Scholars' Mine

Doctoral Dissertations

Student Theses and Dissertations

Spring 2011

Ozone and terpene reactions on indoor surfaces: reaction rates and implications for indoor air quality

Shi Shu

Recommended Citation

OZONE AND TERPENE REACTIONS ON INDOOR SURFACES: REACTION
RATES AND IMPLICATIONS FOR INDOOR AIR QUALITY

by

SHI SHU

A DISSERTATION

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

2011

Approved by

Glenn C. Morrison, Advisor
Joel G. Burken
Fitch Mark
Jianmin Wang
Charles C. Chusuei

PUBLICATION DISSERTATION OPTION

This dissertation has been prepared in the form of four journal articles for peer review. These articles are presented in Paper I through Paper IV. Paper I has been prepared according to the style used by Talanta and pages 25 to 51 have been published. Paper II has been prepared in the style used by Environmental Science and Technology and pages 52 to 78 will be submitted to this publication. Paper III has been prepared in the style used by Atmospheric Environment and pages 79 to 112 will be submitted to this publication. Paper IV has been prepared in the style used by Indoor Air and pages 113 to 131 will be submitted to this publication.

NOTE: The sections of Introduction, Goals and Objectives, Materials and Method, Conclusions, Significance and Impacts, Future Research, and Appendices contain supplemental information for the journal articles. They present some information required to complete this dissertation but not necessary for submission to any of the aforementioned journals.

ABSTRACT

Surface chemistry greatly influences the concentration of reactants and products in indoor environments, thus affecting human exposure. The large amount of surface area serves as a support for heterogeneous reactions such as those taking place between ozone and other species associated with that surface. Ozonation reactions can generate carcinogens, asthma promoters and irritants. Therefore, investigation of the significance of ozone reactions on surfaces is necessary for controlling, and for developing a better understanding of, occupant exposure to ozone and heterogeneous ozone reaction products.

In this dissertation, bench scale experiments were conducted in a plug flow reactor to quantify the reaction rate of ozone with two representative compounds, α-terpineol and dihydromyrcenol, adsorbed on beads representative of indoor surface materials. Both the reaction probability and a second-order rate coefficient were measured. A new method of measuring terpenoids in the presence of ozone was developed. Experiments were also conducted in a room-sized chamber to compare kinetics at lab and full scale. Products of the heterogeneous surface reaction have also been identified. The rate constants suggest that these surface reactions take place at a rate comparable to or higher than the air exchange rate or the rate of gas-phase reactions. Thus, surface conversion is predicted to significantly affect exposure (to reactants and products) and existing indoor air models must be modified to include these reactions.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1. INTRODUCTION

Although the ozone layer in the upper level of the atmosphere prevents potentially

damaging ultraviolet light from reaching the Earth's surface and thus is beneficial to people,

ozone in the lower atmosphere (troposphere) is an air pollutant and harms people's health

(Weschler 2006; Bell et al. 2004). Ozone, a strong oxidant, reacts readily with other

compounds in the atmosphere and in indoor environments. The products of these reactions also

exhibit deleterious health effects. Well studied homogeneous reactions with terpenoid

compounds generate a host of gas-phase and aerosol products of concern. This research is

directed to improving our understanding of the indoor heterogeneous chemical rates of ozone

with terpenoids typical of indoor cleaning and personal care products.

1.1 OZONE AND OZONE CHEMISTRY

Ozone in the troposphere is formed by photochemical reactions that include

hydrocarbons and nitrogen oxides and the energy imparted by sunlight. Hydrocarbons are

emitted into the atmosphere by both anthropogenic activities (e.g., automotive traffic

emissions, industrial processes, application of paint and solvents) and natural processes (e.g.,

emissions from forests and oceans). Nitrogen oxides, in addition to being a precursor of ozone,

are also directly harmful to human health (Chauhan et al. 1998). They are mainly produced and

emitted by fuel combustion (Faiz, Weaver, and Walsh 1996). Reactions between hydrocarbons and nitrogen oxides are facilitated by sunlight, and the reactions generate not only ozone, but also particulate matter (PM) and other components of smog (Atkinson 2000). High outdoor ozone concentrations are generally associated with urban areas which generate high emissions of ozone precursors. In addition, ozone concentrations in rural areas are increasing (Seinfeld and Pandis 2006; Lelieveld and Dentener 2000).

Adverse health effects of ozone range from mild sensory irritation to severe impairment and death. According to the World Health Organization, ozone can irritate the respiratory system and harm lung function (World Health Organization 2003). Correlations between exposure to high ambient ozone level and some symptoms, such as cough, lower and upper respiratory symptoms, and shortness of breath, have been identified in epidemiological studies (Galizia and Kinney 1999; Kinney 1999). Even modest increases (~ 0.010 ppm) in ambient ozone result in measurably higher morbidity and mortality (Nyberg and Pershagen 1996; Hubbell et al. 2005; Jerrett et al. 2009).   In response to these findings, the 8-hr ozone standard has been recently been reduced to between 0.070 and 0.075 ppm by the United States Environmental Protection Agency (US EPA) (National Ambient Air Quality Standards for ozone, 2008).

Ozone is also a continuing problem in indoor environments. Tropospheric ozone enters residential and commercial buildings by infiltration and by natural or mechanical ventilation. Ozone can also be generated indoors by appliances such as laser printers and electrostatic air

cleaners (Kissel 1993; Boeniger 1995; Britigan, Alshawa, and Nizkorodov 2006). In the absence of such indoor sources, indoor ozone concentrations are almost always lower than outdoor ozone concentrations. The indoor to outdoor ratio of ozone concentrations ranges from about 0.1 to 0.8 and this ratio is highly dependent on the air exchange rate (Weschler, Shields, and Naik 1989). Lower indoor ozone concentrations are caused by both gas phase homogenous reactions (e.g., reaction with nitric oxide to form nitrogen dioxide) and heterogeneous reactions on indoor surfaces. Although ozone concentrations are lower indoors, people spend ~ 90% of their time indoors (Klepeis et al. 2001). Because of this, approximately half of ozone exposure occurs indoors (Weschler 2006).

Ozone reactions not only decrease the ozone concentration indoors but also generate hazardous reaction products. Secondary Organic Aerosols (SOA), usually associated with smog, are produced indoors from ozone-terpene reactions, either in air or on surfaces (Sarwar et al. 2004; Waring et al. 2008). Dicarbonyls are also produced from both gas phase (Harrison and Wells 2009; Ham, Proper, and Wells 2006; Forester, Ham, and Wells 2006; Wells 2005; Yu et al. 1999; Calogirou, Larsen, and Kotzias 1999) and surface ozone terpene reactions (Ham and Wells 2009; Ham and Wells 2008).The yield of dicarbonyls from gas phase ozone reaction with some terpenes can vary from ~5% to ~90% (Forester and Wells 2009). The ozonide, an intermediate in the reaction path with olefins, is thought to be responsible for observed eye and membrane irritation in ozone-terpene reaction mixtures (Wilkins et al. 2003; Wolkoff et al. 2000). Exposure to SOA and dicarbonyls may cause lung disease, respiratory

symptoms and occupational asthma (Kreiss et al. 2002; Delfino 2002; Anderson et al. 2007). Furthermore, formaldehyde, an EPA listed carcinogen, is produced by the ozone reaction with latex paint (Reiss et al. 1995) and carpets in   homes (Wang and Morrison 2006; Wang and Morrison 2010).

1.2   INDOOR SURFACES AND POLLUTANT INTERACTIONS

Unlike ambient environments, indoor environments usually incorporate a very large surface area in a relatively small volume. The surface area-to-volume ratio is roughly two orders of magnitude larger than that for an outdoor urban air parcel (Nazaroff, Weschler, and Corsi 2003).

Many kinds of surface materials are present in indoor environments: painted surfaces (wall and ceiling), textiles (carpets, curtains, upholstery, clothing and bed sheets), wood (floors and furniture), glass (windows and mirrors), plastics/polymers (vinyl flooring and coatings), hair and skin (occupants and pets) and so forth. All indoor surfaces are covered with dust, dirt and oils that can also influence their interactions with pollutants.

The morphology of indoor surfaces varies considerably. Some surfaces (e.g. textiles) are fluffy with substantial internal surface area and roughness scales measured in the millimeter to centimeter range. Others, such as latex paint, are porous at a more microscopic scale. The geometric or 'projected' surface to volume ratio of typical indoor environments range from 2 to 4 m^2 m^{-3} (Hodgson, Ming, and Singer 2004). Floor, ceiling and walls account

for most of the projected area, while the furnishings and textiles may account for a large

fraction of the internal surface area. For example, the surface area of the fibers in carpet is

roughly 50-100 times the projected area of the carpet itself (Morrison and Nazaroff 2002).

Many indoor materials serve as adsorptive sink for indoor pollutants (such as volatile

organic compounds), which means they have the potential to reduce the peak concentration of

pollutants, but also to prolong occupant exposure due to their re-emission (Won, Corsi, and

Rynes 2000). The interactions of organic compounds with indoor materials and their effects on

indoor air quality have been studied extensively. Many models have been developed for

organic adsorption on different indoor materials (Singer et al. 2007; Jørgensen 2007; Huang,

Haghighat, and Blondeau 2006) and their emissions from these materials (Yan, Zhang, and

Wang 2009; Xu and Little 2006; Haghighat and Huang 2003). In general, volatile species

adsorb weakly, while low-volatility or polar species adsorb more strongly. For the same

equilibrium air concentration, the surface concentration for a terpene alcohol such as

a-terpineol will be much higher than that for a more volatile, less polar, terpene such as

limonene. Under these conditions, a reactive molecule such as ozone will strike the adsorbed

terpineol much more frequently than adsorbed limonene while the gas-phase collision rates

would be equal.

When ozone encounters an indoor surface it can strike and rebound, adsorb or react

with the substrate, an adsorbed molecule or other debris coating the substrate. Ozone can

spontaneously decompose to oxygen, even on otherwise unreactive surfaces such as clean

glass. Different substrates can have very different ability to "consume" ozone; the products and their yields can also be quite different (Hoang, Kinney, and Corsi 2009; Klenø et al. 2001). Ozone reaction rates and products have been quantified and/or identified from such substrates as latex paint (Reiss et al. 1995), carpet (Morrison and Nazaroff 2002), aircraft cabin materials and clothing fabrics (Coleman et al. 2008), and even human skin lipids (Wisthaler and Weschler 2009; Pandrangi and Morrison 2008). Products from the heterogeneous ozone reaction with these surfaces include aldehydes (e.g. formaldehyde), ketones (e.g. acetone), other carbonyls, dicarbonyls and hydrocarbonyls. Although not precisely quantified, Weschler et al estimated that the reaction with occupants and their clothing were responsible for >55% ozone removal in a simulated aircraft cabin (Weschler et al. 2007). Thus, ozone surface chemistry can significantly alter the concentration of indoor air species, and affect human exposure to indoor pollutants.

