Drew University College of the Liberal Arts

Acid-Catalyzed Heterogeneous Reaction of Limonene with Mineral Aerosols: A New Mechanism for The Organic Coating of Inorganic Aerosols

An Honors Thesis in Chemistry
by
Allison Rose Staniec
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Committee Members:
Dr. Ryan Z. Hinrichs
Dr. Mary-Ann Pearsall
Dr. Jim Supplee
Dr. James Bazewicz

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Abstract: Many uncertainties remain about the reaction of atmospheric volatile organic compounds to form secondary organic matter (SOM) on inorganic aerosols. This thesis describes a previously unstudied reaction between limonene and mineral aerosols involving an acid-catalyzed heterogeneous mechanism by which volatile organics react directly with inorganic aerosols to form condensed phase organic compounds. Kaolinite and α-alumina were exposed to gaseous limonene at varying concentrations and under conditions of varying relative humidity, HNO_3 presence and carrier gases. Product formation was monitored using infrared spectroscopy (DRIFTS), and the products were identified using GC-MS. Kaolinite exposed to limonene formed α-terpineol. Alumina exposed to limonene formed 1-methyl-4-(prop-1-en-2-yl) cyclohex-2-enol (53%), carveol (28%) and limonene glycol (13%). Pre-exposing the mineral surface to gaseous HNO_3 increased the rate of product formation and affected the type of product formed. Limonene concentration and the initial rate of product formation varied linearly indicating an Eley-Rideal type reaction, in which gaseous limonene reacted directly with the surface sites and condensed water. Increasing the relative humidity decreased the initial rate of reaction and the saturation of the products indicating competition of water and product for adsorption sites. This reaction between limonene and mineral aerosols represents an additional mechanism which may work in conjunction with the traditional gas phase oxidation and condensation to adhere organic compounds to mineral aerosols.

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Chapter I: An Introduction to Atmospheric Particulates and Heterogeneous Reactions

The ubiquitous nature of aerosols makes them a highly relevant and well explored topic of current scientific research. One phenomenon of interest is the formation of secondary organic aerosols (SOA), the result of volatile organic compounds (VOCs), like isoprene, reacting to form less volatile liquid and condensed phase products which can partition onto inorganic aerosols. Here we use the term secondary organic matter (SOM), a more general appellation, interchangeably with SOA, to indicate all types of organic molecules present after atmospheric reaction, whether condensed into wholly organic particulates or coated on inorganic aerosols. The organic coating of inorganic aerosols has implications for the impact of aerosols on human health and the environment. Our understanding of SOAs is limited by uncertainties about their presence, composition and structure, and the fact that most studies of inorganic aerosols neglect the organic fraction and vice versa (Jang *et al*., 2002). Traditional models of SOA formation involve reactions solely in the gas phase, with VOCs interacting with ozone, nitrate and hydroxyl radicals. Studies using this model have been found to regularly underestimate the amount of SOA present, indicating that the gas phase model may not represent the whole picture (Kroll and Seinfeld, 2008). Literature indicates the possibility of acid-catalyzed reactions using aqueous acidic droplets and biogenic hydrocarbons where secondary organics are formed in hydration, acetal, hemi-acetal and dimerization reactions (Li *et al*., 2010) (Figure 1).

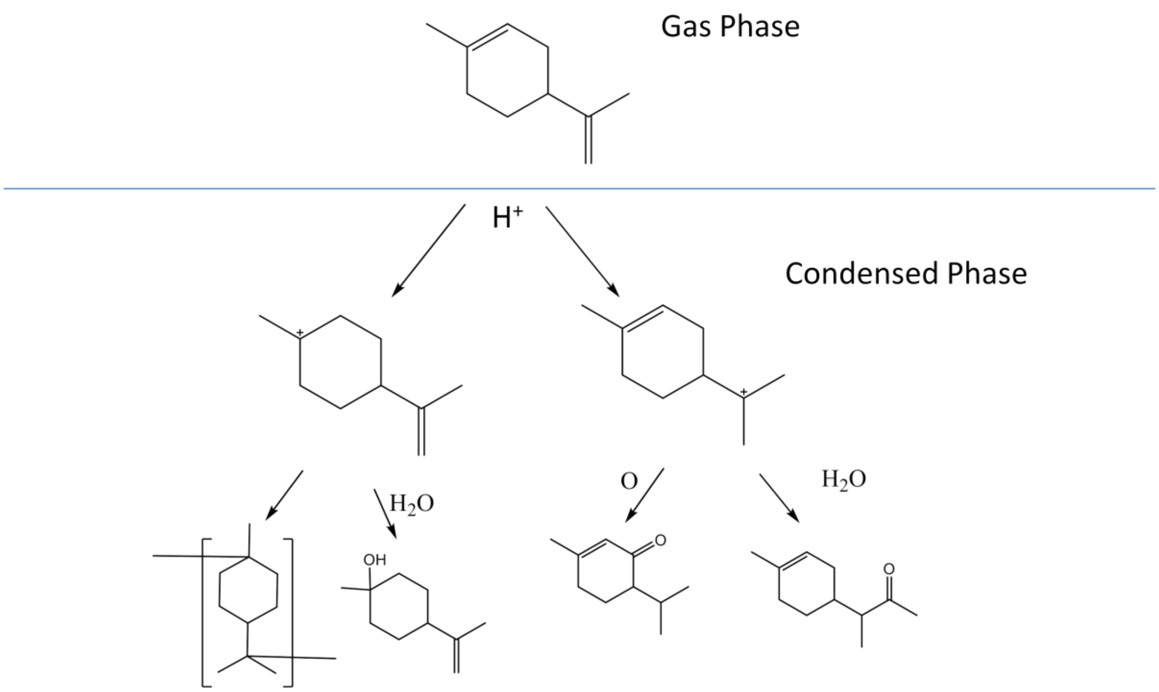


Figure 1. Acidic droplet experiments lead to a variety of products (Li *et al*., 2010)

The interaction of limonene with mineral aerosols explored in this thesis is particularly fascinating because it represents a novel acid-catalyzed heterogeneous mechanism for forming secondary organic aerosols with solid phase mineral dust aerosols, where the products are the result of interactions between gaseous phase organics and condensed phase water and surface sites. Heterogeneous reactions like this may account for the fraction of SOA which traditional models fail to predict.

I. Aerosols and their Implications for Human and Environmental Health

Aerosols are fine particulate matter suspended in the atmosphere, studied for their possible effects on human health and pollution. Because of these effects, the Environmental Protection Agency (EPA) is required to set National Ambient Air Quality Standards for Particulate Matter (PM NAAQS) which are based upon the size of the particles. Particulate matter between 10 and 2.5 μm is referred to as “inhalable coarse particles” (PM_{10}), while particles less than 2.5 μm are “fine particles” ($PM_{2.5}$) (“Particulate Matter”, 2013). Health hazards from particulate matter include respiratory and heart issues, and reductions in $PM_{2.5}$ have been linked to increases in life expectancy of up to 0.61 years for each reduction of 10 $\mu g/m^3$ (“Health”, 2014, Pope *et al*., 2009). EPA standards, however, ignore the potential differences in health and environmental effects caused by compositional differences and instead are solely concerned with the size of the particulate matter which influences the likeliness of human inhalation and exposure (“Health”, 2014).

Visibility and environmental health are also linked to aerosol formation and transformation due to the ability of aerosols to reflect solar radiation. Aerosols can affect the amount of solar radiation which is absorbed into the atmosphere and transmitted downward versus the amount which is reflected back out into space. Reflection or transmittance of this radiation is based upon aerosol composition and size and therefore changes in these properties have implications from a global warming perspective (Figure 2).

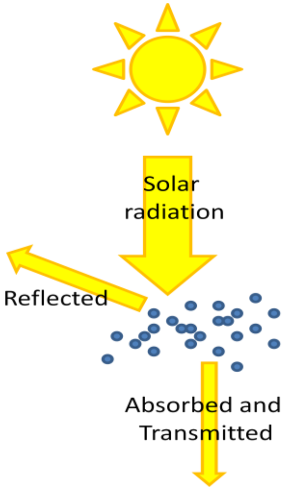


Figure 2. The reflectance and/or transmittance of solar radiation by aerosol particles

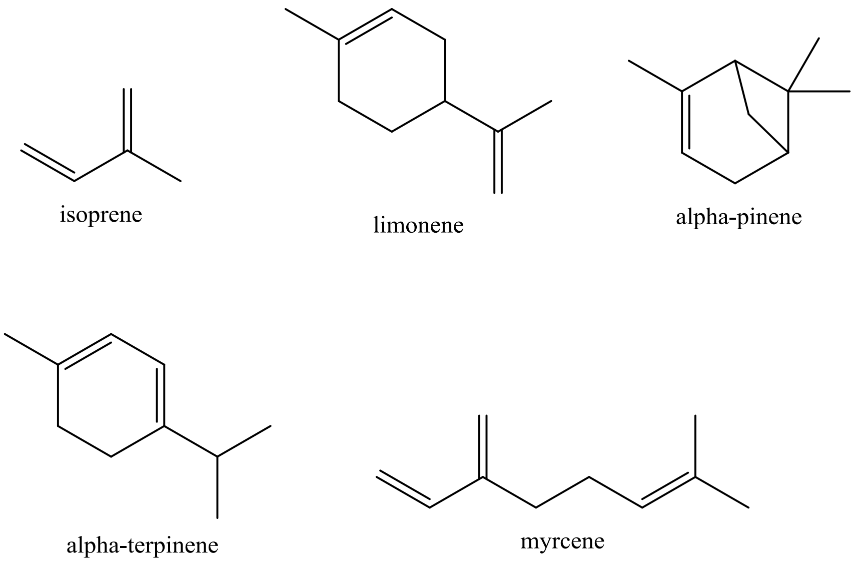
Secondary organic aerosols often influence the properties of other aerosols by coating their surfaces (an interaction which has implications for the formation of ice and cloud nuclei as well as the direct reflection from the aerosol particles themselves) (Hoyle *et al*., 2009). A greater understanding of the formation and transformations of SOAs allows better predictions in climate modeling and better responses to the presence of particulate matter formed from and coated by organic compounds.

Many questions remain about the exact reactions which form SOAs and how those reactions impact their health and climate effects. The major gas-phase reaction mechanism used in current atmospheric models is based on the kinetics of laboratory studies and often under-estimates the amount of organic aerosol present, indicating the presence of unknown formation reaction pathways (Carlton *et al*., 2009). The Intergovernmental Panel on Climate Change (IPCC) cites uncertainties in the emission sources and structure of aerosols along with uncertainties in the results of mixing of aerosols and their subsequent reactions which have implications for the accuracy of climate models (“Uncertainties”, 2007). Studies that measure chemical composition of aerosols in situ are often focused in small areas and therefore may not be representative of larger portions of the atmosphere (Van Beelen *et al*., 2014). Therefore further understanding of the reactions which occur in the atmosphere and the production of secondary organic aerosols is an area of particular interest.

II. Terpenes as Aerosol Precursors

Aerosols come in a variety of types, defined by their chemical composition. Inorganic aerosols include minerals, sulfates, and sea salts (Finlayson-Pitts and Pitts, 2000). These compounds are hardly ever present as pure inorganic aerosols, customarily acquiring a coating of adsorbed organic compounds during their atmospheric lifetime (Eliason *et al*., 2003). Organic compounds tend to be present in the atmosphere either as volatile organic compounds (gas phase) or condensed as secondary organic aerosols on inorganic substrates.

Volatile organic compounds (VOCs) is the term used for all gas phase organic compounds present in the atmosphere. The major source of these compounds is biogenic or vegetation based (Seinfeld and Pandis, 2006). Other sources include vehicle exhaust, industrial processes, volatile solvents, decomposition and animal husbandry (Friedrich and Obermeier, 1999). Isoprene and terpenes form the majority of the vegetation based hydrocarbons and are particularly reactive in the atmosphere because of their double bonds (Figure 3).



isoprene

limonene

alpha-pinene

alpha-terpinene

myrcene

Figure 3. Isoprene and several representative monoterpenes

Isoprene emission is tied to photosynthesis and nearly ceases when light is not present (Seinfeld and Pandis, 2006). Monoterpenes, such as limonene, are formed from the combination of two isoprene units. Emission of terpenes is tied to the biophysical processes of plants and thus continues even at night. They are stored by plants as deterrents to insects and are released into the atmosphere due to their high volatility (Hewitt, 1999). Anyone who has ever broken needles off a Christmas tree or crushed a mint leaf has released these strong smelling compounds into the atmosphere. Isoprene emissions are estimated to be approximately 500 Tg/ year while monoterpene emissions are on the order of 127 Tg/year (Seinfeld and Pandis, 2006).

