solid-liquid comparisons (using the setup in Figure C.1a) are shown in Table C.1. Included in the table are the average mass scattering coefficients for total and back scattered red, green, and blue light. Typical total mass scattering coefficients for organic species are between $3\text{--}7\text{ m}^2/\text{g}$.¹ The values measured here are lower and the reason for this discrepancy is unknown. It was found after these experiments that the

calibration parameters that were stored in the software were wrong however it is not known by how much this may have affected the results. Nevertheless, if we assume that whatever is causing the discrepancy is independent of particle phase, it is apparent that solid particle mass scattering coefficients are reproducibly ~30% higher than liquid particle mass scattering coefficients.

Table C.1. Mass scattering coefficients for solid and liquid elaidic acid

	Average mass scattering coefficient (m ² /g)		solid/liquid
	Supercooled (liquid)	Precooled (solid)	
Total Blue	2.3	3.0	1.30
Total Green	1.2	1.5	1.25
Total Red	0.58	0.70	1.21
Backscattered Blue	0.77	1.0	1.30
Backscattered Green	0.38	0.51	1.34
Backscattered Red	0.18	0.24	1.33

Using the scattering coefficients above to indicate whether the particles were liquid or solid, the supercooling lifetimes (i.e. how long the particles may stay in a metastable, supercooled state) may be explored by increasing the amount of time between particle formation and the scattering measurement. This was accomplished by the addition of known volume flasks after the particle source and before the nephelometer and the time was calculated based on the volume flow rate. These results are shown in Figure C.2.

As evident in Figure C.2, it appears as if the mass scattering and back scattering coefficients resemble liquid particles (according to Table C.1) at 0.5-1.5 minutes but then the scattering coefficients begin to increase and then plateau around the scattering coefficient values of solid particles after ~2.5 minutes suggesting all of the particles have frozen. This technique may prove to be a useful and relatively simple way to measure supercooling

lifetimes. All of the scattering coefficients show the same trends so any one of these metrics may be selected to measure supercooling lifetimes.

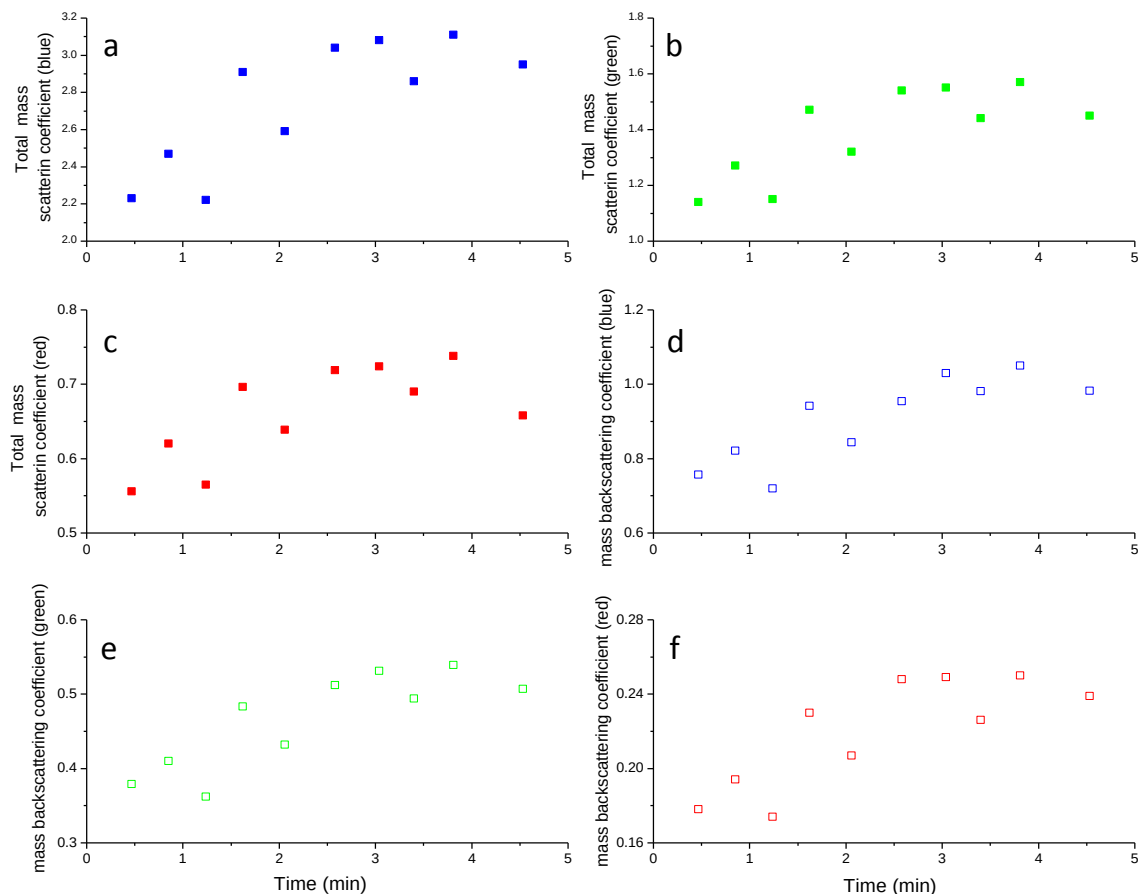


Figure C.2. a-c) Total mass scattering coefficient of blue, green, and red light **d-f)** mass backscattering coefficient of blue, green, and red light as a function of time the particles spent before entering the nephelometer.

It is not clear whether the particles start out as completely liquid and then freeze over time or if some of the particles, even initially, are partially frozen and that over time more of the particles freeze. What is clear, however, is that there is no further change in mass scattering coefficients after 2.5 minutes so this may be considered as an upper bound for the supercooling lifetime of elaidic acid particles. These experiments are worth repeating with a

properly calibrated nephelometer and the effects of experimental parameters such as particle source temperature, particle size, flow rates, cooling rates, etc. should be explored.

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