1.3   TERPENE CHEMISTRY

The *terpene* is a category of hydrocarbons built up from isoprene sub-units (Zubay and Atkinson 1988). They are naturally emitted from flowers and plants and usually can be found in essential oils and resins (Kesselmeier and Staudt 1999). Strictly speaking, a terpenoid is modified terpene, wherein methyl groups are moved or removed, or oxygen functionality added (IUPAC 1978). However, as is common usage, the terms terpene and terpenoid are used interchangeably throughout this dissertation. Terpenes are emitted in large quantities into the
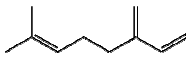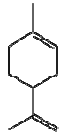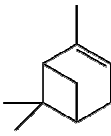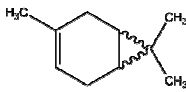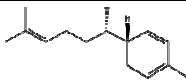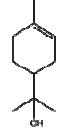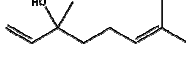
atmosphere (Isidorov, Zenkevich, and Ioffe 1985) and participate in atmospheric chemistry, which is why there is a much higher concentration of aerosols in the atmosphere above forest (Tunved et al. 2006). Many terpenes contain carbon-carbon double bonds which react readily with ozone. These important atmospheric reactions have been studied for many years. See reviews in (Yu et al. 1999; Atkinson and Arey 2003).

Because many terpenes have a pleasant odor, they have been extensively used as fragrance compounds in household products, including but not limited to perfume, soap, shampoo, detergents, air fresheners, candles, and cosmetics. Large quantities of terpenes are produced by chemical synthesis each year. For d-limonene only, the worldwide annual production was ~70 million kg in 2009 (Kerton 2009). Because of this, indoor concentrations tend to be much higher than outdoors and can be the dominant components of indoor VOCs (Singer et al. 2006; Nazaroff and Weschler 2004).

Some terpenes that dominate indoor measurements include limonene and α-pinene (Nazaroff and Weschler 2004). These are used as "top-notes" and are the first compounds to evaporate and develop the fragrance desired by the manufacturer (McDaniel and McDaniel 2010). Others emit somewhat more slowly and provide a longer-lasting experience. For example, the terpene alcohol α-terpineol is a major component of pine oil (Nazaroff and Weschler 2004), and has been found in liquid cleaner/disinfectant, liquid floor detergent (Colombo et al. 1991) and air fresheners (Salthammer and Uhde 2009). Dihydromyrcenol is one of the principal components of lavender (Nazaroff and Weschler 2004) and has been found

in liquid floor detergent (Colombo et al. 1991). The formulas and structures of some typical

terpenes are listed in Table 1.1.

Table 1.1 List of terpenes

Category	Name	Formula	Structure	Found in
Monoterpene	α-myrcene	$C_{10}H_{16}$		Bay, wild thyme
	limonene	$C_{10}H_{16}$		Orange peel
	α-pinene	$C_{10}H_{16}$		Pine resin
	Δ-3-carene	$C_{10}H_{16}$		Turpentine
Sesquiterpene	zingiberene	$C_{15}H_{24}$		Ginger oil
Triterpene	squalene	$C_{30}H_{50}$		Shark liver oil, human skin
Monoterpene alcohol	α-terpineol	$C_{10}H_{18}O$		Pine tree oil
	linalool	$C_{10}H_{18}O$		Kiwifruit and apple
	dihydromyrcenol	$C_{10}H_{20}O$		lavender

Ozone-terpene reactions in the gas phase have been studied for many years. The

products include gaseous and particulate products (Yu et al. 1999). Nøjgaard et al. found that

limonene oxidation products can cause trigeminal stimulation and possibly eye irritation when ozone and limonene concentration were in their high end of indoor related concentrations (Nøjgaard, Christensen, and Wolkoff 2005). The ozone terpene reactions are generally believed to initially form a primary (unstable) ozonide which reacts further to form a semi-stable secondary ozonide. The mechanism is shown in Figure 1.1 .
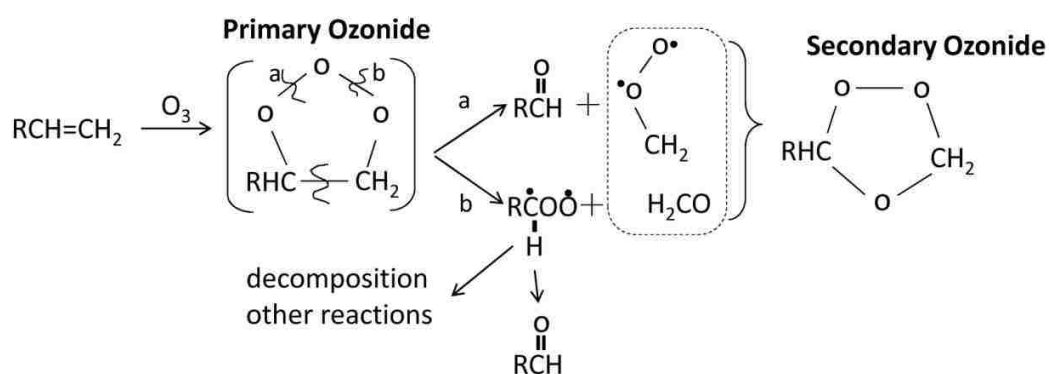
Figure 1.1 Ozone terpene reaction mechanisms

This secondary ozonide further decomposes to form aldehydes, dialdehydes, ketones, carboxylic acids, hydroxycarbonyls, and others; some are much less volatile than the original terpene and condense to form secondary organic aerosols (Claeys et al. 2004).

Specific gaseous products include glyoxal, methylglyoxal, glycolaldehyde, and dicarbonyls such as these have been identified as irritants and sensitizers (Anderson et al. 2007). For example, workers at a microwave popcorn plant were exposed to diacetyl (a

dicarbonyl similar to glyoxal) and they have twice expected rates of asthma (Kreiss et al. 2002). Even irritation can exact a toll. As Mendell et al. (Mendell et al. 2002) pointed out, there are up to 60 million people in the United States working in indoor office environment have one or more weekly building-related symptoms. The annual cost due to illness or performance losses was estimated to range from 20-70 billion. Exposure to indoor volatile organic compounds was ascribed as one major reason for building related symptoms (Spengler, Samet, and McCarthy 2001). At the cellular level, some VOCs can induce cellular damage to lung cells and cause inflammatory response (Doyle et al. 2007; Sexton et al. 2004; Kasper et al. 2000).

Ozonation of terpenes generates secondary organic aerosols in the ~0.015 to 0.7 μm size range (Rohr et al. 2003). Particles which have aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) are correlated with daily mortality. A 10 μg m^{-3} increase in two-day mean $PM_{2.5}$ was associated with a 1.5% (95% CI 1.1% to 1.9%) increase in total daily mortality (Schwartz, Dockery, and Neas 1996).

In buildings, the rates of chemical reactions determine whether this chemistry is "important" relative to other phenomena such as emissions or ventilation. There are three major removal mechanisms for reactive pollutants: air exchange, adsorption/absorption and reaction. In general, the rate of chemical reactions must be a substantial fraction of the air exchange rate to significantly influence the steady-state indoor concentrations of reactants, assuming rates are reported on the same basis (usually first-order, or units of h^{-1}). The gas phase reaction rate of ozone and some terpenes (e.g. citronellol, d-limonene, Δ-carene,

α-pinene, α-terpineol, dihydromyrcenol, isoprene, and geraniol) have been quantified, in terms of bimolecular second-order reaction rate coefficient (Ham, Proper, and Wells 2006; Forester, Ham, and Wells 2006; Wells 2005; Forester, Ham, and Wells 2007; Khamaganov and Hites 2001). At typical ozone concentrations in buildings, pseudo-first-order rates of many terpenes compete with air exchange as the dominant removal mechanism for these compounds.

Surface reactions of ozone with terpenes may also have rates that compete with air exchange, but have only recently been studied. The products of surface ozone reactions with α-terpineol and dihydromyrcenol have been investigated (Ham and Wells 2008; Ham and Wells 2009). Some of the same products were identified from both surface reaction and gas phase reaction. However, the relative yields of products were different. It was suggested that large molecular weight products (not observed directly) were formed from the surface reactions. Springs et al. (Springs and Morrison 2007.) studied the surface reaction probability of ozone and two volatile terpenes: Δ-3-carene and d-limonene. The surface ozone reaction probability of Δ-3-carene and d-limonene were roughly 10 to 100 times greater than the corresponding gas-phase values. However, to achieve measurable adsorption on surfaces, the concentrations of Δ-3-carene and d-limonene used in this research were ~1000 ppb, which is very high compared with typical indoor concentrations (10-100 ppb). Extrapolation of results suggested that ozone uptake on indoor surfaces would not be substantially increased due to adsorbed Δ-3-carene and d-limonene. However, terpene removal and product formation rates may be a non-significant fraction of the whole. The research reported in this dissertation was

motivated by the fact that terpenes with similar gas phase ozone reactivity but a much lower vapor pressure (e.g. α-terpineol) could achieve high surface coverage at low air concentrations and thus may substantially increase ozone-terpene conversion rates in buildings.

1.4   OZONE INTERACTIONS WITH SURFACES

The reaction probability, γ, is defined as the probability that a reaction occurs when two particles (molecules in this case) undergo a collision (McNaught and Wilkinson 1997). Its value ranges from 0 to 1 and depends on the physical and chemical properties of the reactant molecules and the reaction, such as activation energy, the energy of molecules before and after collision, the cross sectional area of reactant molecules. It is independent of the macro scale conditions, such as fluid flow or the concentration of each reactant. When the collision of ozone and a second molecule takes place in the gas phase, the gas phase reaction probability, γ_{gas}, is proportional to their bimolecular reaction rate constant, as shown in Equation (1).

$$\gamma_{gas} = \frac{k_{2,gas} \cdot \rho_{gas}}{z} \tag{1}$$

where the $k_{2,gas}$ is the bimolecular reaction rate constant (cm^3 molecule^{-1} s^{-1}), ρ_{gas} is the density of gas, which is 2.5×10^{19} molecule cm^{-3} at 25°C, and z is the collision frequency, which is 3×10^9 s^{-1} (Springs and Morrison 2008).