Monoterpenes are important precursors of secondary organic aerosols. The dominant mechanism for SOA formation involves volatile organic compounds (VOCs), such as isoprene and limonene, reacting in the gas phase to become oxidized by ozone (O_3), hydroxyl (OH) or nitrate (NO_3) radicals. The parent organic compounds are defined by their volatility and are present only in the gas phase in the atmosphere.

As the VOCs react with oxidizing reagents in the gas phase they form primary products which lose volatility. The semi-volatile product exists in equilibrium between the gas phase and bound to a substrate (in this case our inorganic dust aerosol). It can undergo further oxidation in the gas phase to form a secondary organic aerosol which has lost nearly all of its volatility and remains bound to the substrate (Figure 4).

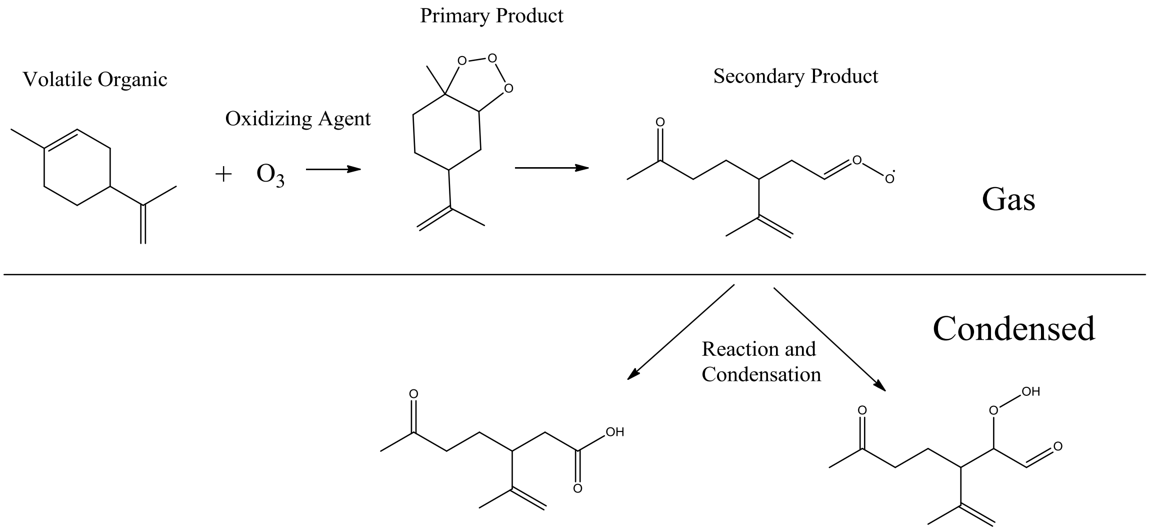


Figure 4. The traditional view of secondary organic aerosol formation is that reactions are conducted in the gas phase. (Maksymiuk *et al.*, 2009)

Limonene, in particular, is a well known candidate for these reactions, possessing two reactive double bonds which can form low vapor pressure, SOM-forming products (Maksymiuk *et al.* 2009). The reaction of limonene with ozone to form secondary organic aerosols uses this gas phase mechanism and is of particular interest for comparison to our proposed heterogeneous mechanism. In the traditional limonene/ozone reaction, ozone is known to attack the endo-cyclic double bond and the terminal double bond at different rates and to produce primary products which exist partitioning between gas and condensed phases (Zhang *et al.*, 2006). The initial ozonolysis creates Criegee intermediates (Figure 5), radical carbonyls which can react with many different compounds to form a large distribution of products, and favors breakage of the endocyclic double bond (Jonsson *et al.*, 2006).

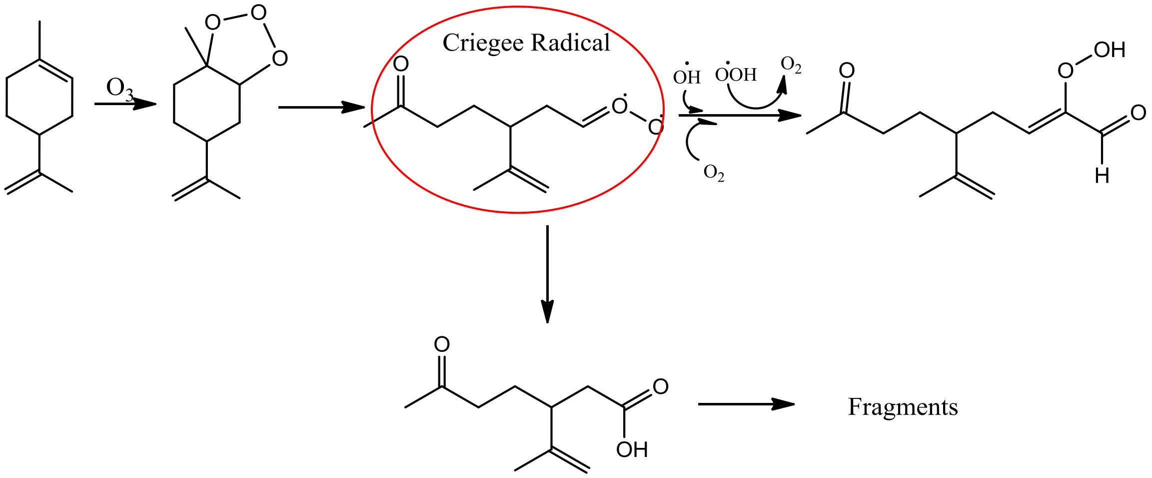


Figure 5. Criegee radicals and various secondary products formed from limonene (Maksymiuk *et al.*, 2009)

The Criegee radical products can undergo further reaction in either phase due to the original limonene possessing a second reactive double bond. Here we see two separate pathways which Criegee radicals may pursue, involving rearrangement and addition of OH groups. The ozonolysis of limonene results in a variety of products and is known to be particularly efficient at forming secondary organic aerosols (Jonsson *et al.*, 2006). Limonene ozonolysis has therefore been studied as a model for SOA aging (undergoing further reaction in the atmosphere) (Zhang *et al.*, 2006, Matsymiuk *et al.*, 2009).

Gas phase SOA forming reactions (like the ozonolysis of limonene described above), which act as the major sink for volatile organics, are atmospherically relevant but may not represent the whole picture. As previously stated, models using only gas phase reactions for estimating SOA formation consistently underestimate the actual SOM presence measured *in situ*. The mechanism proposed in this work may provide a key to the formation reactions which remain unaccounted for in current models.

III. Heterogeneous Reactions in the Literature

The possibility of acid based heterogeneous reactions contributing to secondary organic aerosol formation is addressed as early as 2002 in the literature. Jang *et al.* postulate that sampling techniques which allow the products to return to their original configurations lead to the lack of easily identified products and thereby mask the true amount of acid-catalyzed reactions which may be occurring. Their particular focus is carbonyl primary products which are vulnerable to secondary acid-catalyzed heterogeneous reactions. They show reaction of gaseous aldehydes with acidic seed aerosols leading to five times more SOA product than a neutral aerosol system indicating the viability of acid-catalyzed reaction of primary products (Jang *et al.*, 2002).

Volatile organics have long been known to bind to inorganic substrates and react on those surfaces. Li *et al.* (2001) focused on volatile carbonyl compounds, the result of VOC reactions in the atmosphere. While my work is concerned with the precursors of these carbonyl compounds, the work done by Li *et al.* proves that volatile organics can bind in appreciable amounts to compounds like alumina and iron oxide and undergo further reaction while bound there.

Perhaps the most relevant to the limonene/ mineral aerosol interaction addressed in this thesis is the reactions of volatile organics with liquid acidic droplets investigated by Li *et al*. (2010). They exposed sulfuric acid droplets equilibrated at various humidities to gaseous limonene and terpineol. Li *et al*. observe a large variety of products based upon an initial protonation mechanism for limonene (Figure 6). Hydration is their most atmospherically relevant reaction pathway based upon equilibration time (approx 4 hours) and relative humidity (Li *et al*., 2010).

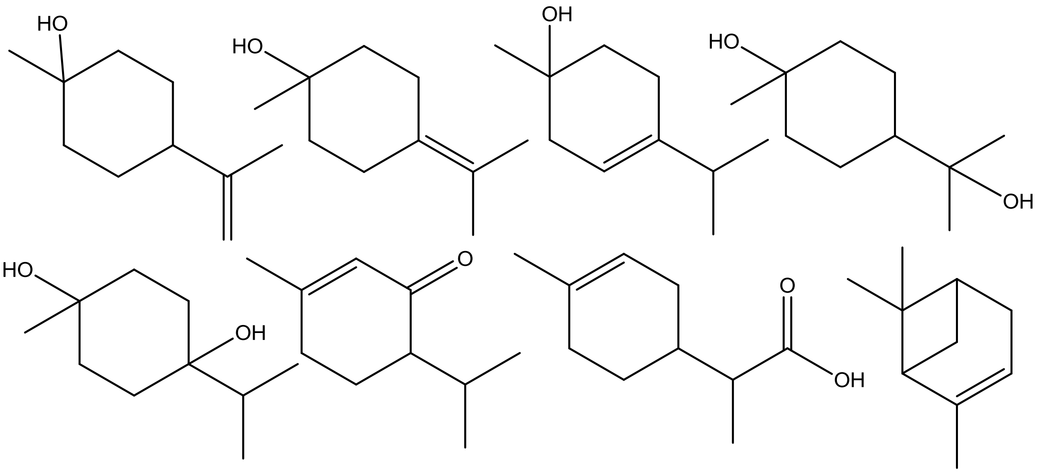


Figure 6. A sampling of the products formed in reactions between gaseous limonene and acid droplets (Li *et al*., 2010)

In this thesis we hope to elucidate whether the interactions of limonene and mineral aerosols could proceed by similar acid-catalyzed mechanisms to adsorb organic products to mineral aerosols.

When VOCs undergo gas phase reaction, the resultant products will condense onto almost any type of aerosol substrate, regardless of composition. In this thesis we propose a heterogeneous mechanism which involves direct reaction between the particulates and the VOC. Thus the composition and surface structure of the aerosol plays an important role in determining reactivity.

IV. Mineral Dust Aerosols

Mineral dusts are important atmospheric particulates which are known to act as catalysts and major sinks for both volatile organics and nitric acid. In particular, volatile carbonyls adsorbing to mineral dusts (alumina, iron oxide etc.) have been well documented using IR and UV/vis spectroscopy (Li *et al*., 2001). These factors led us to consider the direct reaction of VOCs and mineral aerosols as a possible alternate mechanism for secondary organic matter (SOM) coating of aerosols. Mineral dust aerosols are usually the result of dust storms and are defined as soil particles which have become air-borne (Usher *et al*., 2003). Their composition is usually weathered rock, like quartz, feldspars and clays. These particles, which exist in large quantities and have relatively long atmospheric lifetimes, are important both as part of reaction mechanisms and for their health and atmospheric effects (Usher *et al*., 2003). Kaolinite and other mineral dust aerosols can also carry newly bound organics longer distances than might be expected and retain these compounds in the atmosphere (Dentener *et al*., 1996). In addition, organics are known to alter the properties of mineral aerosols, such as the ability to act as ice or cloud nuclei. For example, coating inorganic aerosols with organics has been found to reduce their efficacy as cloud condensation nuclei by creating a hydrophobic layer on the normally fairly hydrophilic mineral (Woodill *et al*., 2013).

Kaolinite is a layered mineral with alumina and silica sheets alternating. The alumina sheets have hydroxyl groups situated along each side, one facing outward and the other facing the silica sheet allowing hydrogen bonding and reactivity (Miranda-Trevino and Coles, 2003). Adsorption tends to take place on the surfaces and edges of this well packed structure (Miranda-Trevino and Coles, 2003) (Figure 7A). Pure alumina appears naturally as corundum, a mineral which makes up rubies and sapphires. Alumina consists of a hexagonal oxygen ion lattice with holes occupied by aluminum ions (Davis, 2010) (Figure 7B). Both of these surfaces are well suited to act as catalytic sites for heterogeneous reaction mechanisms. Clays, in particular, are capable of supporting acid-catalyzed reactions because of their inherent Bronsted acidity (Varma, R. S., 2002). They also involve surface hydroxyl groups and are widely used for support of other reagents (Varma, R. S., 2002). They have been noted as suitable replacements for even nitric and sulfuric acids (Varma, R. S., 2002).