The calculation of surface reaction probability is briefly discussed here. The overall flux of a reactive pollutant to a surface depends on boundary layer mass-transfer conditions and the probability of reaction with the surface itself. However, flux to an indoor surface has traditionally been parameterized by a single combined parameter known as the deposition velocity, v_d. To provide a rationale for using the deposition velocity, Cano-Ruiz et al. (Cano-Ruiz et al. 1993) derived an equation that combined the resistance of boundary layer mass transfer and the resistance of the surface to pollutant "uptake". The relationship between deposition velocity, surface reaction probability, and transport-limited deposition velocity is shown in Equation (2) (Cano-Ruiz et al. 1993).

$$\frac{1}{\gamma_{sur}} = \left[\frac{<v>}{4} \left(\frac{1}{v_d} - \frac{1}{v_t} \right) \right] \tag{2}$$

where $<v>$ is the Boltzmann velocity for pollutant, which is pollutant specific and temperature specific and v_t is the transport-limited deposition velocity (i.e. when $\gamma_{sur}=1$). Under typical indoor air velocity conditions, the ozone deposition to surface is limited by transport through the boundary layer to the surface when $\gamma_{sur} > {\sim}3\times10^{-4}$, and is limited by surface kinetics alone when $\gamma_{sur} < {\sim}5\times10^{-7}$.

Several studies have quantified the ozone uptake to specific surfaces (Hoang, Kinney, and Corsi 2009; Klenø et al. 2001) and some of these studies were done *in situ*, in occupied homes (Wang and Morrison 2006; Wang and Morrison 2010). In these studies, ozone was

assumed to be reacting with "the surface", regardless of its composition. Further, the surfaces were isolated (using a flow-through reactor with clean gases) from the rest of the building, meaning that the conditions were not entirely "real". Real indoor surfaces adsorb and interact with numerous gas-phase species in the building. Thus, ozone consumption and reactions with adsorbed species were necessarily neglected. Thus, models that attempt to assess occupant exposure to reactants and products (Carslaw 2007) do not include this very important component of the reaction system.

1.5 OZONE REACTION PROBABILITY WITH SURFACE ATTACHED SPECIES

The reaction probability of ozone and surface-bound compounds has been investigated, mainly to advance our understanding of ambient atmospheric chemistry. In these studies, the compounds were attached to an inert substrate (e.g. silicon and gold) so that the orientation of molecules on the surface was well defined. Then ozone was introduced to react with the compound loaded surface and other surface chemistry techniques were used to investigate surface reactions.

Dubowski et al. studied the ozone oxidation of three-carbon and eight-carbon vinyl terminated self-assembled monolayers (SAMs, C3= and C8=) on a silicon Attenuated Total Reflectance (ATR) crystal (Dubowski et al. 2004). The ozone concentrations ranged over 5 orders of magnitude for different experiments and the initial ozone reaction probabilities were quantified. As the ozone concentration increased, the measured initial reaction probability

decreased. The rate of change in the C=C and C=O bonds were measured. The kinetics

suggested that ozone was rapidly adsorbed onto the surface and then reacted more slowly with

the alkene moiety. This overall reaction mechanism is known as the Langmuir-Hinshelwood

mechanism. Molecular dynamics calculations also supported this mechanism. In a similar

SAMs experiment focused on the products, McIntire et al. found large organic aggregates (~

0.1 – 1 μm) were formed on the substrate, while the surrounding substrate was depleted of

carbon (McIntire et al. 2005). This was consistent with other studies which suggested stable

secondary ozonides were formed on surfaces (McIntire, Ryder, and Finlayson-Pitts 2009).

Geiger and colleagues also developed a linker strategy to bind tropospherically

relevant alkenes onto a glass surface, and used Sum Frequency Generation (SFG) to

characterize the terpene loaded surfaces and track their interaction with ozone (Voges et al.

2007). The surface reaction probability of several terpenes were quantified and also a

Langmuir-Hinshelwood type mechanism was suggested (Stokes et al. 2008; Stokes et al. 2009).

Their studies suggested that the surface reaction probability was affected by stereochemistry

and orientation. When the C=C double bonds were oriented toward the gas phase, the reaction

probability was higher than when C=C double bonds were oriented towards the substrate

(Stokes et al. 2009).

A key observation has been that reaction probabilities of substrate-attached alkenes are

larger than observed for gas-phase reactions. Stokes et al. (Stokes et al. 2009) measured the

surface reaction probability of several compounds and compared the results with that of other

studies. The compilation comparisons along with the data reported by Springs and Morrison

(Springs, Wells, and Morrison, submitted to Indoor Air) are shown in Figure 1.2.
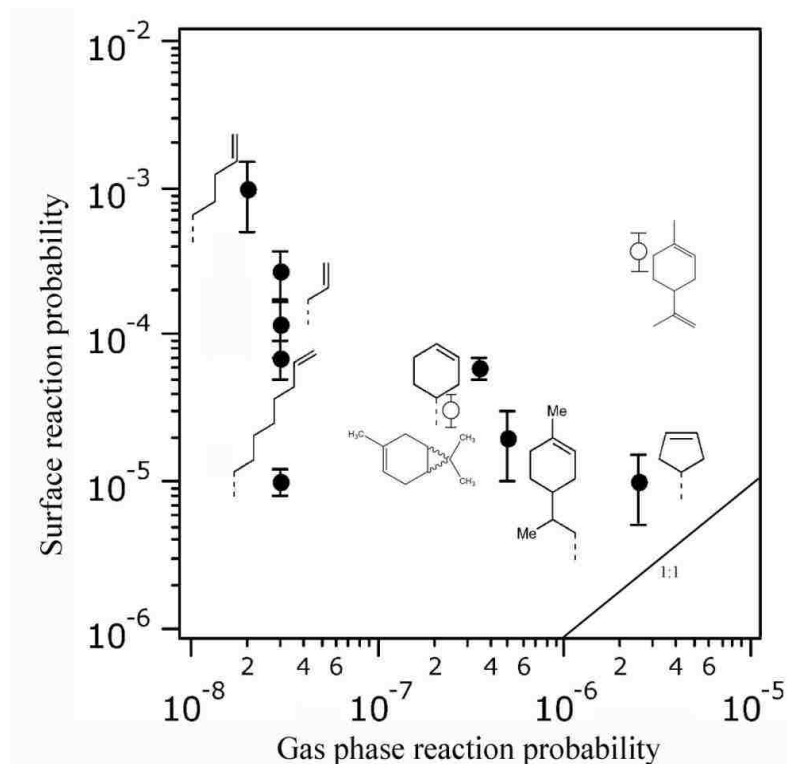
Figure 1.2 Comparison of the surface reaction probability with the gas phase reaction probability. Solid dots are from Stokes et al. (Stokes et al. 2009), and hollow dots are from Springs and Morrison (Springs, Wells, and Morrison, submitted to Indoor Air).

Note that 1) the surface reaction probabilities do not appear to be correlated with

gas-phase reaction probabilities, 2) all reaction probabilities are greater than their gas-phase

counterparts and 3) surface reaction probabilities are up to *five* orders of magnitude greater

than in the gas phase.

When these observations are extrapolated to compounds which adsorb to indoor surfaces, we may predict that low volatility and high ozone reactivity compounds can substantially alter our expectations of indoor conversion rates of these compounds. Low volatility compounds can potentially cover a substantial portion of indoor surface, even at low indoor air concentrations. Further, the surface reaction probability is likely to be greater than the gas phase reaction probability, which may already be high enough to cause gas-phase chemistry to substantially alter indoor concentrations of reactants and products.

The reaction probability for the reaction of ozone with an adsorbed species can be determined by comparing ozone flux to a surface with and without the adsorbed compound. For clean bare surfaces, the "background" reaction probability, γ_{bkg}, can be determined by quantifying the flux and deposition velocity to that surface and applying equation (2). For a surface supporting an adsorbed species, the new area-averaged reaction probability can be found by quantifying the ozone flux and deposition velocity and again applying equation (2). The resulting (or total) reaction probability, γ_{total}, is, theoretically, a linear combination of the individual reaction probabilities of all available surface sites. Thus, the total reaction probability, γ_{total}, is the linear combination of background reaction probability, γ_{bkg}, and ozone reaction probability with surface-bond compounds, γ_{com}, as shown in Equation (3).

$$\gamma_{total} = \gamma_{com} f_{com} + \gamma_{bkg} (1 - f_{com}) \tag{3}$$

where f_{com} is the fractional coverage of the compound on the surface. There are two key assumptions in defining the compound reaction probability in this way:

1. The heterogeneous ozone surface reaction follows the Eley-Rideal mechanism. In this mechanism, the reactant (terpene in this research) is adsorbed to the surface and ozone directly reacts with it from gas phase, without initially adsorbing. This assumption is in conflict with the aforementioned observation that heterogeneous ozone surface reactions are more likely to follow a Langmuir-Hinshelwood mechanism, in which ozone initially adsorbs before it reacts. However, this continues to be an active area of research and the "jury is still out" on the full mechanism. Further, it is very difficult to quantify how fast adsorbed ozone migrates on surface, collides and reacts with other species. Finally, this "effective" surface reaction probability (even if fictitious) can be used directly in conjunction with reactor or building models to calculate conversion rates, and ultimately estimate personal exposure to reactants and products.

2. The adsorbed molecules form no more than a monolayer on surfaces. This assumption is more likely to be true when the adsorbed amount is small and the surface coverage is low (e.g. <1%). As more molecules adsorb, they are more likely to interact with each other, and even form multi-layer 'islands' on surfaces. Thus the calculated fractional coverage, f_{com}, based on adsorption isotherms, is equal to or larger than the true surface coverage. The compound reaction probability, γ_{com}, resulting from application of equation (3) will be less than or equal to the true value. Therefore, the compound-specific surface reaction

probability quantified in this dissertation is called the 'minimum effective' reaction

probability.

1.6   INDOOR AIR QUALITY MODELS AND SURFACE REACTIONS

Existing mass balance models used to calculate indoor concentrations of reactants

generally include air exchange, deposition to surface due to background reactivity, and gas

phase reaction as removal mechanisms for ozone and reactive VOCs. The mass balance at

steady state is expressed as in Equation (4).

$$QC_{O3,in} = QC_{O3,out} + v_{d,bkg}AC_{O3,out} + k_{2,gas}C_{O3,out}C_{com,out}V \tag{4}$$

where the $v_{d,bkg}$ is the area-averaged background ozone deposition velocity (cm s^{-1}), Q is the

flow rate through the room (cm^3 s^{-1}), A and V are surface area and volume of the room

respectively (cm^2 and cm^3), $C_{O3,out}$ and $C_{O3,in}$ are the inlet and outlet of ozone concentration

(molecule cm^{-3}), and $k_{2,gas}$ is the bimolecular second-order reaction rate constant (cm^3

molecule^{-1} s^{-1}). The surface reaction element of Equation (4) can further be sub-divided by

taking into account differences in the reactivity and flow characteristics of specific surfaces ($v_{d,bkg,1}A_1 + v_{d,bkg,2}A_2 + \ldots$).

Where sufficient information about surface coverage (f) is available, the change in the

surface deposition velocity due to an adsorbed reactant can be related to the reaction

probability of the background and the adsorbed compound as in Equations (2) and (3).

However, the fractional coverage may not be available, as it can be difficult to determine in

field settings. In lieu of using the reaction probability directly, an overall rate coefficient that is

related to the gas-phase concentration of the adsorbing reactant may instead be applied.

Assuming that the surface reactivity is the dominant resistance to ozone uptake, the reactant

molecule (e.g. a terpenoid) has a much higher reaction probability than the background surface,

but also that the fractional coverage of the reactant is small, the total ozone deposition velocity

can be expressed as in Equation (5).

$$v_{d,total} = v_{d,bkg} + k_{2,sur} \cdot C_{com} = v_{d,bkg} + v_{d,com} \tag{5}$$

where $v_{d,total}$ is the total ozone deposition velocity of compound loaded surface (cm s^{-1}),

$k_{2,sur}$ is an effective second-order surface reaction rate coefficient (cm^4 molecule^{-1} s^{-1}), C_{com}

is the gas-phase concentration of the reactant (molecule cm^{-3}), $v_{d,bkg}$ is the ozone deposition

velocity associated with background surface reactivity (cm s^{-1}), and $v_{d,com}$ is the ozone

deposition velocity associated with surface-bond compound. Incorporating the adsorbed

compound, Equation (4) becomes,

$$QC_{O3,in} = QC_{O3,out} + (v_{d,bkg} + v_{d,com})AC_{O3,out} + k_{2,gas}C_{O3,out}C_{com}V \tag{6}$$

Thus, Equations (5) and (6), can be used to estimate indoor concentrations of reactants and the conversion rates due to heterogeneous and/or homogeneous mechanisms. Further, the surface reaction rate coefficient, $k_{2,sur}$, can be determined at bench scale or in field experiments and compared directly. If comparable, bench-scale measurements then become a powerful tool for estimating exposure in buildings for multiple compounds under many different conditions.

2. GOALS AND OBJECTIVES

Although indoor ozone chemistry has been studied in great detail, little of the existing research allows us to estimate the impact of adsorbed reactants on the resulting indoor concentrations of ozone, reactants and products. Evidence points to this surface chemistry as being particularly important for low-volatility terpenes. Specific questions that remain unanswered include: how fast does this surface reaction take place? Is this surface reaction fast enough to significantly alter the indoor concentration of reactants and products? Can bench-scale measurements of these reaction rates be extrapolated to full-scale environments?

Therefore, in this research, an experimental method to quantify the ozone reaction rate with surface-bounded terpene species was developed. Also, mathematical models for my experiment system that allow us to calculate the rate parameters from the resulting experimental data were developed. A second-order surface reaction rate was newly defined and demonstrated to be a more useful term than the reaction probability for characterizing the flux (or surface conversion rates) at least for the two compounds studied in this research. The objectives of this research were:

(1) to develop a reliable analytical method to quantify ozone reactive terpenes, for single compound and also terpene mixtures, in the samples where ozone is present.

(2) to quantify the adsorption, surface reaction rates, and surface reaction probability of ozone with terpenes (α-terpineol and dihydromyrcenol) adsorbed on relevant indoor materials, for a relevant range of relative humidity conditions;

(3) to compare the surface bound reaction probability with reported values of the gas-phase reaction probability;

(4) to determine by extrapolation and experiment to what extent the ozone surface reaction alters the concentration of specific terpenes and ozone, and

(5) to identify some of the heterogeneous reaction products that result from ozone reacting with spontaneously adsorbed terpenes.

3. MATERIALS AND METHOD

To fulfill the aforementioned objectives, the following experimental plan has been implemented:

1) Develop a reliable sample preparation and analytical method to measure the concentration of reactive organic compounds in the presence of ozone.

Please refer to paper I.

2) Quantify the ozone/α-terpineol surface reaction kinetics on polyvinyl chloride, glass, and latex paint surfaces using a bench-scale reactor and mathematical modeling.

Please refer to paper II.

3) Quantify the ozone/dihydromyrcenol surface reaction kinetics on polyvinyl chloride, glass, and latex paint surfaces using a bench-scale reactor, and evaluate and compare these kinetics in a room-sized chamber equipped with latex painted wallboard.

Please refer to paper III.

4) Identify some of products of heterogeneous surface reaction between ozone and two terpene alcohols (α-terpineol and dihydromyrcenol)

Please refer to paper IV.

PAPER

I. Dynamic solid phase microextraction sampling for reactive terpenes in the presence of ozone

(Talanta, 2010, 82, 1884-1891)

SHI SHU AND GLENN MORRISON*

Department of Civil, Architecture and Environmental Engineering, Missouri University of

Science and Technology

*Corresponding author phone: (573)341-7192; e-mail: gcm@mst.edu;

Fax: (573)341-4729

ABSTRACT

Dynamic gas sampling using solid phase micro-extraction (SPME) was evaluated for recovery of reactive terpenes and terpenoids in the presence of ozone. For limonene, α-terpineol and dihydromyrcenol in the 20-60 ppb range, this method achieves > 80% recovery for ozone mixing ratios up to 100 ppb. Both the experimental results and a model analysis indicate that higher ozone concentrations and longer sampling times result in lower percent recovery. Typically greater than 90% recovery and ppb level method detection limits were achieved with a 5 minute sampling. Increasing the flowrate from 100 sccm to 400 sccm flow (5 to 20 cm s^{-1}) through the active sampler did not significantly affect sensitivity or recovery in most cases, probably due to negligible mass-transfer improvements. The recovery for each

compound improves when sampling from a mixture of different species than that from a single compound sample. This may be due to competition for ozone amongst adsorbed species. Dynamic SPME sampling can improve detection and quantification of terpenes in reactive environments, especially for low vapor pressure (< 5mmHg at 25°C) compounds that can be lost to ozone scrubbers used in other methods.

KEYWORDS

SPME, terpene, ozone, recovery, α-terpineol, dihydromyrcenol

1. Introduction

Quantification of the concentration and emission rates of biogenic terpenes and terpenoids is important for both atmospheric and indoor air quality research. Biogenic terpenes such as isoprene and pinene contribute to the formation of photochemical oxidants and aerosols in the atmosphere [1,2]. In recent simulations, Curci et al. [3] estimated that biogenic VOCs contribute to, on average, 5% of ozone maxima over Europe, but 15% or greater in some urban areas.   In buildings, ozone reactions with unsaturated terpenes can generate formaldehyde, aerosols and irritants [2,4-6].   Many terpenes are present at much higher concentrations indoors relative to outdoors, because they are widely used as fragrances and solvents in cleaning products, air fresheners, and personal care products [4,7-9]. Thus quantification of terpenes in either environment is crucial for understanding and predicting the concentrations of the products of this chemistry.

In both indoor and outdoor environments, ozone and other oxidants coexist with reactive terpenes, making measurement problematic. Although smog levels have improved, outdoor urban ozone concentrations can still rise over 100 ppb [10]. Indoor ozone concentrations tend to follow outdoor concentrations, and are between 10 and 70% of outdoor levels [11]. Even the lower indoor concentrations of ozone can interfere with the measurement of terpenes [12]. Analytical methods that collect and concentrate compounds on surfaces may be especially prone to recovery problems if ozone is not removed prior to collection. Unsaturated compounds attached or sorbed to surfaces tend to react rapidly with ozone. For example, Stokes et al. [13] showed that a surface bound unsaturated organic such as 1-pentene can react with ozone at rates nearly five orders of magnitude faster than it would in the gas phase. Surface conversion rates may be more related to the orientation and availability of double-bonds rather than to the gas-phase rates [14]. As surface coverage of the terpene increases, the rate of terpene-ozone reactions increase and recovery suffers. Relative to higher volatility terpenes, reduced recovery would also be anticipated for lower volatility or polar terpenes with higher equilibrium surface coverage.

Evidence for this effect has been observed during the collection of terpenes on sorbent surfaces [15-17]. Tenax, Carbosorb, and other sorbents are widely used to collect and concentrate gas-phase compounds for thermal desorption, separation and quantification by GC-MS or other methods [18]. At the inlet of a sorbent cartridge, analytes rapidly approach equilibrium surface coverage (maximum for those conditions) and are exposed to ambient

concentrations of ozone during the entire duration of sampling. Surface conversion rates are thereby maximized in the inlet region. Several authors [15,19,20] have shown that when ozone is present, reactive terpenes degrade during sampling on Tenax, reducing recovery. Calogirou et al. [15] showed that recovery was reduced for lower volatility compounds, polar oxygenates and compounds with multiple unsaturations. Several methods, such as adding an ozone trap before the sorption tube [21-28] or adding trans-2-butene to the sample gas as ozone scavenger [29], have been developed to overcome this problem. However, lower-volatility and polar terpenes tend to adsorb to traps, again reducing recovery [15]. The addition of scavenger gases increases the complexity and cost of sampling. Calogirou et al. also improved recovery by reducing the total sample time, thereby reducing the ozone-terpene contact time on the sorbent surface. However, even for very short sampling times, some terpenes still exhibited low recovery (<50%) due to their very high reaction rate with ozone on the surface of the sorbent.

Solid phase micro extraction (SPME) is widely used in analysis of organic compounds in both air and water [30-33]. By concentrating sorbates into a thin layer of sorbent material, SPME combines sampling, extraction, and concentration, and does not require a solvent for sample introduction and analysis [34]. While it is common to use SPME as an equilibrium sampler, a potential advantage of this method is that it can be applied such that the sorbent material surface does not reach equilibrium with the gas. The surface coverage of the analyte is minimized, reducing the average rate of ozone-terpene collisions. Researchers have studied SPME sampling of low-reactivity aromatic compounds in the presence of ozone [35] and also

verified that the SPME fiber will not be affected or damaged when the ozone mixing ratio is as high as 1000 ppb.   Several ozone-terpene kinetics studies have used SPME in the presence of ozone to detect terpenes [36, 37]. Harrison et al. [36] measured ozone-citronellal kinetics using a polydimethylsiloxane divinylbenzene (PDMS/DVB) coated SPME fiber in the presence of 0.3-0.5 ppm citronellal and 0.05-0.15 ppm ozone. No explicit determination of how ozone would affect recovery was reported, but kinetic results with reference terpene compounds suggested that ozone did not significantly impact recovery.

In an effort to improve terpene measurements in reactive environments and eliminate the need to trap ozone or introduce other species into the collecting media, we have evaluated the impact of ozone on terpene and terpenoid recovery in a dynamic SPME sampling system. Our objective was to identify conditions, such as the sampling time, that result in good recovery and sensitivity.