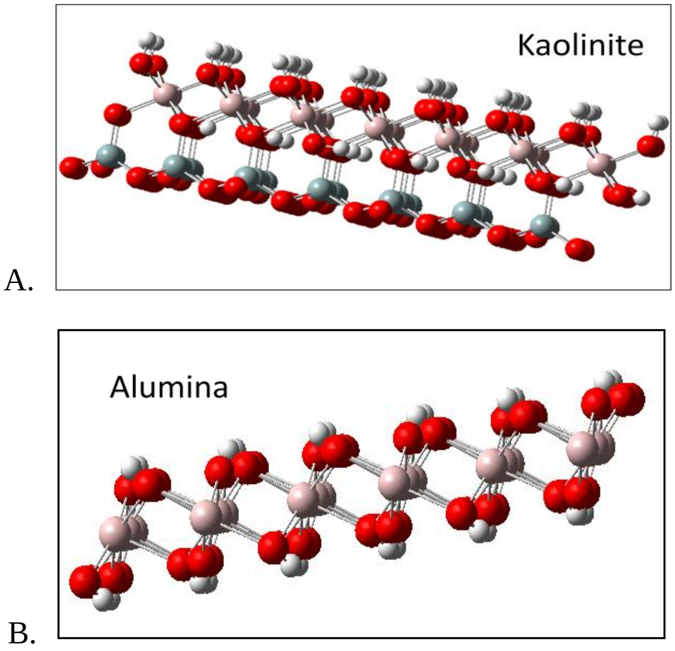


Figure 7. Surface Structure of A. Kaolinite and B. Alumina. Atoms are identified by color Pink: Aluminum, Gray: Silicon, Red: Oxygen, White: Hydrogen (Gaussian figure)

V. Implications of a Heterogeneous Mechanism

The interaction of limonene with mineral aerosols has implications for the binding of organic compounds to inorganic substrate aerosols. In this thesis we show that mineral substrates can support heterogeneous acid-catalyzed interactions with VOCs, in particular, gaseous limonene with kaolinite and with alumina. This interaction was explored using kinetics. The impact of various parameters on the interaction was investigated to assess the atmospheric viability of the reaction itself as a possible alternative acid-catalyzed heterogeneous mechanism for SOA formation (Figure 8). Detailed here are experiments to identify products of this reaction (using GC-MS) for comparison to other acid-catalyzed aerosol interactions and to elucidate the kinetics of this interaction under varying conditions.

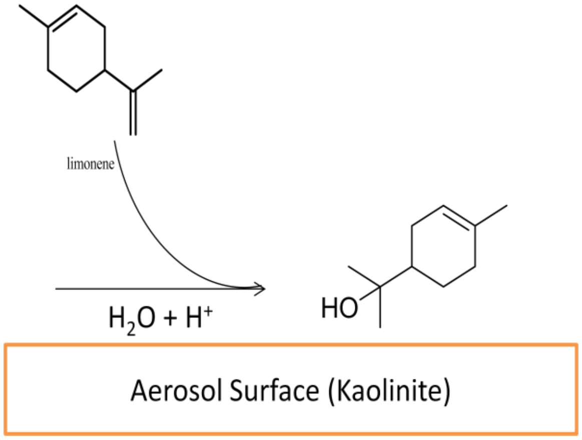


Figure 8. The proposed mechanism (heterogeneous) by which limonene interacts with kaolinite

In the mechanism proposed in this thesis a gaseous reactant interacts directly with a condensed phase substrate to create products with immediate rather than stepwise loss of volatility. The gaseous limonene reacts with condensed water and surface sites on the kaolinite or alumina. The resulting products are bound to the substrate and have their volatility reduced by three orders of magnitude with the addition of a hydroxyl group (Kroll and Seinfeld, 2008). They coat the inorganic substrate in a layer of organic compounds which may change the reactivity of the aerosol. The presence of this organic layer is a validation of the possibilities for atmospherically relevant heterogeneous reactions which may contribute to overall SOA formation.

Chapter II details the experimental methods used to obtain proof of SOA formation via heterogeneous mechanism. Chapter III will discuss the kinetics data as a function of various parameters and its use for validating the proposed mechanism. Product identification via GC-MS will also be discussed. The results of varying parameters such as nitric acid presence for the interaction of kaolinite and limonene and relative humidity for alumina and limonene will be examined. Chapter IV will contain the conclusions and comparison of our results with those of similar studies.

Chapter II: Experimental Methods

I. Methods and Materials

α-alumina and kaolinite powders were exposed (+)-(R)-limonene to facilitate reaction with the surface and adsorbed compounds. Gaseous limonene was introduced to the solid mineral powders via carrier gas, usually compressed air and nitrogen. The reaction of this volatile organic was monitored using Diffuse Reflectance Infrared Spectroscopy (DRIFTS) and Gas-cell Infrared Spectroscopy. Surface concentration of forming products (terpineol, etc.) was monitored throughout the course of a reaction and later analyzed using first order kinetics. Gas Chromatography-Mass Spectroscopy was used to identify products and their relative abundances.

A. Infrared Spectroscopy

Infrared Spectroscopy uses the infrared portion of the electromagnetic spectrum to excite vibrational motion of molecules through stretching and bending along bonds. Each of these bond vibrations has a particular range of frequencies to which it corresponds according to its constituent atoms. For example the O-H stretching vibration causes a broad peak around 2500-3600 cm^{-1}. These peaks and their corresponding bonds have been extensively studied and their correlations are well known. They can be expressed in absorbance or transmittance. Absorbance is the energy absorbed by the molecule to fuel the bend and stretch of the bond. Transmittance is the amount of light energy which is allowed to pass through the sample without being absorbed. Here all spectra are expressed in absorbance versus wavenumber (cm^{-1}).

Gas-cell IR Spectroscopy is used to monitor the amount of limonene present in experiments. Gas-cell IR spectroscopy measures the concentration of a compound present in the gaseous phase by reflecting an IR beam up and down an open column; our gas-cell has a pathlength of ten meters, allowing us to work at very small concentrations. A background spectrum of humidified air is taken so that only limonene is present in the series of spectra taken before and during the reaction (Figure 9).

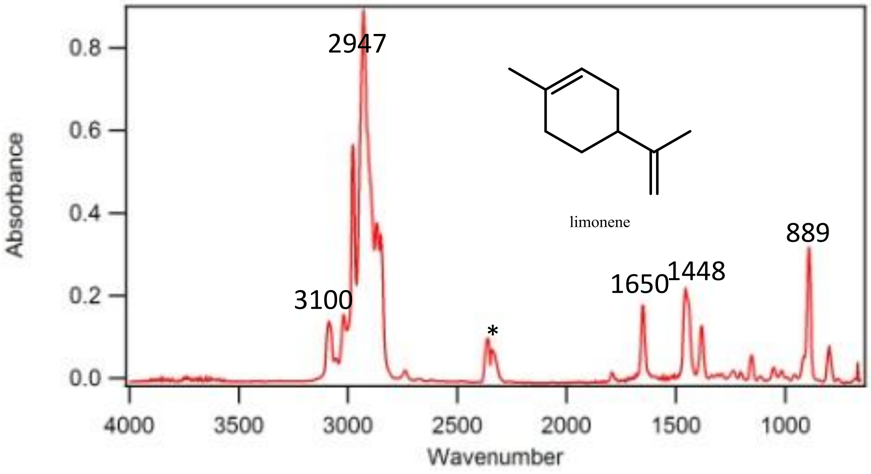


Figure 9. Gas phase infrared spectrum of limonene. Note the presence of characteristic C-H stretch peaks around 2900 cm^{-1}. The CO_2 peak (*) can be ignored as it fluctuates with the environment and is easily identified

The peaks in the spectrum correspond to the amount of energy required to cause the bending or stretching vibrations in the bond. The series of peaks around 2900 cm^{-1} are the stretch of the various C-H bonds present in limonene. The peaks at approximately 2400 cm^{-1} are the stretch of the carbon dioxide C=O bonds. CO_2 is a fairly difficult molecule to remove from the spectrometer and is easily identified by this characteristic peak. It tends to vary freely throughout the experiment. The 1600 cm^{-1} peak is typical of the C=C double bond stretch. There are two present in limonene.

Table 1. Major IR peaks of limonene

Peak (cm-1)	**Vibrational Mode**
3100	=C-H stretch
2947	C-H stretch
1650	C=C stretch
1448	C-H bend
889	=C-H bend

These spectra are obtained by averaging 256 scans, requiring approximately 4 minutes per average. The 2900 cm^{-1} peak, associated with C-H groups in the limonene, can be fitted to give the concentration of limonene present using Beer's Law (Equation 1).

$$1.\quad Abs(\nu) = \sigma(\nu) * l * N$$

Beer's law relates the absorbance of a peak with the concentration of the compound (*N*) through the pathlength (*l*) and the cross section (*σ*). We can fit a known cross section to our experimental data by multiplying it by the known pathlength and varying the concentration until it matches (Figure 10).

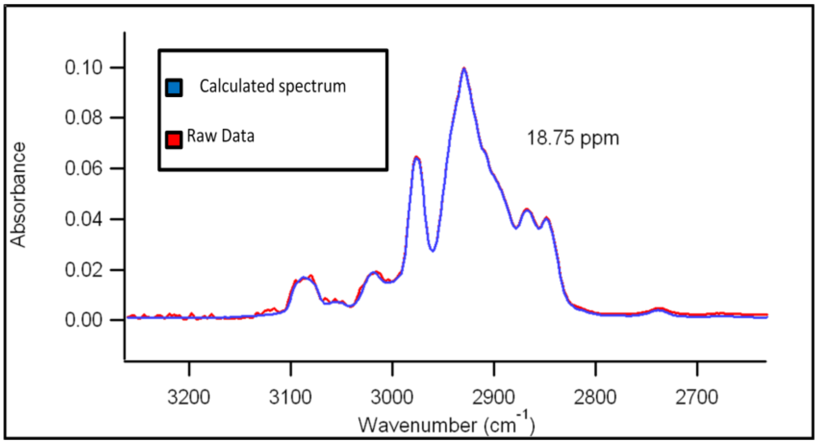


Figure 10. The calculated cross section (blue) fitted to raw data (red).

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is used to monitor the mineral surface. This is accomplished by diffusely reflecting infrared beams off the surface of the mineral dust and recollecting the reflected beams using a parabolic mirror. The DRIFTS chamber itself is rather simple (Figure 11).

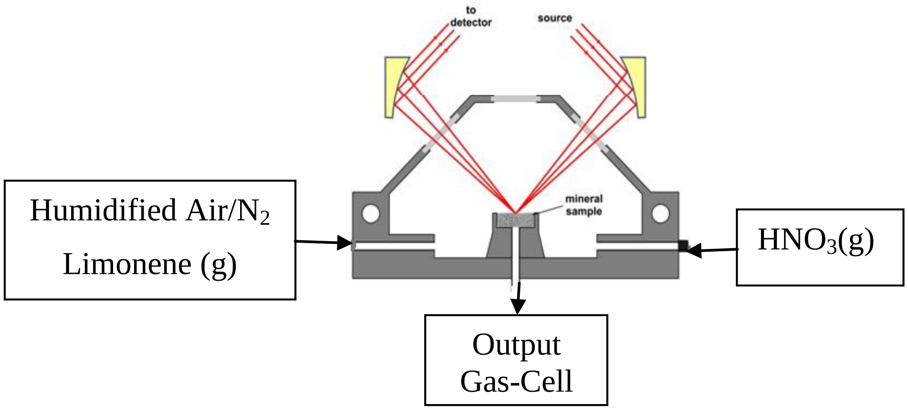


Figure 11. The DRIFTS chamber, side view (Dr. Ryan Z. Hinrichs)

A small cup is packed with approximately 0.1g of the chosen mineral aerosol substrate.. For most of our reactions water is already present on the substrate, the result of continuously running humidified air through the chamber. This water and the surface of the substrate itself are part of the background spectrum and are therefore automatically subtracted from the reaction spectra. The volatile organic is then allowed to flow through the powder sample where it can react with any adsorbed compounds as well as the substrate itself.