2. Experimental

2.1 Reagents and supplies

(R)-(+)-Limonene, dihydromyrcenol (DHM), tetrahydromyrcenol (THM), α-terpineol, citronellal, (1R)-(+)-α-pinene,   (1S)-(+)-3-carene, linalyl acetate, linalool, and β-citronellol were obtained from Sigma Aldrich (St. Louis, MO) at the highest purity available. They were chosen to represent volatile and semi-volatile terpenes and terpenoids with high and low reactivity. The vapor pressure and gas phase ozone reaction rates are listed in Table 1. THM is fully saturated and not expected to react with ozone. It is used as a control and an

internal standard for sampling in the presence of ozone. Supelco StableFlex™ SPME fibers (65μm PDMS-DVB coating; manual holder) were obtained from Sigma-Aldrich (St. Louis, MO).

2.2 Experimental apparatus

A sketch of the apparatus used to produce the gas mixture is shown in Fig 1. A Parker Balston (Haverhill, MA) zero air generator was used to deliver clean air to the system, and MKS (Crewe, UK) flow controllers were used to control the flow at desired rates. In this study, the relative humidity of the gas mixture was 50% for all experiments. Ozone was generated and monitored by a Dasibi (Glendale, CA) ozone generator and monitor. The ozone concentration in the gas standard was controlled by adjusting the voltage to the UV lamp in the ozone generator. To minimize the extent of analyte-ozone reactions in the gas phase, ozone was introduced through a port 10 cm upstream of the sampling port, for a residence time of 0.1 s prior to reaching the SPME fiber. Terpenes were generated using a temperature controlled flow-through system consisting of diffusion tubes in a glass reservoir. A range of diffusion tube sizes (diameter and length) were used to adjust the concentration of terpenes. The temperature was maintained at $25.0 \pm 0.5°C$ for all experiments. The concentrations of terpenes were measured in the absence of ozone using thermal desorption tubes (Markes International Ltd., Llantrisant, UK). To verify that the concentration of the gas standard was stable during experiments, a standalone SRI (Torrance, CA) flame ionization detector (model 110) was used to draw a sample from the exhaust at 80 sccm and its signal was recorded.

2.3 Dynamic sampler

A 3/8 inch (95 mm) stainless steel compression tee (Swagelok, Solon, OH) was used as the main body of the SPME sampling device (Fig 2a). A modified Teflon Mininert valve body (Supelco, Bellefonte, PA) with a septum seal was inserted into the tee to center and stabilize the SPME needle. The two other ports of the tee were used as the gas inlet and outlet. The flow rate through the dynamic sampler was controlled at 100 sccm or 400 sccm, by a flow controller attached to vacuum. To sample, the SPME fiber was inserted through the valve and exposed (parallel) to the flowing gas mixture (Fig 2b). Exposing the fiber to a flowing stream reduces the sampling time by decreasing the boundary layer resistance to mass transfer [42]. The dynamic sampling device was placed in a temperature controlled cabinet maintained at 25.0±0.5°C.

2.4 SPME/GC/FID

Each SPME sample was analyzed immediately after sample collection. An Agilent 6890 gas chromatograph with a flame ionization detector (GC/FID) was used in this study. For SPME fibers, a liner with a 0.75 mm inner diameter was used in the injection port. The injection port was maintained at 250°C for fast desorption in splitless mode. The SPME fiber was retained in the injection port for 5 minutes. A single fiber was used repeatedly for all experiments. A HP-5 capillary column (30.0m×320µm; 0.25µm film thickness) was used under 8 psi constant pressure. The oven temperature ramp was 50°C to 250°C at a rate of 20°C/min. FID detector temperature was set to 250°C. The total run time was 10 minutes.

2.5 Calibration of thermal desorption tubes

The concentrations of terpenes were measured in the absence of ozone using thermal desorption tubes filled with Tenax-TA (Markes, Llantrisant, UK), thermal desorber (Markes, Llantrisant, UK), and Agilent 6890 GC/FID system [18]. The standard solution was prepared by dissolving a small amount of each terpene into methanol. The solution concentration of the 9 terpenes ranged from 20.6 – 23.3 ng/μL. To develop a gravimetric calibration curve for TD tubes, different volumes of the standard solution (10, 20, 40, 80 μL) were injected into 5 different TD tubes, purged with high purity nitrogen to drive off methanol, and injected and analyzed on the GC/FID system. To verify the terpene concentration in the dynamic sampler, gas (without ozone) was drawn through a TD tube at 100 sccm for 10 minutes. Triplicates were used to ensure the accuracy of the sampling. Resulting FID peak areas were compared against the gravimetric calibration.

3. Procedures

3.1 Internal standard

THM was chosen as an internal standard since it is saturated and not expected to react readily with ozone. To ensure that THM itself does not react with ozone, the peak areas were compared for THM at 80 ppb, with and without ozone at 580 ppb (an arbitrarily large value). Five replicates were collected at each condition using two sampling times (5 and 30 minutes). During all other experiments, THM was maintained at 18 ppb as an internal standard.

3.2 Competitive adsorption with internal standard and reaction products

It has been reported that analytes compete with each other for adsorption sites on SPME fibers that contain divinylbenzene [42]. Ozone-terpenoid reaction products may also compete with the reagents. The effect of potential competitive adsorption between the analytes, internal standard, and ozone reaction products was tested using gas mixtures containing limonene only, limonene with 18 ppb THM, and limonene with 18 ppb THM and 100 ppb ozone. Sampling time ranged from 2 minutes to 930 minutes. Two limonene concentrations were used for each condition (17ppb and 29ppb). Here and throughout, terpene concentrations were chosen to reflect the low-ppb range (< 100 ppb) that may be observed in buildings [43].

3.3 Effect of ozone concentration, sampling time and flowrate on recovery of individual analytes

For this recovery assessment, the gas mixture contained a single compound (d-limonene, α-terpineol or DHM), the internal standard and/or ozone. The sample was collected for sampling times ranging from 2-30 minutes at 0, 30, and 100 ppb ozone, at a high and low terpenoid mixing ratio, and at a 100 and 400 sccm sample flowrate (equivalent to mean velocity in the sampler equal to 5 and 20 cm s^{-1} respectively). The high and low mixing ratios (ppb) for each terpenoid were as follows: d-limonene (17, 29), α-terpineol (15, 48), DHM (18, 45). The SPME fiber was also exposed to clean air and ozone to test for any coating specific reaction products.

3.4 Effect of ozone concentration and sampling time on recovery of multiple analytes

The following gas mixture was generated and the SPME recovery evaluated with 0, 30, and 100 ppb ozone: 51 ppb pinene, 60 ppb carene, 16 ppb limonene, 39 ppb DHM, 39 ppb

THM, 35 ppb citronellal, 17 ppb terpineol, and 14 ppb linalyl acetate. The flow rate was 100

sccm and samples were collected for times ranging from 2 to 30 minutes.

3.5 Qualitative sorption-reaction model

A model was developed to evaluate the qualitative dynamics of sampling in a reactive

environment. During the early period of sampling, the concentration near the surface of the

SPME film is very small relative to the mean gas concentration [42]. The concentration at the

surface is at equilibrium with this near-surface concentration, but the inner pores of the DVB

may not be at equilibrium. At the concentrations of terpenes used in this study, the surface

density of terpenes is low and the ozone-terpene reaction rate at the surface is negligible. We

also apply the reasonable assumption that ozone does not react readily with PDMS or DVB.

Therefore, the ozone concentration adsorbed to the surface is constant and proportional to the

measured gas-phase concentration. Finally, the reaction of ozone with the surface bound

terpene is first-order in each of the reactants. By applying a mass balance, the rate of mass

adsorbed per unit area of fiber surface (m_A) equals to the adsorption rate minus the desorption

rate and the loss rate due to reaction. The model is expressed in Equation 1.

$$\frac{dm_A}{dt} = v_t C_A - \left(\frac{v_t}{K_A^E} + K_2 K_A^E K_{O3}^E C_{O3}\right) m_A \qquad (1)$$

where v_t is the transport limited deposition velocity (expressed in terms of boundary layer

thickness and diffusion coefficient by Koziel et al. [42]), C_A and C_{O3} are the concentration of

analyte and ozone in the gas sample, respectively, K_A^E and K_{O3}^E are adsorption equilibrium

constants for the analyte and ozone, respectively and K_2 is the rate constant for the

ozone-analyte reaction on the fiber surface. The adsorption equilibrium constant is defined as

the gas phase concentration divided by the equilibrium value of m_A. The following expressions

are constant:

$$A = v_t C_A \tag{2}$$

$$B = \frac{v_t}{K_A^E} + K_2 K_A^E K_{O3}^E C_{O3} \tag{3}$$

For an initial adsorbed mass equal to zero, Equation (1) can be solved and simplified:

$$m_A = \frac{A}{B}(1 - e^{-Bt}) \tag{4}$$

This qualitative model predicts that as sampling time increases, analyte percent

recovery is expected to diminish. Also, as v_t increases the mass on the fiber reaches

equilibrium more rapidly, but the equilibrium mass is larger and recovery will be higher.

Therefore, a flowing sampler operated for short sampling time periods (time-weighted

sampling) may be more advantageous for sampling in reactive media than a static sampler

operated for long time periods. Equilibrium sampling results in the lowest possible recovery.

4. Results and discussion

4.1 Internal standard

THM recovery averaged 100% ± 7% in the presence of ozone under all conditions and

was therefore considered to be a suitably non-reactive internal standard for this study. No

products of a reaction with THM were observed.

4.2 Calibration of Tenax sorption tubes and SPME

The Tenax sorption tubes calibration curves exhibited good linearity (R^2 varied from 0.9942 to 1 for different compounds) in the range of 0 - ~2500 ng. The instrumental detection limits varied from 15 - 25 ng. The detection limits for dynamic SPME sampling and GC/FID analysis depended on the SPME sampling time. For a 5 minute sampling time, the detection limits varied from 1.6 – 5.8 ppb for different compounds. Reproducibility for all compounds evaluated was 5% or better.

4.3 Competitive adsorption with internal standard and reaction products

In Fig. 3 are shown the results of competitive adsorption experiments with limonene, THM and (potentially) ozone reaction products. For very long sampling times, THM significantly reduces the mass of limonene collected on the SPME fiber. Competitive adsorption was not significant for sampling times less than 10 minutes. For lower-volatility compounds (terpineol and DHM), we observed no significant competition up to 30 minutes. Therefore, up to 10 minutes, any observed reduction in the recovery of limonene and species with similar or lower vapor pressures, is likely due to reactions and/or competition with reaction products. A reduced recovery of limonene was observed in the presence of 100ppb ozone and the reduction increased with increasing sample time (Fig. 4). This corresponds qualitatively with anticipated mass reduction due to a combination of ozone reactions reducing limonene concentration on the surface and reaction products competing with limonene adsorption. Since the contact time of limonene and ozone in gas phase is less than 0.1 second,

reaction products generated by gas-phase reactions are not likely to influence recovery. No reaction products were observed for the reaction of ozone in clean air with the coating on the fiber.