The DRIFTS spectrometer is programmed to take continuous spectra, averaging approximately once per minute during the course of a reaction. This allows us to monitor the reaction as product forms on the surface. Because the limonene is introduced via air/nitrogen flow as a gas we do not see it in our DRIFTS spectra, which monitor the surface only. This series of spectra can be overlaid to show the progress of the reaction over time (Figure 12).

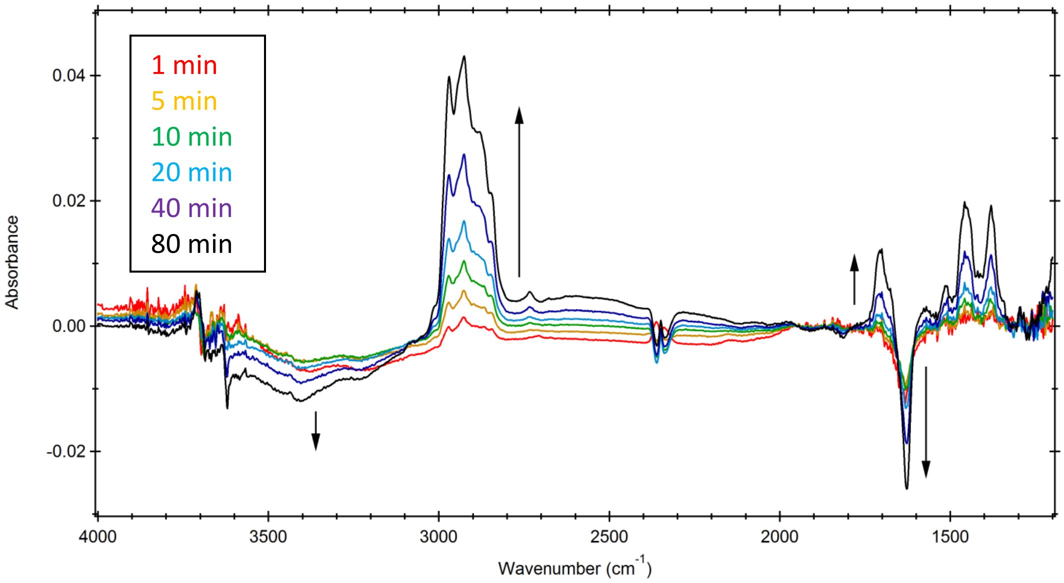


Figure 12. DRIFTS reaction spectra taken over time. Each spectrum represents a certain time point in the reaction.

These two IR techniques are part of a larger set up which allows us to vary limonene concentration, humidity of air and presence of other reactants and to control the parameters of the reaction closely (see Figure 13).

B. Chamber Setup and Introduction of Reagents

Prior to reaction, the DRIFTS chamber is lightly packed with the substrate, either alumina or kaolinite powder. The amount of substrate present in the cup is roughly the same between experiments (≈0.1g). Liquid limonene is kept in a bubbler through which nitrogen gas is flowed at various rates. These flow rates allow us to control the amount of limonene which is present in the carrier gas (N_2 and air) and thus in the DRIFTS chamber, where the reaction takes place. The limonene bubbler is sometimes immersed in dry ice baths in order to obtain very low limonene concentrations, on the order of 1 ppm.

A schematic is included for clarity (Figure 13).

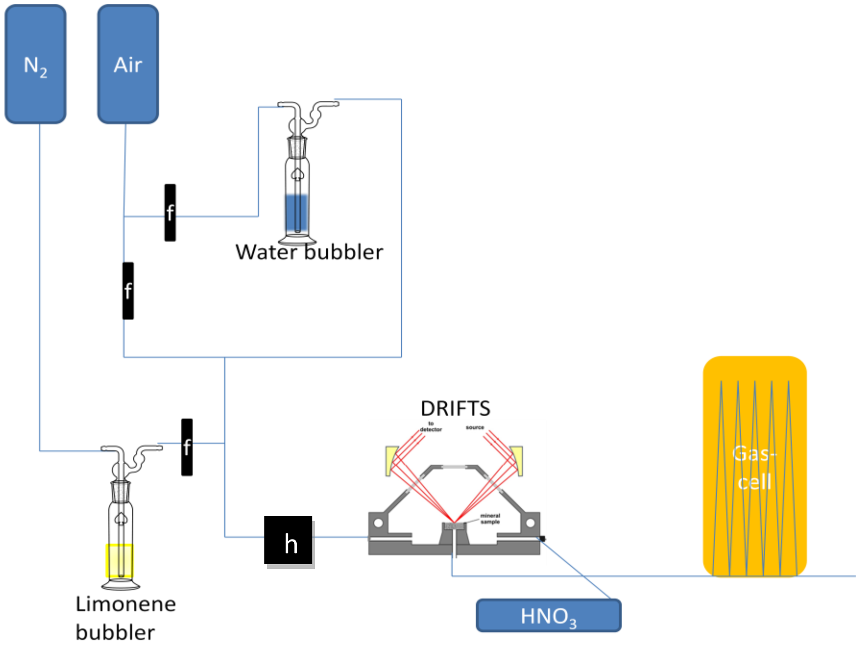


Figure 13. Schematic of the lab set up. “f” denotes flow meter. “h” denotes humidity monitor.

Air is flowed through two channels; one “dry,” which flows directly to the chamber, and one “wet,” which is flowed through a water bubbler of deionized water kept at a constant 25 °C, before recombining to flow through the chamber. The overall flow is maintained at approximately 1030 sccm (standard cubic centimeter per minute). The ratio of the flow rates for the two air channels can be changed to acquire a range of relative humidities from 0 to 80% RH. When limonene flow is introduced the “dry” air flow is reduced accordingly to maintain the relative humidity which is monitored by a humidity meter.

The background spectra for both the DRIFTS and gas-cell are taken before the introduction of the limonene, while the chamber and gas-cell are equilibrated at the chosen relative humidity (RH). The limonene is routed around the DRIFTS chamber and monitored via gas-cell IR series until it is determined to have reached the desired concentration and stabilized. It is then rerouted to flow through the DRIFTS chamber before reaching the gas cell. The DRIFTS series begins when the DRIFTS chamber is opened to limonene.

For certain experiments, gaseous nitric acid was introduced before the reaction began (after equilibration at the chosen RH) to test the effects of additional acidic sites. The vapor from a nitric/sulfuric acid mixture was diluted in a lecture bottle to approximately 200 psi with air. The lecture bottle was attached to an inlet on the DRIFTS chamber. Outflow to the gas-cell was rerouted to a hood and the gaseous nitric acid was allowed to flow into the DRIFTS chamber to coat the substrate, monitored by an infrared series. After the nitric acid was exhausted the lecture bottle was removed and the flow rerouted through the gas-cell. The reaction then proceeded as usual.

Gas Chromatography Mass Spectroscopy (GC-MS) was used to identify the products of the reactions which varied with substrate and addition of nitric acid. Products were extracted from the substrate using acetonitrile followed by filtration through a syringe filter. The substrates with adsorbed product were allowed to sit in acetonitrile for several hours. Several samples were sonicated for up to 30 minutes with no discernable shift in product distribution.

Chapter III: Results and Discussion

I. Kaolinite and Limonene: Product Identification

The reaction between kaolinite and limonene was monitored by DRIFTS. The most prominent peaks which grow in on the IR spectra correspond to organic C-H stretching (Figure 14).

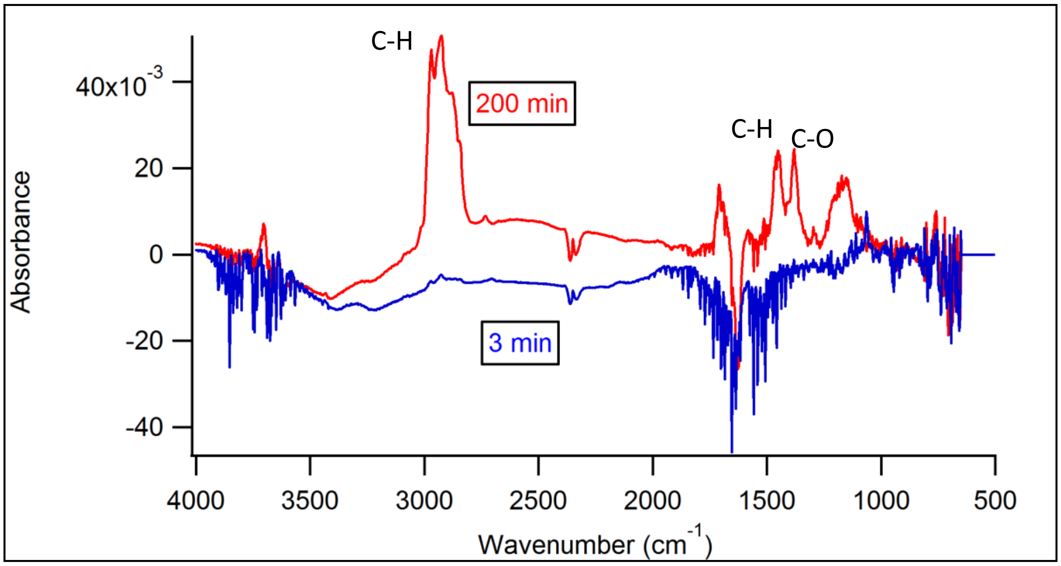


Figure 14. DRIFTS spectra of kaolinite exposed to gaseous limonene. The peaks are consistent with an organic product bound to the kaolinite surface.

It was therefore concluded that the products on kaolinite were, in fact, the result of gaseous limonene interactions resulting in organic product. Gas Chromatography-Mass Spectroscopy identified the major product of the kaolinite/limonene interaction as α-terpineol (Figure 15).

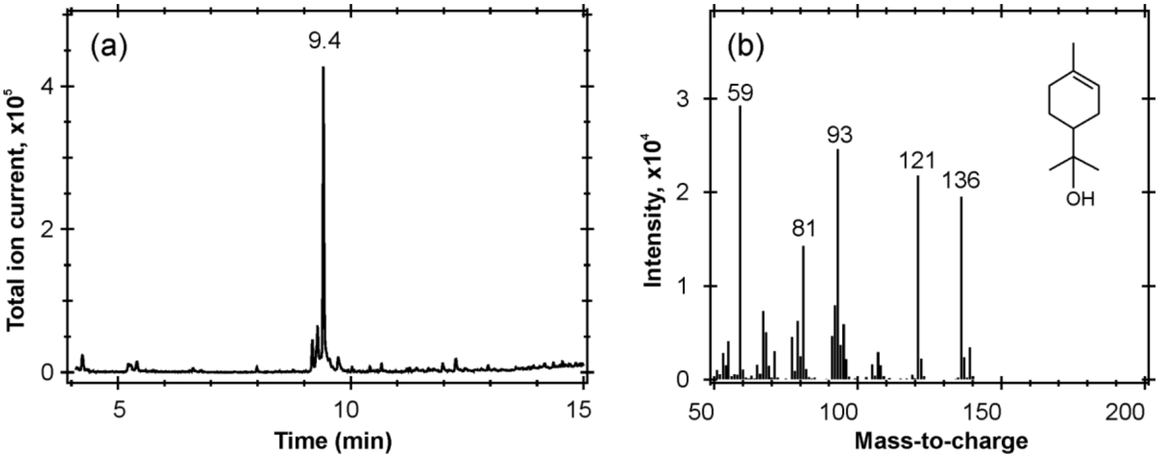


Figure 15. a) Gas Chromatograph of α-terpineol from kaolinite sample b) Mass spectroscopy identifying α-terpineol (All samples assessed by Mr. Daryl Van Ry)

This identification is further corroborated by the presence of C-H stretch peaks around 2900 cm^{-1}, the C-H bend at 1454 cm^{-1}, and the C-O stretch at 1143 cm^{-1} in the IR spectrum. While we would normally see a broad O-H peak around 3000 cm^{-1} the loss of water on the surface compensates so that we actually see a loss of the O-H stretch at 3000 and the O-H bend at 1613 cm^{-1}. This loss of water indicates a hydrolysis type reaction as proposed below (Figure 16).

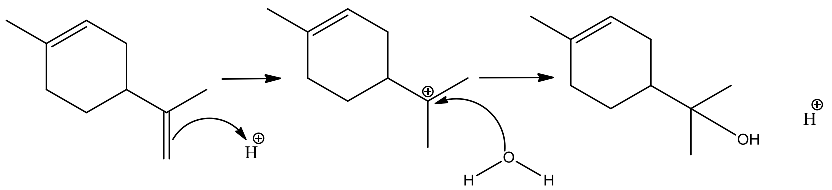


Figure 16. Hydrolysis Mechanism for the exocyclic double bond of α-terpineol

The DRIFTS spectra could then be used to assess the speed and productivity of the reaction via kinetics calculations.

II. Kaolinite and Limonene: Kinetics

Interpretation of the kinetics of the limonene/mineral dust reaction was an important overall goal of the experiments conducted in order to assess both the mechanism and the atmospheric relevance of the reactions. Chemical reaction rates can be dependent on several factors including the concentrations of reactants, temperature and the presence of catalysts. The limonene/mineral dust reaction is an example of a heterogeneous reaction, occurring at the interface between gas (the airborne limonene) and condensed (the solid mineral dust and attached water) phases meaning that it is also dependent on the structure of the surfaces on which it occurs. All of these factors must be accounted for when comparing or calculating rates.

The kinetics of this reaction are assessed using the area under the C-H stretch peak versus time. A typical kinetics plot of the kaolinite spectrum is shown below with initial rate fit (Figure 17).

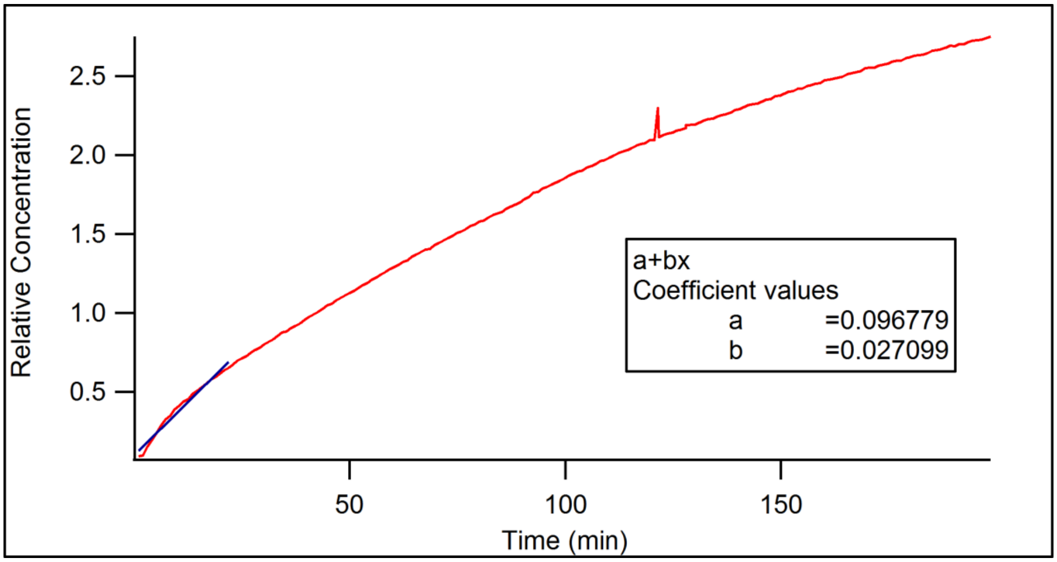


Figure 17. Plot of Area under the curve versus time for the kaolinite and limonene reaction. The blue line is a linear fit of the initial rate of reaction

A. Initial Rates

The rate of reactions can be represented as the rate of disappearance of reactants or the change in the concentration of reactant over time. This can be represented as in Equation 2 where [A] is the concentration of reactants.

$$A \rightarrow Products$$

2. $$Rate = -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

This equation assumes a constant temperature and directly correlates rate and concentration of reactants. We expand upon this by the addition of a temperature dependent rate constant, k. We also take into account the order of the reaction in Equation 3 where x is the order of the reaction.

3. $$Rate = k[A]^x$$

Our reaction requires limonene and water as reactants and uses the surface sites present on the alumina or kaolinite as catalytic sites (Equation 4).

4. $$limonene \quad + H_2O \quad + surface\ sites \rightarrow product$$

Thus the reaction rate can be written as Equation 5.

5. $$Rate = k[limonene\quad]^x[H_2O]^y[surface\ sites]^z$$

For individual reactions the concentration of water remained constant throughout the experiment, provided by the steady flow of air through a water bubbler maintained at 25 °C. The series of reactions used for mechanism determination were conducted at 30% RH so that water concentration could be assumed to be constant and folded into the experimental rate constant. Initial rate is defined to be the first 20 minutes of reaction because that is the portion of the reaction which remains fairly linear. Initial rates were used for determination of mechanism so that the concentration of surface sites (which is reduced over time by products adsorbing to the mineral dust) can also be assumed to be constant. Thus we obtain equation 6 where k_{exp} includes the water and surface site concentrations as constants (equation 7).

6. $$Rate_{(initial)} = k_{exp}[limonene\ \ ]^x$$

7. $$k_{exp} = k[H_2O]^y[surface\ sites]^z$$

For comparison of individual reactions we initially vary limonene concentration only. This allows us to compare the major types of heterogeneous reactions and determine our overall mechanism.

$$Limonene_{(g)} + H_2O_{(ads)} + surface\ sites \rightarrow \alpha - terpineol$$

Adsorption reactions tend to use one of two major mechanisms to react. The Eley-Rideal reaction mechanism assumes a reaction which occurs heterogeneously. In our case the gaseous limonene would be able to react directly with the condensed phase water and the surface sites. An Eley-Rideal type reaction would have a direct correlation between rate of reaction and concentration of gaseous limonene (8).

8. $$Rate = \frac{d[terpineol]}{dt} = k_{exp}\left[limonene_g\right]$$

The Langmuir-Hinshelwood mechanism assumes that the reactants must be in the same phase to react. This means that the gaseous limonene would need to adsorb onto the surface before reacting with the water and surface sites leading to a two step mechanism (9, 10).

9. $$limonene_{(g)} \leftrightarrows limonene_{(adsorb)}$$

10. $limonene_{(adsorb)} + H_2O_{(adsorb)} + surface\ sites \overset{k_2}{\rightarrow} terpineol_{(adsorb)}$

This means that the relationship between the rate of reaction and reactant concentration is non-linear due to the rate limiting adsorption step (11).

11. $$\frac{d[terpineol]_0}{dt_0} = k_{exp}\left[limonene_{(adsorb)}\right]$$

Thus the rate of the reaction is tied to the relationship between gaseous and adsorbed limonene.

In a Langmuir-Hinshelwood reaction we see maximum adsorption when we reach a monolayer. The saturation, $\theta_{limonene}$, relates the concentration of adsorbed limonene to the number of sites and also to the gaseous limonene concentration by equation 12;

12. $$\theta_{limonene} = \frac{\left[limonene_{(adsorb)}\right]}{N_{sites}} = \frac{K_1\left[limonene_{(g)}\right]}{1+K_1\left[limonene_{(g)}\right]}$$

where N_{sites} is the number of available sites on the kaolinite. Combining equations 11 and 12 we see that the initial rate of reaction is related to the concentration of gaseous limonene by equation 13.

13. $$\frac{d[terpineol]_0}{dt_0} = k_{exp}N_{sites}\left(\frac{K_1\left[limonene_{(g)}\right]}{1+K_1\left[limonene_{(g)}\right]}\right)$$

Thus the Langmuir Hinshelwood mechanism and Eley-Rideal mechanisms show different dependences of initial rate on limonene concentration (Figure 18).

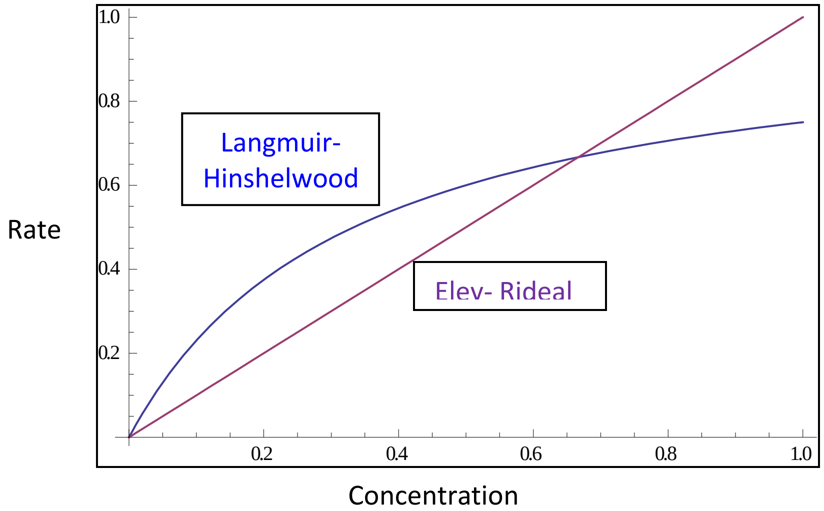


Figure 18. A sample plot of Langmuir-Hinshelwood (blue) and Eley-Rideal (purple) mechanism where rate is plotted versus concentration of gaseous limonene

We can use this correlation to determine our mechanism. Several experiments were conducted where limonene concentration was the only variable changed (Table 2).

Table 2. Limonene Concentration and Initial Rate (kaolinite reactions at 30% RH

[limonene] (ppb)	Initial Rate (abs/min)
218	0.0002263
1050	0.0010943
6640	0.034061
10500	0.00635
18750	0.027099
20500	0.015676

When initial rate is plotted versus limonene concentration the correlation fits linearly indicating an Eley-Rideal mechanism (Figure 19).

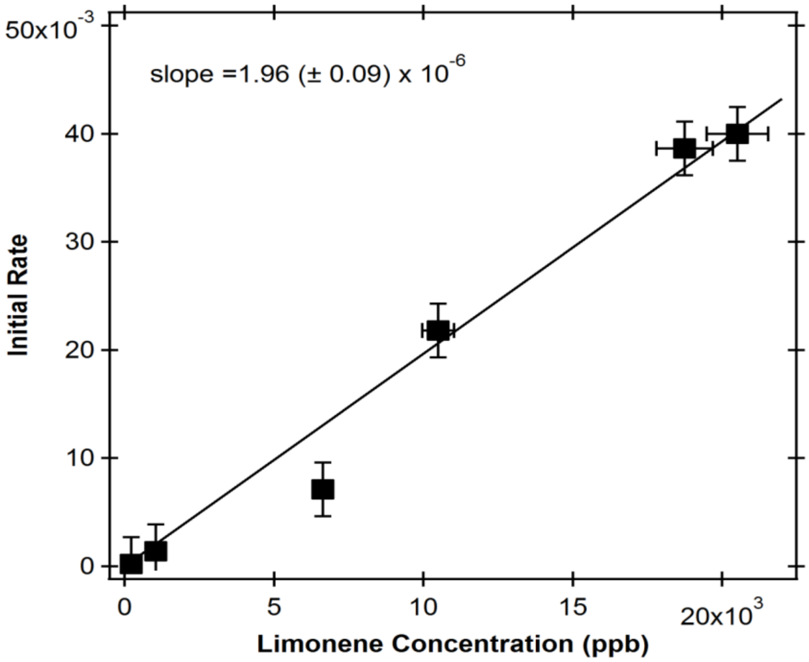


Figure 19. Initial rate of α-terpineol formation plotted versus limonene concentration. Each point represents an experiment conducted at a different limonene concentration. Relative Humidity was maintained at 30%

This makes sense considering the relatively high volatility of limonene. We would not expect spontaneous condensation down to the surface sites. Thus we can conclude that the gaseous limonene reacts directly with water present on the surface and the surface sites, consistent with the acid catalyzed heterogeneous mechanism that we postulated earlier.

B. Overall Kinetics

As can be seen in the typical kinetics plot presented at the beginning of this chapter the reaction rate slows as it moves out of its initial rate until it appears to reach a plateau. We postulate that this acid catalyzed mechanism has its access to acidic sites reduced by the adsorption of product at long reaction times. With the sites continually covered as the reaction goes further, finding uncovered sites requires more time and the reaction slows. This subsection aims to model the long term reaction rather than simply the initial rate.