4.4 Recovery of single compound

Shown in Fig. 5 are normalized FID responses for each set of conditions (low concentration low flow, high concentration low flow, and high concentration high flow) for d-limonene, α-terpineol, and DHM. The curves qualitatively match model predictions: 1) under the same conditions (terpene concentration, flow rate, and ozone concentration), longer sampling times results in lower recovery, and 2) higher ozone concentrations result in lower analyte mass accumulated on the fiber if other conditions (terpene concentration, flow rate, and sampling time) are the same.

Recoveries are shown in Fig. 6. Overall, the recovery ranges from 65% to 115%. For 10 minute sampling at 100 ppb ozone, recoveries were ~80% or better. For 5 minute sampling at 30 ppb, recovery was generally not significantly lower than 100%. Thus, this method is sufficient for quantification of reactive semi-volatile compounds, even in the presence of ambient ozone levels. Interestingly, although limonene has a gas phase reactivity that is 300 times greater than that of dihydromyrcenol, the recovery of limonene is very similar to the recovery of DHM for the same sampling conditions. Thus, the method appears to be fairly robust for a both low and high reactivity terpenoids. Recovery is reduced as the ozone concentration increases and (usually) as sampling time increases.

We observed higher velocity does not significantly increase mass accumulated on the fiber, except in the case of terpineol (Fig. 5). Therefore, the mass transfer coefficient did not significantly increase over this range. This was observed by Koziel et al. [42], but for a somewhat higher velocity system and for perpendicular flow. The apparent difference in terpineol uptake with increased velocity was reproducible but a satisfactory explanation is not apparent. The difference in mass-transfer characteristic due to slight differences in diffusivity is not likely to have a significant impact on v_t.

Increasing the flow rate from 100 to 400 sccm does not significantly increase the recovery except, perhaps, in the case of DHM. If DHM had a significantly larger adsorption equilibrium constant, K_A^E, v_t would more strongly influence recovery (Equation 4). However, this does not appear to be the case as equilibrium mass uptake on the fiber is similar for terpineol and for DHM. As the present conditions result in adequate recovery, we did not operate the system at a lower flowrate. However, we anticipate that recovery would be somewhat reduced for a much lower flowrate, as predicted by Equation 4.

4.5 Multiple compounds in the presence of ozone

Shown in Fig. 7 are normalized FID responses for individual compounds in the multiple compound mixture. For the higher volatility compounds (pinene, carene, and limonene), the adsorption profile is not linear for sampling times greater than 20 minutes. This is likely due to the competition for the adsorption sites with the other, lower volatility, compounds.

Recoveries for individual compounds in the multiple compound mixture are shown in Fig. 8. In the presence of ozone, the recoveries of limonene, dihydromyrcenol, and terpineol in the mixture are higher than their recoveries in the single compound samples. At a high adsorbed surface density, reactive compounds can compete with each other for ozone and, potentially, improve recovery for individual compounds by spreading out reactive losses across all adsorbed species. All else being equal, more of the lower-volatility species (smaller adsorption constant) will be present on the fiber and out-compete the higher-volatility species for ozone. Amongst the lower-volatility species, gas-phase reactivity appears to correlate roughly with recovery. At 100 ppb ozone, DHM, exhibits significantly higher recoveries than terpineol, citronellal or linalyl acetate which have gas-phase reactivity approximately 100 times greater than DHM. This competition and improved recovery is not anticipated to occur for very low gas-phase terpene concentrations (a few ppb). Low adsorbed surface density on the SPME fiber would reduce ozone uptake, resulting in higher near-surface ozone concentrations and higher relative rates of terpene oxidation on the SPME fiber. The recovery of pinene and carene (Fig. 8) was not affected by the displacement phenomenon shown in Fig. 7.

4.6 Sensitivity and detection limit in the presence of ozone

Because of the improved mass transfer conditions, dynamic sampling is more sensitive than static sampling for the same time-weighted averaging period [44]. The method detection limit was estimated based on twice the standard deviation of the peak areas of the lowest mass

injection by SPME. For the eight compounds studied in the presence of ozone, the MDL

ranged from 1.6 – 5.8 ppb for a 5 minute sampling time, and the presence of 30 or 100 ppb

ozone does not affect the MDL significantly.

4.7 Effect of relative humidity

The effect of humidity was not evaluated in this research. Equilibrium mass collected

by SPME can be influenced by relative humidity [45]. SPME sampling of BTEX was not

affected by the relative humidity when the humidity was lower than 45% [46]. For

time-weighted sampling, and short sample times, uptake on the fiber is transport limited and

relative humidity is not anticipated to significantly alter the results. However, polar terpenoids

such as terpineol and DHM are alcohols and strong interactions with water may influence

equilibrium partitioning (K_A^E in Equation 1). The quantity of water on the fiber may also

influence the rate of the reaction with ozone and distribution of products generated.

The application of SPME for rapidly quantifying gas-phase concentrations of reactive

terpenoids in the presence of ozone was demonstrated. We observed good recovery for

environmentally relevant concentrations, even in the presence of 100 ppb ozone. Properly

applied, this method improves upon recovery using flow-through sorbent samplers and

eliminates the need for ozone traps or scavenger gases.   However, if sampling conditions are

favorable for surface reactions, ozone and other oxidants can consume reactive terpenes

adsorbed onto the SPME fiber resulting in poor recovery. Interference may also result from

accumulation of reaction products on adsorption sites in the SPME coating.

Acknowledgements

The authors thank Honglan Shi, research chemist in Environmental Research Center of Missouri University of Science & Technology, and Jonathan McKinney, graduate student in Environmental Engineering Program of Missouri University of Science and Technology, for their great help on the experiment and their comments on this paper.

References

[1]   M.R. Papiez, M.J. Potosnak, W.S. Goliff, A.B. Guenther, S.N. Matsunaga, W.R. Stockwell, Atmos. Environ. 43 (2009) 4109-4123.

[2]   C. Geron, S. Owen, A. Guenther, J. Greenberg, R. Rasmussen, J. Hui Bai, Atmos. Environ. 40 (2006) 1759-1773.

[3]   G. Curci, M. Beekmann, R. Vautard, G. Smiatek, R. Steinbrecher, J. Theloke, Atmos. Environ. 43 (2009) 1444-1455.

[4]   H. Su, C. Chao, H. Chang, P. Wu, Atmos. Environ. 41 (2007) 1230-1236.

[5]   B. Singer, B. Coleman, H. Destaillats, A. Hodgson, M. Lunden, C. Weschler, Atmos. Environ. 40 (2006) 6696-6710.

[6]   J. Yu, D.R. Cocker, R.J. Griffin, R.C. Flagan, J.H. Seinfeld, J. Atmos. Chem. 34 (1999) 207-258.

[7]   W.W. Nazaroff, C.J. Weschler, Atmos. Environ. 38 (2004) 2841-2865.

[8]   G. Sarwar, D. Olson, R. Corsi, C. Weschler, J. Air Waste Manage Assoc. 54 (2004) 367-377.

[9]   C. Weschler, H. Shields, Atmos. Environ. 33 (1999) 2301-2312.

[10] Latest Findings on National Air Quality - Status and Trends through 2006, US Environmental Protection Agency, 2007, http://www.epa.gov/air/airtrends /2007/report/groundlevelozone.pdf

[11] C. Weschler, Indoor Air. 10 (2000) 269-288.

[12] A. Calogirou, B. Larsen, D. Kotzias, Atmos. Environ. 33 (1999) 1423-1439.

[13] G.Y. Stokes, A.M. Buchbinder, J.M. Gibbs-Davis, K.A. Scheidt, F.M. Geiger, J. Phys. Chem. A. 112 (2008) 11688-11698.

[14] G. Stokes, E. Chen, A. Buchbinder, W. Paxton, A. Keeley, F. Geiger, J. Am. Chem. Soc. 131 (2009) 13733-13737.

[15] A. Calogirou, B. Larsen, C. Brussel, M. Duane, D. Kotzias, Anal. Chem. 68 (1996) 1499-1506.

[16] J. Bunch, E. Pellizzari, J. Chromatogr. 186 (1979) 811-829.

[17] F. Jüttner, J. Chromatogr. A. 442 (1988) 157-163.

[18] EPA method-Compendium of methods for the determination of toxic organic compounds in ambient air, 1999.

[19] P. Clausen, P. Wolkoff, Atmos. Environ. 31 (1997) 715-725.

[20] H. Wang, G. Morrison, Environ. Sci. Technol. 40 (2006) 5263-5268.

[21] J. Fick, L. Pommer, B. Andersson, C. Nilsson, Environ. Sci. Technol. 35 (2001) 1458-1462.

[22] D.D. Riemer, P.J. Milne, C.T. Farmer, R.G. Zika, Chemosphere. 28 (1994) 837-850.

[23] S.A. Montzka, M. Trainer, P.D. Goldan, W.C. Kuster, F.C. Fehsenfeld, J. Geophys. Res. 98 (1993) PP. 1101-1111.

[24] A. Stromvall, G. Petersson, J. Chromatogr. 589 (1992) 385-389.

[25] D. Grosjean, E.L. Williams, J.H. Seinfeld, Environ. Sci. Technol. 26 (1992) 1526-1533.

[26] D. Helmig, J.P. Greenberg, J. Chromatogr. A. 677 (1994) 123-132.

[27] D. Helmig, J. Greenberg, J. High Resolut. Chromatogr. 18 (1995) 15-18.

[28] R.S. Martin, H. Westberg, E. Allwine, L. Ashman, J.C. Farmer, B. Lamb, J. Atmos. Chem. 13 (1991) 1-32.

[29] R.R. Arnts, Environ. Sci. Technol. 42 (2008) 7663-7669.

[30] S. Tumbiolo, J. Gal, P. Maria, O. Zerbinati, Anal. Bioanal. Chem. 380 (2004) 824-830.

[31] J. Regueiro, C. Garcia-Jares, M. Llompart, J. Lamas, R. Cela, J. Chromatogr. A. 1216 (2009) 2805-2815.

[32] N. Yassaa, J. Williams, J. Chromatogr. A. 1141 (2007) 138-144.

[33] G. Pieraccini, S. Furlanetto, S. Orlandini, G. Bartolucci, I. Giannini, S. Pinzauti, J. Chromatogr. A. 1180 (2008) 138-150.

[34] J. Pawliszyn, Handbook of solid phase microextraction, Chemical Industry Press of China, 2009.

[35] G. Xiong, J. Koziel, J. Pawliszyn, J. Chromatogr. A. 1025 (2004) 57-62.

[36] J. Harrison, J. Ham, J. Wells, Atmos. Environ. 41 (2007) 4482-4491.

[37] J. Ham, S. Proper, J. Wells, Atmos. Environ. 40 (2006) 726-735.