Throughout the course of an individual experiment both the limonene and water concentrations remain constant, as a result of the airflow through both bubblers continually flushing the reaction chamber. The water bubbler is kept in a temperature controlled water bath and the limonene bubbler is maintained at room temperature. Our initial reaction rate equation encompasses limonene, water and the catalytic surface sites as contributing factors (14).

14. $$Rate = k[limonene][H_2O][surface\ sites]$$

With the water and limonene concentrations maintained as constants for individual experiments we can fold them into our observed rate constant (15, 16).

15. $$Rate = k_{obs}[surface\ sites]$$

16. $$k_{obs} = k[limonene][H_2O]$$

Thus the rate of reaction is how quickly the surface sites become covered with product and therefore inaccessible for reaction.[1] The concentration of surface sites changes over time as in Equation 17.

17. $$\frac{d[surface\ sites]}{dt} = -k_{obs}[surface\ sites]$$

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[1] Note that we postulate that the amount of surface sites initially present may be related to the amount of water introduced by the relative humidity because water may adsorb competitively with the product. This explanation will be further explored in the data analysis of the variation of parameters.

Integrating Equation 17 from initial (t=0) to time (t) gives us Equation 18.

18. $$[surface\ sites]_t = [surface\ sites]_0 e^{-k_{obs}t}$$

The initial amount of surface sites, $[\text{surface sites}]_0$, becomes the amount of surface sites left after some time has passed added to the amount that have been covered with product (we take terpineol as an example here) by Equation 19.

19. $$[surface\ sites]_0 = [surface\ sites]_t + \left[terpineol_{(ads)}\right]_t$$

Solving for the amount of surface sites left after time t and plugging into equation 18 gives us equation 20.

20. $$[surface\ sites]_0 - \left[terpineol_{(ads)}\right]_t = [surface\ sites]_0 e^{-k_{obs}t}$$

This equation can then be solved for the amount of product generated to give equations 21, 22.

21. $$\left[terpineol_{(ads)}\right]_t = [surface\ sites]_0 - [surface\ sites]_0 e^{-k_{obs}t}$$

22. $$\left[terpineol_{(ads)}\right]_t = [surface\ sites]_0 (1 - e^{-k_{obs}t})$$

The overall product formation is plotted as the area under the C-H peak (acquired using integration in IGOR) versus time. This is then fitted to the exponential equation above where A is the total number of surface sites and k_{obs} is the observed rate constant. We add a constant offset, x, to account for the shift up or down of spectra as a result of repacking the chamber each experiment (Figure 20).

$$Area = A\left(1 - e^{-k_{obs}t)}\right) + x$$

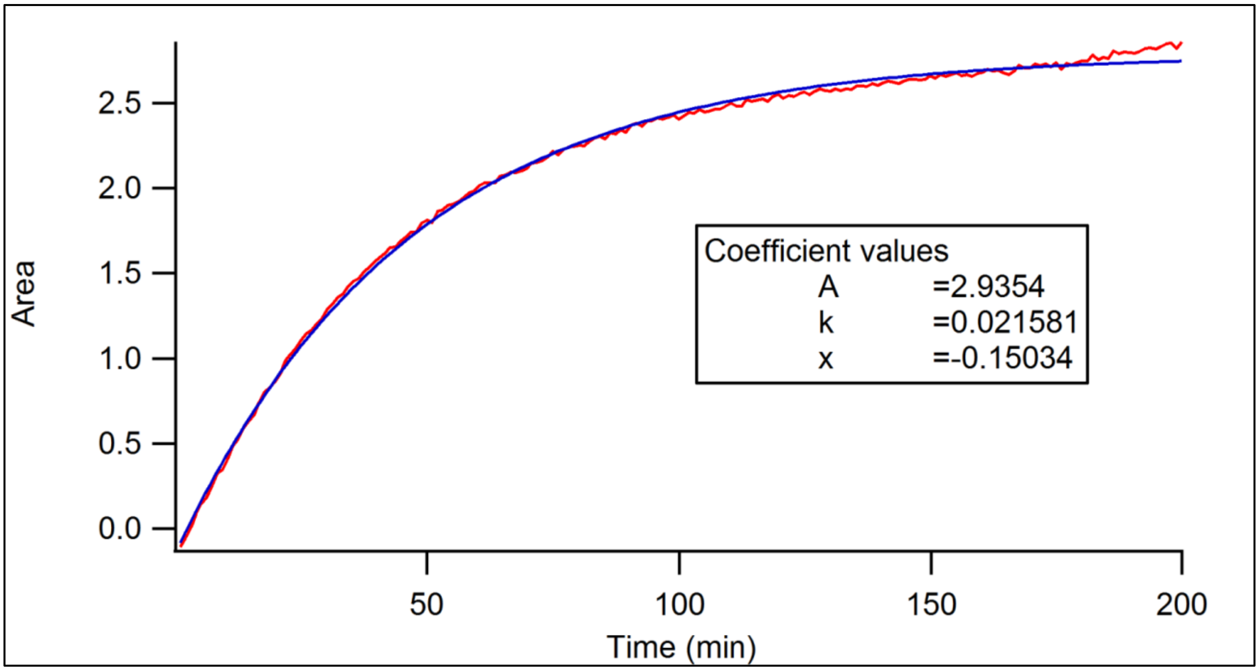

Figure 20. The overall curve can be fitted to an exponential kinetics equation

The parameter, A, can be understood as both the total amount of initial surface sites and the total concentration of product formed when the reaction runs to completion (coating all initial surface sites) and may also be notated as P_{∞}. This is because the reaction is assumed to go to completion when there are no more surface sites for the limonene to react with and product (terpineol etc) to bind to. The parameter k is, of course, k_{obs}, which includes both limonene and water concentration throughout the reaction as defined in equation 16.

As can be seen in Figure 20 our theoretical equation provides a very good fit for the experimental data and the reaction can therefore be assumed to be first order with respect to acidic sites.

III. Effect of Different Parameters on Kinetics of Reaction and Products Formed

Once our mechanism (and therefore our major reactants and contributors to the reaction) has been identified we can explore the possibility of influencing the rate of reaction. The presence and number of acid sites, the amount of water present and the particular substrate used were all found to influence the type of products formed and the rate of reaction. These parameters are also very relevant because of their natural variation in the atmosphere. Relative humidity, acid content and composition of mineral aerosols can fluctuate throughout the course of a single day.

A. Effect of Nitric Acid on the Kaolinite and Limonene Reaction

The reaction of limonene with kaolinite is believed to be an acid catalyzed hydrolysis so that addition of acidic sites could have one of two effects. It could bind to and block sites used by the limonene and so slow the reaction or it could speed up the reaction by increasing the amount of catalytic acid sites available. Addition of nitric acid could also provide further proof of the proposed mechanism which includes acidic sites as a necessary catalyst. A change in the rate of reaction with addition of acidic sites would indicate that acid is a major part of the mechanism. Gaseous nitric acid was generated from liquid nitric acid under vacuum and the substrate was exposed to this gaseous nitric acid before being exposed to limonene/ air flow. Nitric acid was thereby adsorbed to the substrate for the duration of the experiment. This was confirmed by the growth in of an N-O condensed phase infrared peak around 1400 cm^{-1}. The catalytic nature of the acid was confirmed by little to no loss of the nitrate peak after reaction (Figure 21).

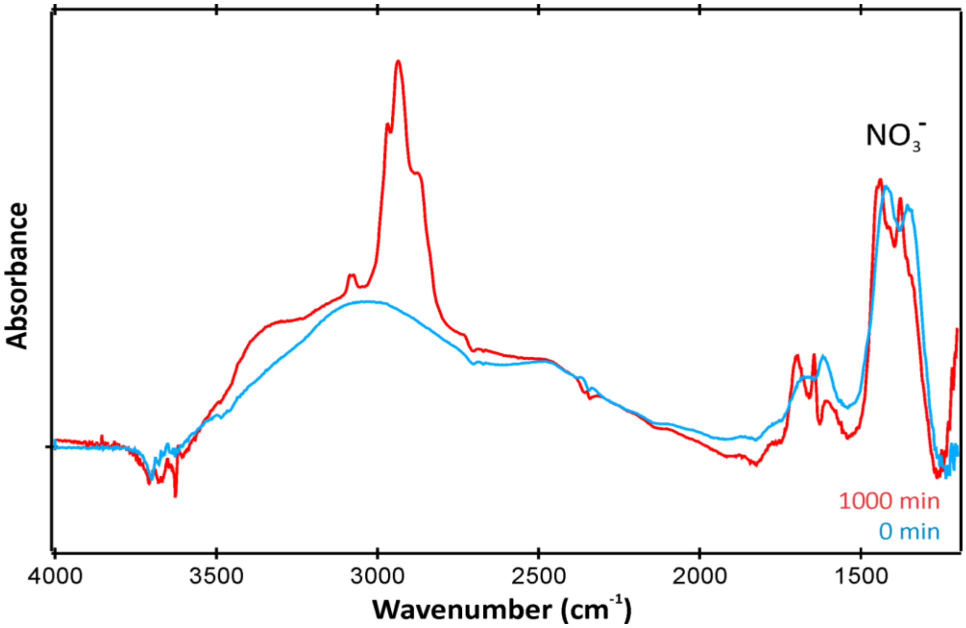

Figure 21. A typical spectrum of kaolinite after exposure to nitric acid. Note the characteristic NO peak at 1400 cm^{-1}. Nitrate Peaks remain in evidence even after 1000 minutes of reaction.

Nitric acid was chosen both because it was fairly simple to generate and because it is a highly atmospherically relevant acid which adsorbs readily to aerosol surfaces. Kaolinite is a known sink for nitric acid, capable of collecting up to 40% of the nitric acid available in the atmosphere (Dentener *et al*., 1996). Sulfuric acid was also considered as a possible reagent but difficulties in generating gaseous sulfuric acid prevented its use.

Nitric acid was shown to increase the rate of reaction for kaolinite (Figure 22).

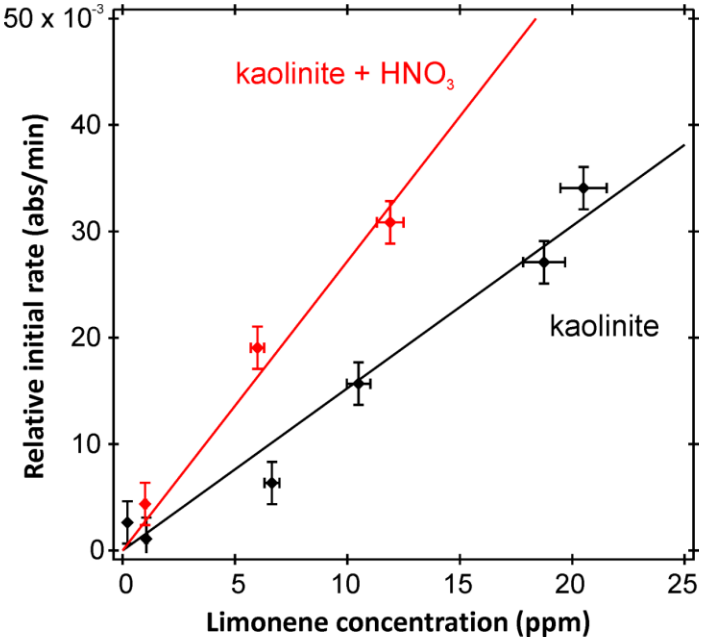

Figure 22. Rate of reaction plotted versus limonene concentration. Note that nitric acid presence enhances initial rate of reaction. These studies were conducted with kaolinite.

The increase in initial rate for kaolinite is attributed to the increase in the number of acidic sites available, catalyzing the hydrolysis more efficiently. Interestingly, this also leads to the production of a minor secondary product where both alkene bonds undergo hydrolysis. This can be understood, as more acidic sites could lead to hydrolysis of the less favored alkene bond after the initial hydrolysis took place (Figure 23).