[38] US EPA, Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.00, 2010.

[39] J. Fick, L. Pommer, B. Andersson, C. Nilsson, Atmos. Environ. 36 (2002) 3299-3308.

[40] C.D. Forester, J.E. Ham, J.R. Wells, Int. J. Chem. Kinet. 38 (2006) 451-463.

[41] J.R. Wells, Environ. Sci. Technol. 39 (2005) 6937-6943.

[42] J. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178-5186.

[43] A. Hodgson, H. Levin, Volatile organic compounds in indoor air: A review of concentrations measured in north america since 1990, Lawrence Berkeley National Laboratory, 2003.

[44] F. Augusto, J. Koziel, J. Pawliszyn, Anal. Chem. 73 (2001) 481-486.

[45] M. Chai, J. Pawliszyn, Environ. Sci. Technol. 29 (1995) 693-701.

[46] Y. Gong, I. Eom, D. Lou, D. Hein, J. Pawliszyn, Anal. Chem. 80 (2008) 7275-7282.

Table 1. CAS #, purity, vapor pressure, and gas phase ozone reaction rates of terpenes

Chemical Name	CAS #	Purity	Vapor Pressure at 25°C [a] (mmHg)	Gas phase ozone reaction rate (cm^{3}molecule^{-1}s^{-1})
Limonene	5989-27-5	97%	1.45	6.40E-16[b]
Dihydromyrcenol	18479-58-8	99%	0.124	<2.00E-18[c]
Tetrahydromyrcenol	18479-57-7	95%	0.114	(anticipated ~ 0)
Terpineol	98-55-5	96%	0.0196 *	3.00E-16[d]
Citronellal	106-23-0	93%	0.254	2.40E-16[e]
Pinene	7785-70-8	98%	4.54	8.20E-17[b]
Carene	13466-78-9	99%	2.09	1.20E-16[b]
Linalyl acetate	115-95-7	97%	0.131	4.30E-16[f]

a. Vapor pressures are reported as the mean of estimated values by Antoine and Grain methods, except for terpineol, whose vapor pressure is estimated by modified Grain methods. All of the values are calculated by EPI Suite [38].

b. Measured value. [39]

c. Measured value. [40]

d. Measured value. [41]

e. Measured value. [36]