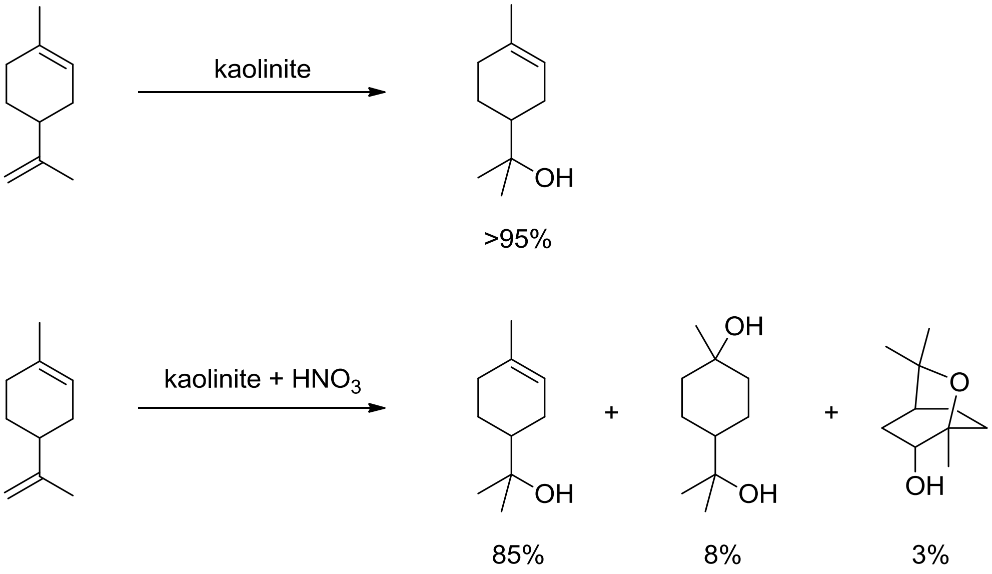

Figure 23. Products and relative abundances for kaolinite reaction

Kaolinite reactions produce only α-terpineol, the result of a normal acid catalyzed hydrolysis of the aliphatic double bond. Adding nitric acid produces a small amount of the di-hydrolyzed product, where both the aliphatic and the ring double bonds undergo hydrolysis, and a trace of a cyclized version of the di-hydrolyzed product.

B. Effects of Relative Humidity on the Rate of the Reaction between Alumina and Limonene

After kaolinite had undergone testing with nitric acid and the mechanism had been well established, we chose to replace the kaolinite with alumina, a related mineral aerosol substrate. Despite alumina and kaolinite being related compounds the use of pure alumina as a substrate led to a surprising mix of products which did not include α-terpineol, the major product of the kaolinite reaction (Figure 24). The products of the alumina reactions were also identified using GC-MS.

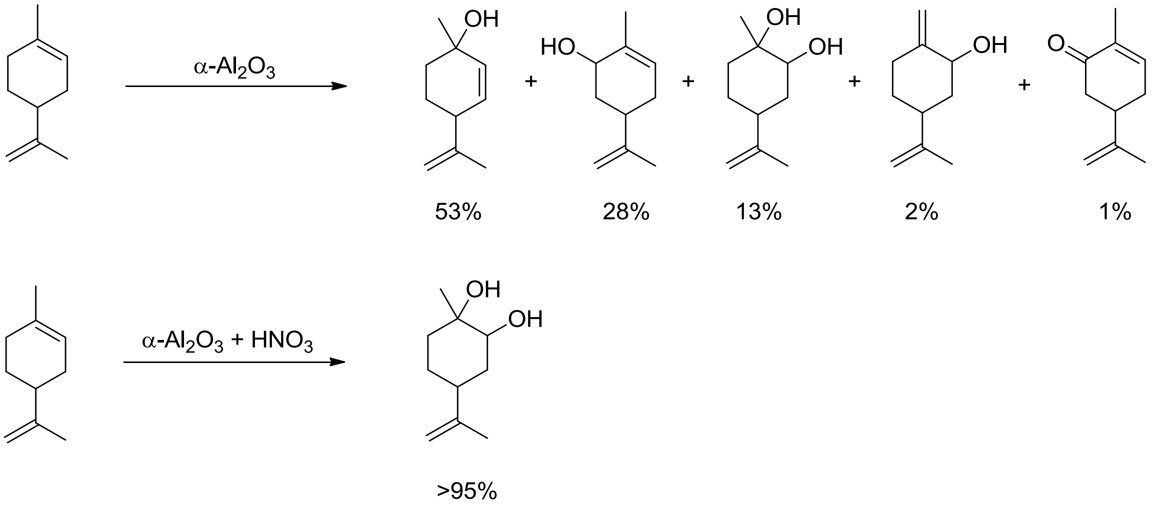

Figure 24. The major products of alumina/ limonene reactions with relative yields.

α-alumina forms a mix of oxidation products including 1-methyl-4-(prop-1-en-2-yl)cyclohex-2-enol (53%), carveol (28%) and limonene glycol (13%) (Figure 24). Tests were run with the alumina reaction under nitrogen carrier gas exclusively, which resulted in the same mix of products as the reaction under air. Thus the source of oxygen for these reactions is almost certainly either the water introduced by the relative humidity or a reduction of the alumina surface.

This is surprising in some ways because kaolinite is a chemical mixture of alumina and silica. We would normally expect similar results for kaolinite and alumina based reactions. This difference in mechanism may be due to structural differences between solid alumina and solid kaolinite surfaces. Interestingly the alumina follows the preference observed for direct ozonolysis for the endocyclic double bond whereas kaolinite preferentially hydrolyzes the terminal double bond. One possibility for the oxidation products of the alumina reaction involves an epoxide intermediate (Figure 25).

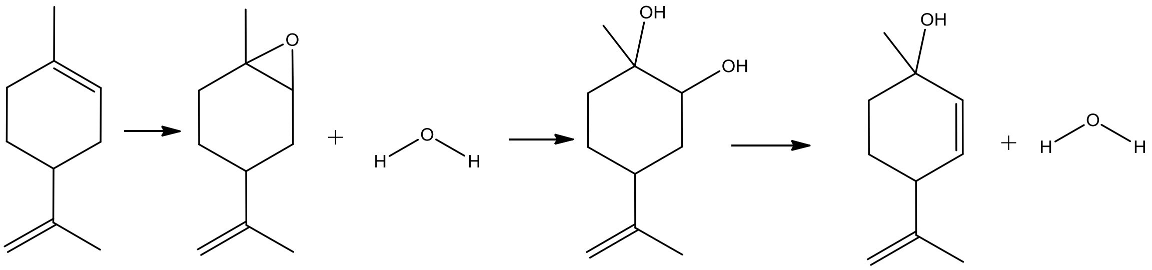

Figure 25. The proposed mechanism for 1-methyl-4-(prop-1-en-2-yl)cyclohex-2-enol

Regardless of mechanism, water is a major reactant in both the alumina and the kaolinite interactions. Initial tests were performed to test the effect of water presence by varying the relative humidity over the alumina substrate. This was accomplished by altering the relative amounts of wet (having flowed through a water bubbler) and dry air flowing through the chamber and monitoring with a humidity monitor. Overall flow rates were maintained in order to keep the amount and velocity of the air flowing consistent between experiments.

We might expect to see an increase of rate of reaction with increase in relative humidity because water is a reactant in our mechanism. Surprisingly we found the exact opposite to be evident; increased relative humidity was actually found to have a dampening effect on the initial rate of reaction (Figure 26).

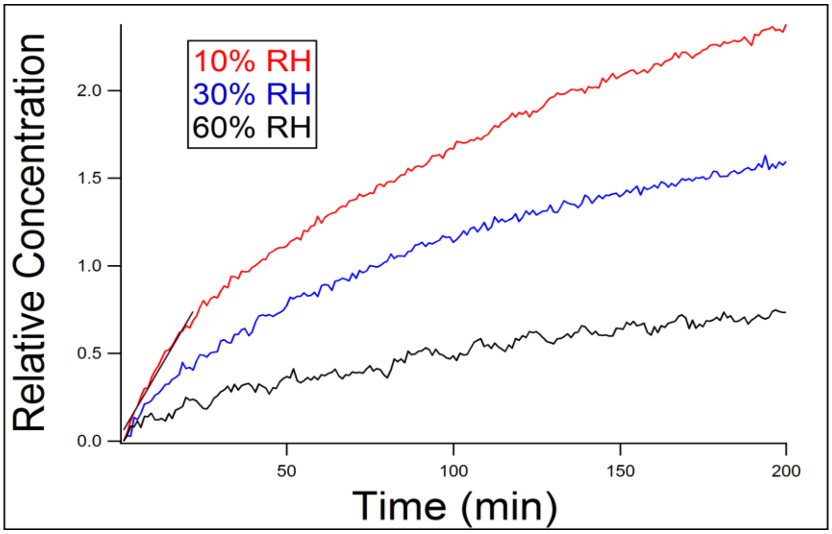

Figure 26. Relative concentration of products (1-methyl-4-(prop-1-en-2-yl)cyclohex-2-enol carveol and limonene glycol) plotted versus time. Note that the 10% RH curve shows both the fastest initial reaction rate and the highest concentration at which the reaction begins to slow down (approaches saturation).

This dampening effect may be attributed to water covering the acid sites which the limonene interacts with, slowing the reaction. Increased presence of water also reduces the saturation point of the reaction, the point at which the rate of reaction appears to level off and no more product is bound to the substrate (Figure 26). This agrees with a competitive adsorption model in which water is attached to sites which the limonene uses to react and binds to once reacted.

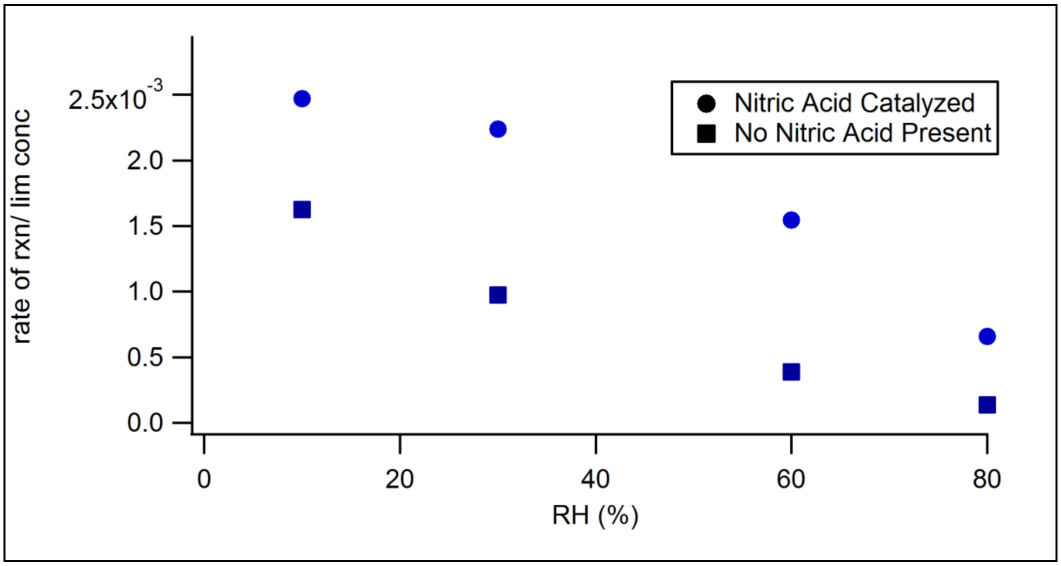

Figure 27. Initial rate of reaction (normalized to limonene concentration) plotted versus relative humidity for α-alumina substrate. Relative humidities were varied from 0 to 80%. The 45% RH data was omitted because it was suspected to have been affected by pressure build-up

Initial rate was plotted versus relative humidity, showing a marked decrease in reaction rate as relative humidity is increased (Figure 27).For example; the 10% relative humidity has the greatest initial rate. It also begins to level off at the highest concentration indicating that more product is bound at lower humidities (Figure 26). The higher relative humidities level off at lower concentrations. This result defies the normal expectations that an increase in the reactant concentration would lead to increase in product formation and indicates that the sites used for this reaction are most likely coated by the water, reducing both the rate of reaction and product formation.

The area under the curve versus time can be fit to a saturation curve according to equation 23 which was derived in earlier chapters.

$$[P(t)] = [P_\infty](1 - e^{-kt}) + x \qquad (23.)$$

Product concentration as a function of time is equated to the product concentration at infinity (P_∞) multiplied by an exponential growth factor (x merely accounts for the vertical shift of the graph). The product concentration at infinity should be directly related to the amount of sites present. We see an increase in catalytic site concentration at lower relative humidities (Figure 28). Thus we can conclude that water adsorbs competitively with our product, covering the reactive acidic sites as relative humidity increases and decreasing the amount of product produced and bound to the substrate.

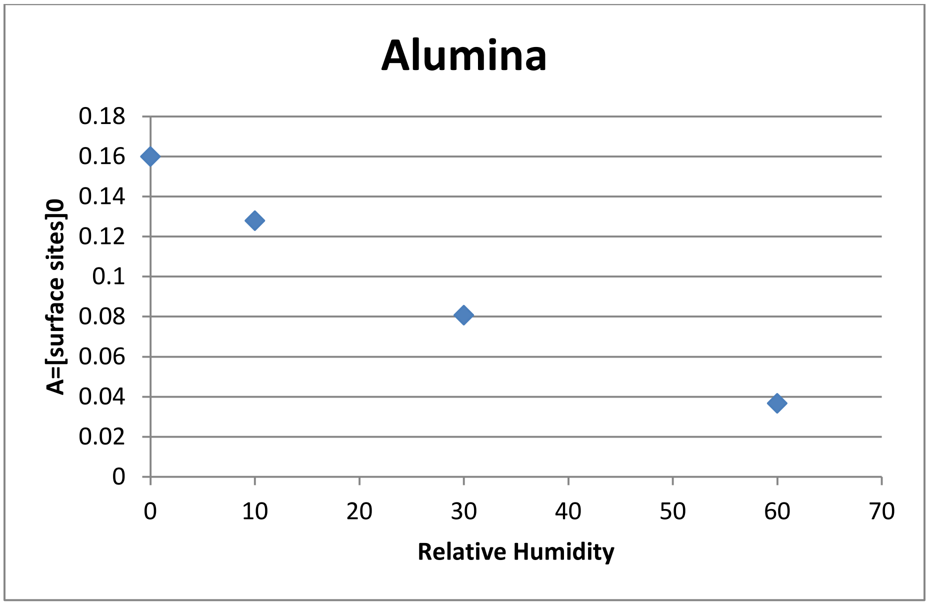

Figure 28. A (surface site concentration at time zero) plotted versus relative humidity.

The parameter, k, represents the observed rate constant and includes the concentration of water and limonene present throughout the experiment. All experiments with relative humidity were conducted at limonene concentrations of ≈20 ppm and k was later divided by limonene concentration so that the k was merely the general rate constant times the concentration of water (which is relative to relative humidity). Thus the only parameter changed between experiments was the concentration of water present. We would expect to see an increase in k proportional to increased relative humidity. Instead we see little to no change except for experiments conducted at 0% RH[2] and 80% RH (Table 3). This indicates that k may, in fact, be decreasing with the addition of more water. This could perhaps be attributed to the covering of the catalytic sites which make this reaction possible.

Table 3. Relative Humidity and k_{obs}

RH (%)	[lim] (ppm)	k_{obs}	k_{obs}/[lim]
10	20	0.008537	0.000427
30	21	0.01035	0.000489
45	20.5	0.0043	0.000209
60	23	0.007299	0.000317
80	18	0.01858	0.00103

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[2] 0% RH experiments may represent a special case due to water not being replenished throughout the experiment as it was in experiments performed at higher relative humidities.

<u>Chapter IV:</u> Conclusions

The limonene/mineral dust reactions explored here show promise as possible alternate mechanisms of hydrolysis and oxidation of volatile organics to form secondary organic aerosols which are bound to inorganic (mineral) substrates.

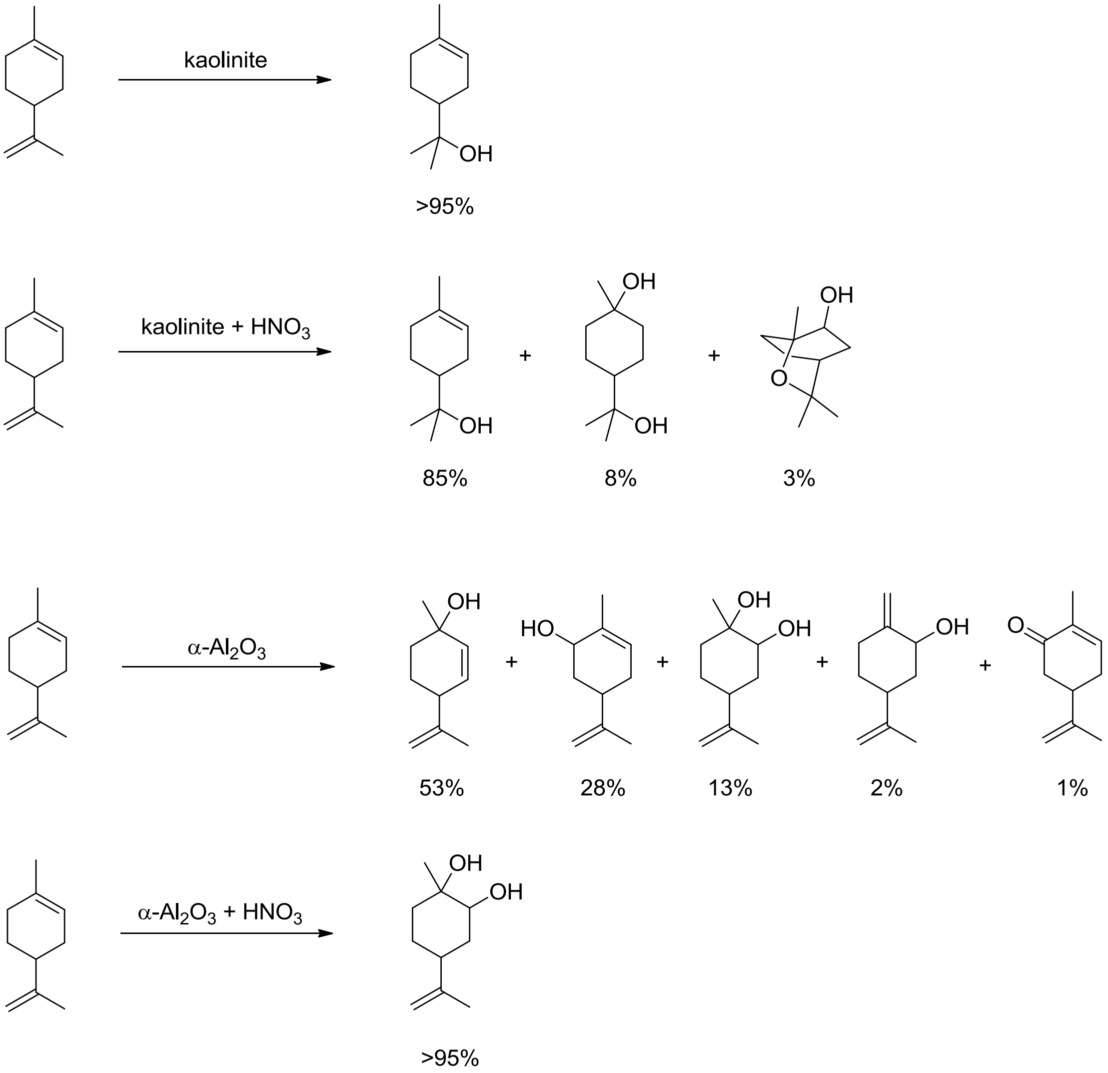

Figure 29. The products of all reactions. Kaolinite produces hydrolysis products. In contrast, alumina produces an entirely separate group of oxidation products.

They differ from traditional homogeneous gas phase reactions in that gaseous limonene appears to be reacting directly with condensed phase water and acidic sites in a heterogeneous Eley-Rideal type reaction. This agrees with previous work in the literature which indicates the viability of aqueous droplet based heterogeneous reactions with limonene as precursors to secondary organic matter on aerosols (Li *et al*., 2010). Expansion of this work beyond acid droplets to the perhaps more atmospherically relevant acid coated mineral aerosols, in fact, increases the general viability of acid-catalyzed heterogeneous reactions as contributors to SOA.

Li *et al*. see some of the same products as our limonene/ kaolinite reactions, the result of gaseous limonene interactions with acid droplets and water and, in fact, cite this type of hydration as the major pathway under mildly acidic, humidified conditions, which are representative of ambient atmospheric conditions (2010) (Figure 30).

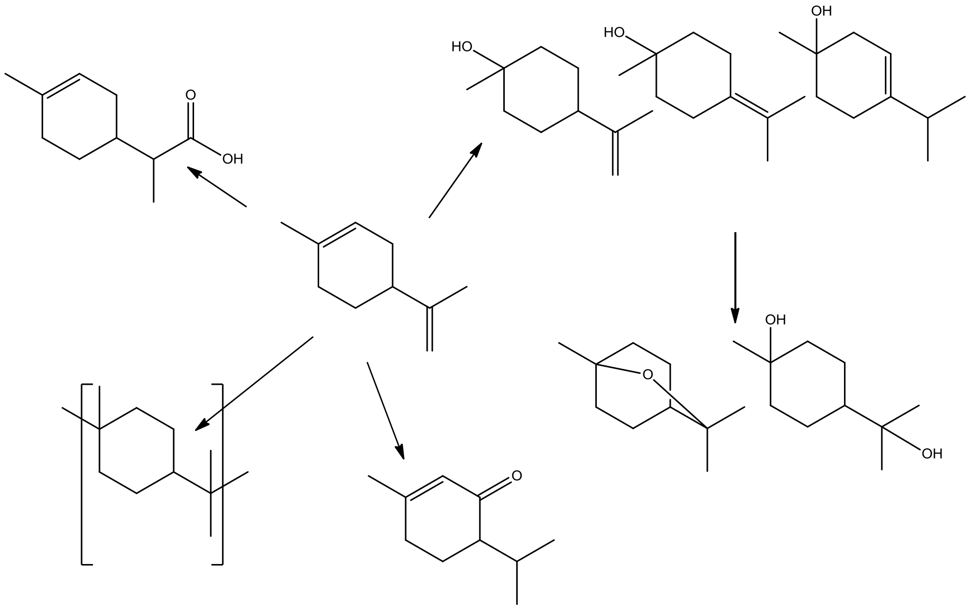

Figure 30. Some of the products observed by Li *et al*. (2010) when reacting limonene with acidic droplets.

Their system seems to favor the endocyclic bond for reaction which agrees with the selectivity of the normal gas phase ozonolysis for reaction where we see the exocyclic double bond react first. This may be the result of differences in the availability of acid sites. With liquid droplets which are composed entirely of acid the endocyclic bond may react first. The sites on the kaolinite will be more difficult to access and therefore may prefer the freer terminal double bond.

Limonene concentration is shown to increase rate of reaction in a linear manner indicating first order kinetics with respect to limonene confirming the postulated Eley-Rideal, heterogeneous mechanism. Increase in presence of water (RH) causes decrease in amount of products made and rate of reaction. This is postulated to be the result of water adsorbing competitively with product thereby reducing limonene access to the catalytic sites present on the mineral dust and the amount of sites present for product to bind to.

The difference in products for alumina and kaolinite indicate entirely different types of reaction and the exact mechanism of the oxidation to form alumina products is also under investigation. The possibility of an epoxide intermediate is currently under consideration. Kaolinite and alumina are related compounds; kaolinite is composed of alternating sheets of alumina and silica, which makes the entirely separate set of products rather surprising. The difference can perhaps be attributed to the silica component of kaolinite providing the acidic catalysis. Another explanation could be the difference in the configurations of surface sites. Kaolinite provides smooth sheets where alumina is a rougher surface. These questions should be answered in further explorations of this mechanism and different mineral substrates.

The exposure of kaolinite to nitric acid leads to an increase in variety of products, consistent with the hydrolysis of the endocyclic double bond. This can be understood in the context of gas phase ozonolysis which shows oxidation of both double bonds though the favorability is reversed in the gas phase versus our condensed phase. (Maksymiuk *et al.*, 2009). Exposing alumina to nitric acid has the opposite effect, decreasing the product variety, a further indicator of a different type of mechanism.

Atmospherically relevant reactions conducted at 30%RH with nitric acid weathering indicate that reactions with kaolinite and alumina may lead to products capable of remaining bound to aerosol and undergoing further reaction with ozone, hydroxyl, etc.

The dominant mechanism for secondary organic aerosols is still, undoubtedly, the gas phase interaction of volatile organic compounds with oxidizers in the atmosphere which then partition down to coat inorganic aerosols. However, models which use these mechanisms alone have been shown to underestimate the amount of SOA which is actually present in the atmosphere. Acid-catalyzed heterogeneous reactions such as this interaction between limonene and mineral aerosols represent a promising alternate mechanism which could account for that gap in our knowledge of SOA formation.

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