f. Estimated value by using AOPWIN module in EPI Suite [38].
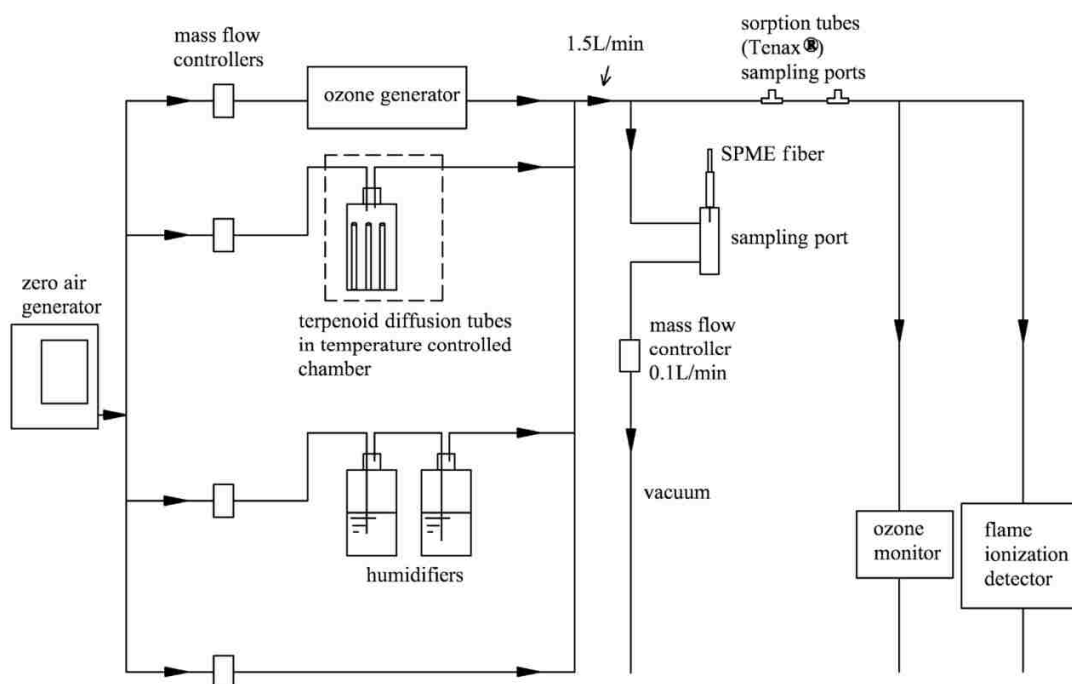
Figure 1. Apparatus used for gas standard generation and experimental determination of recovery.
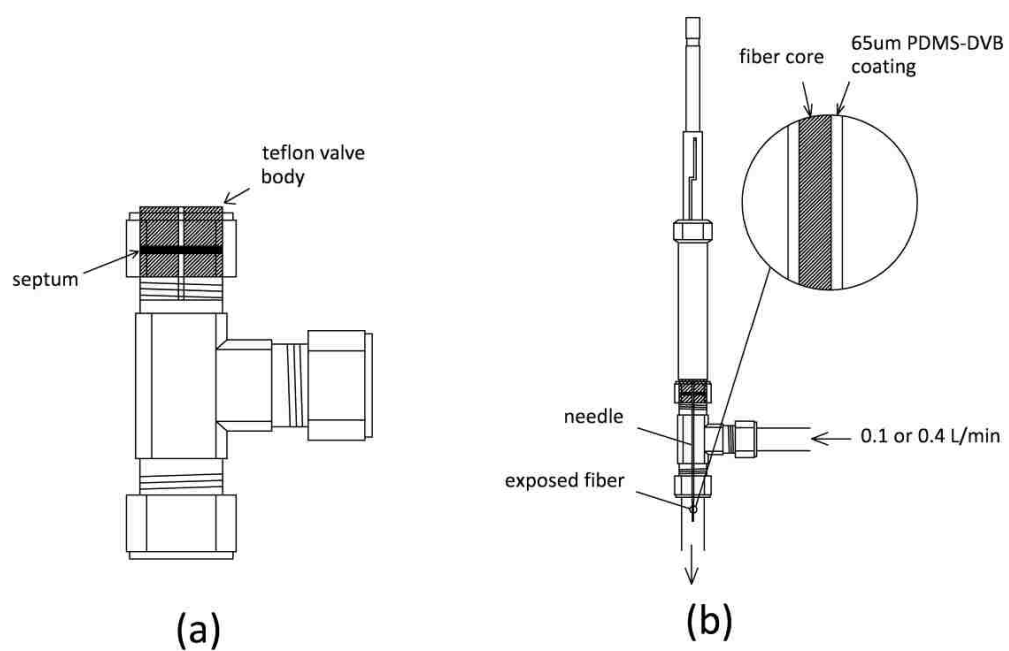
Figure 2. (a) Schematic of the dynamic sampler. (b) The dynamic sampler coupled with a SPME fiber assembly.
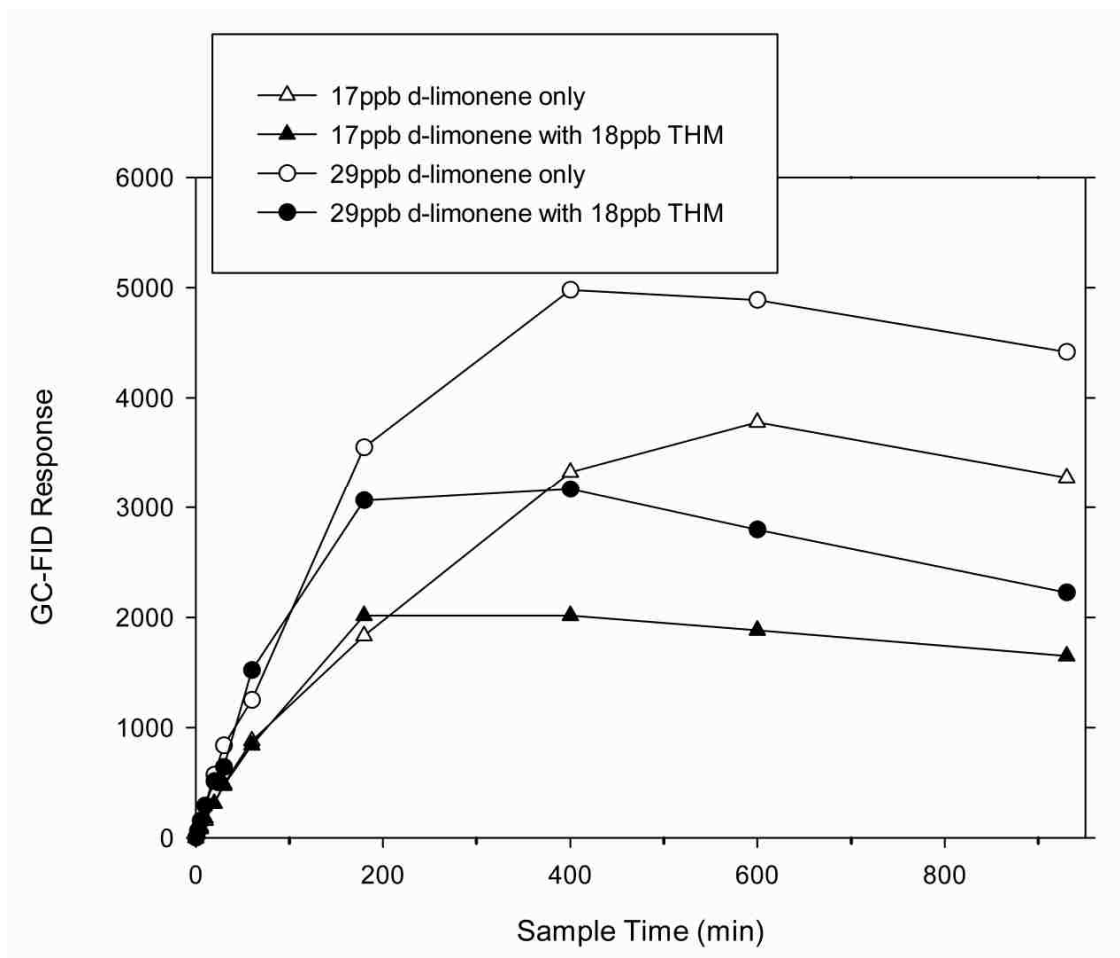
Figure 3. The effect of 18 ppb THM on the mass collected (FID signal) of 17ppb limonene.
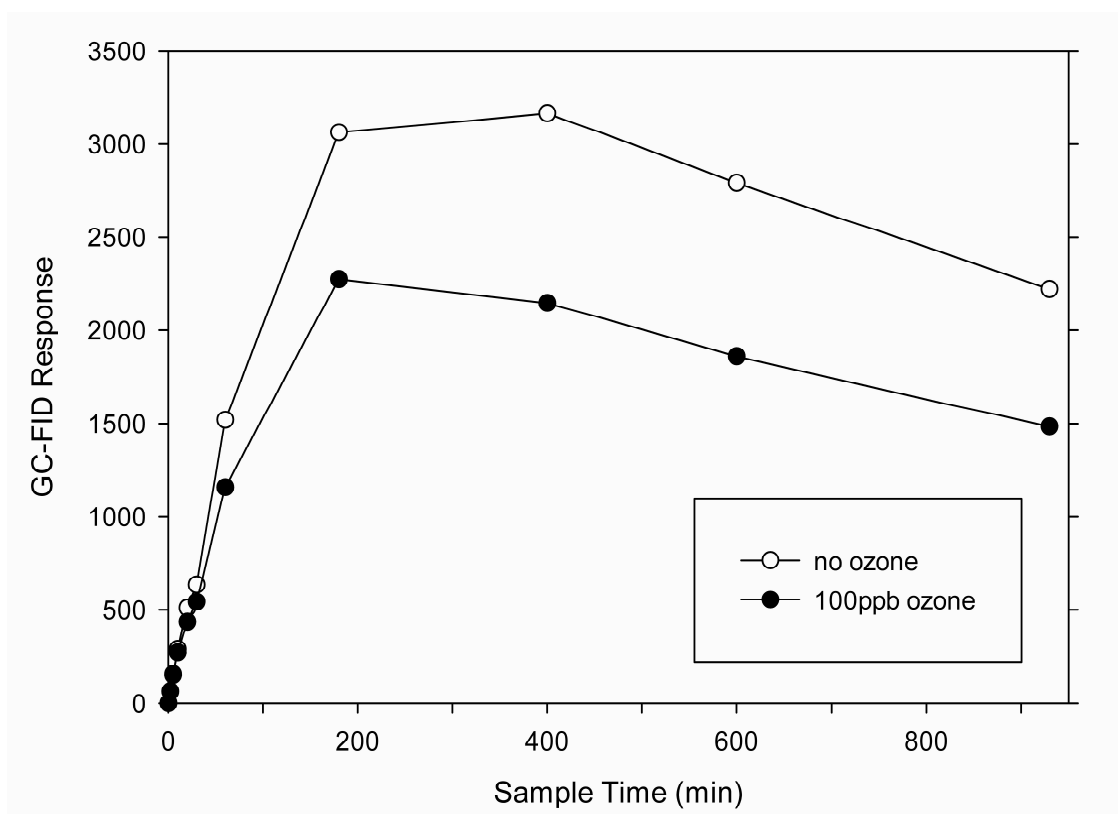
Figure 4. The effect of 100 ppb ozone on the mass collected (FID signal) of 17 ppb limonene, with 18 ppb THM.
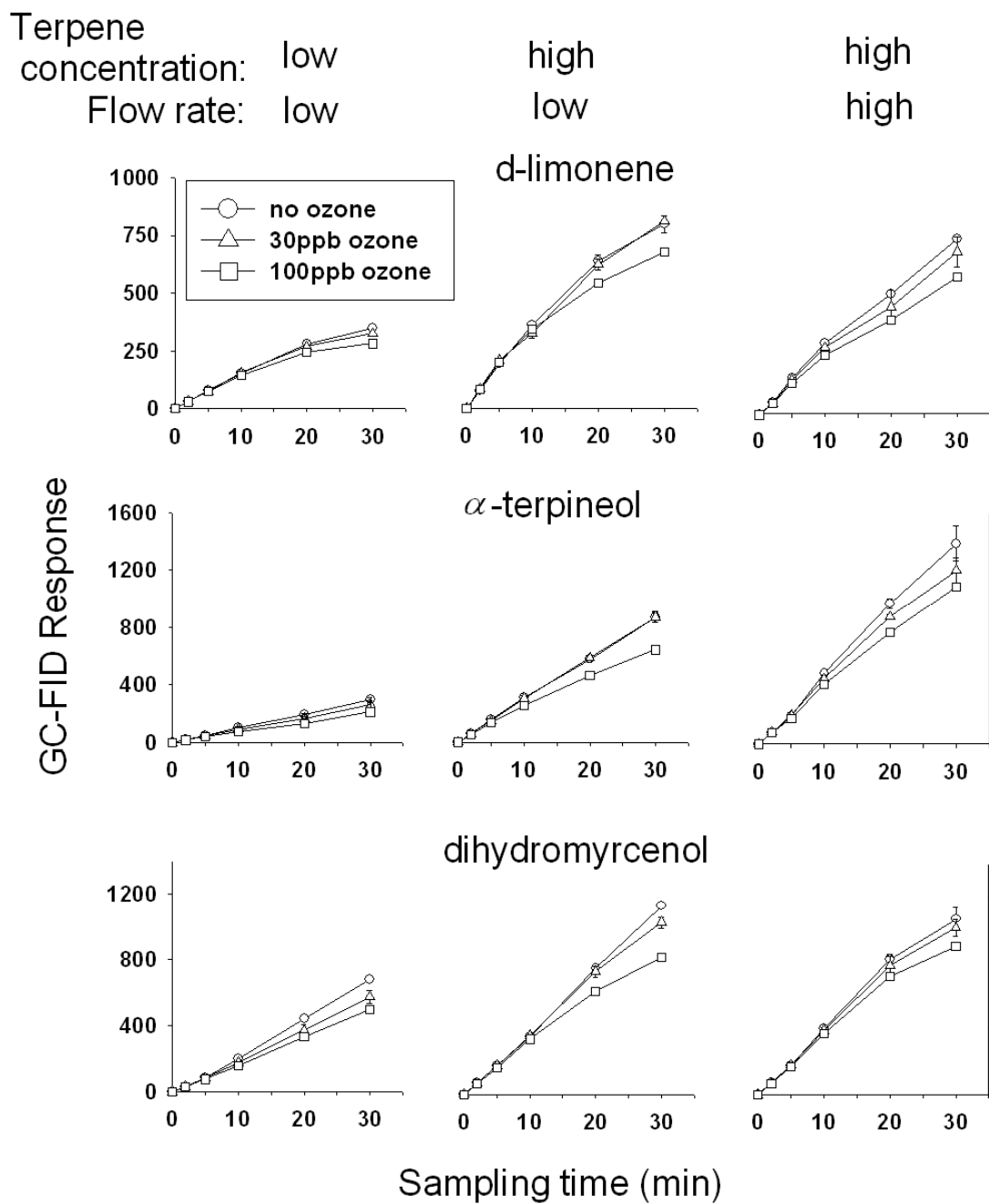
Figure 5. Single compound responses for different concentrations, flow rates and ozone levels.
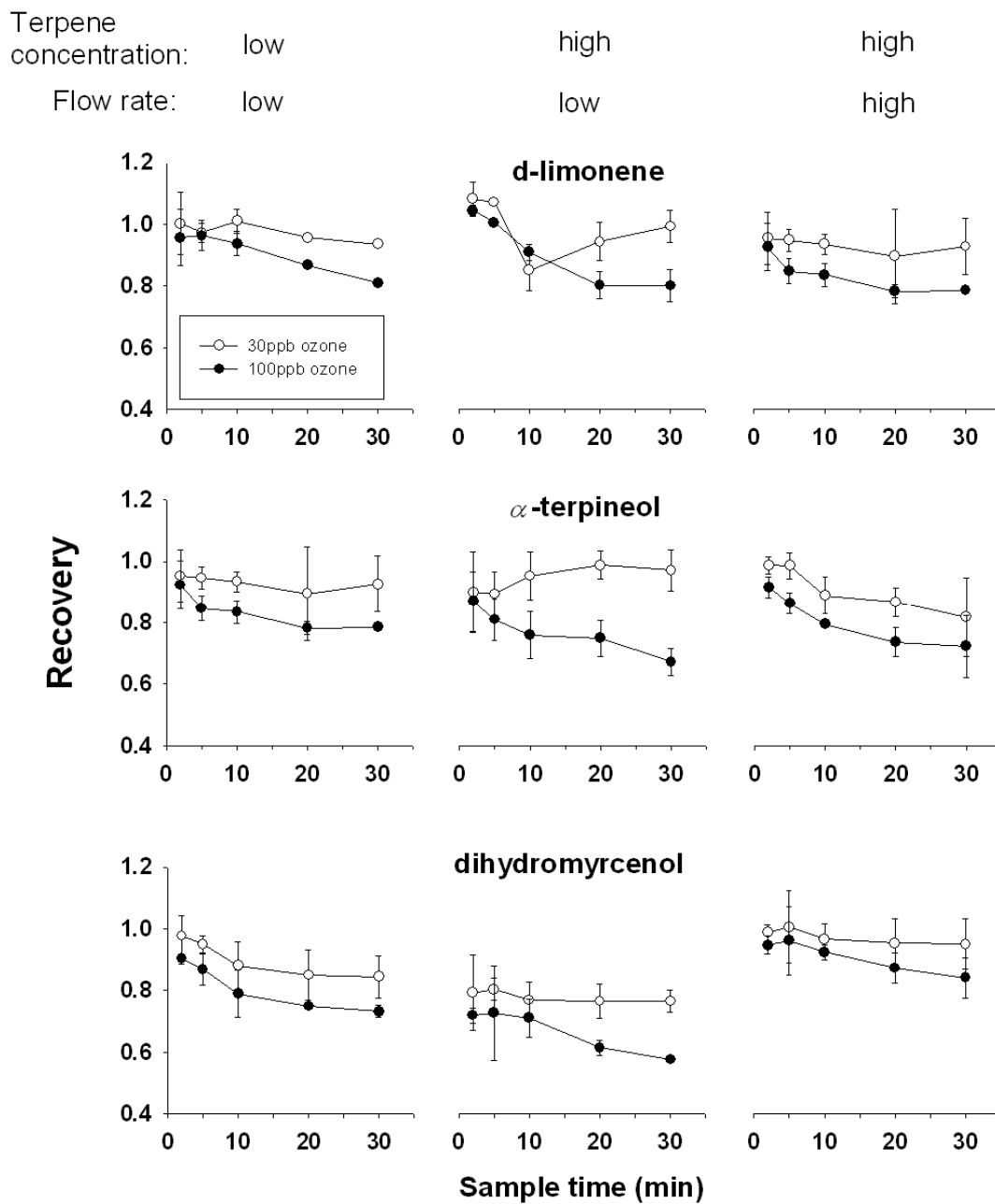
Figure 6. Single compound recovery for different concentrations, flow rates, and ozone mixing ratios.
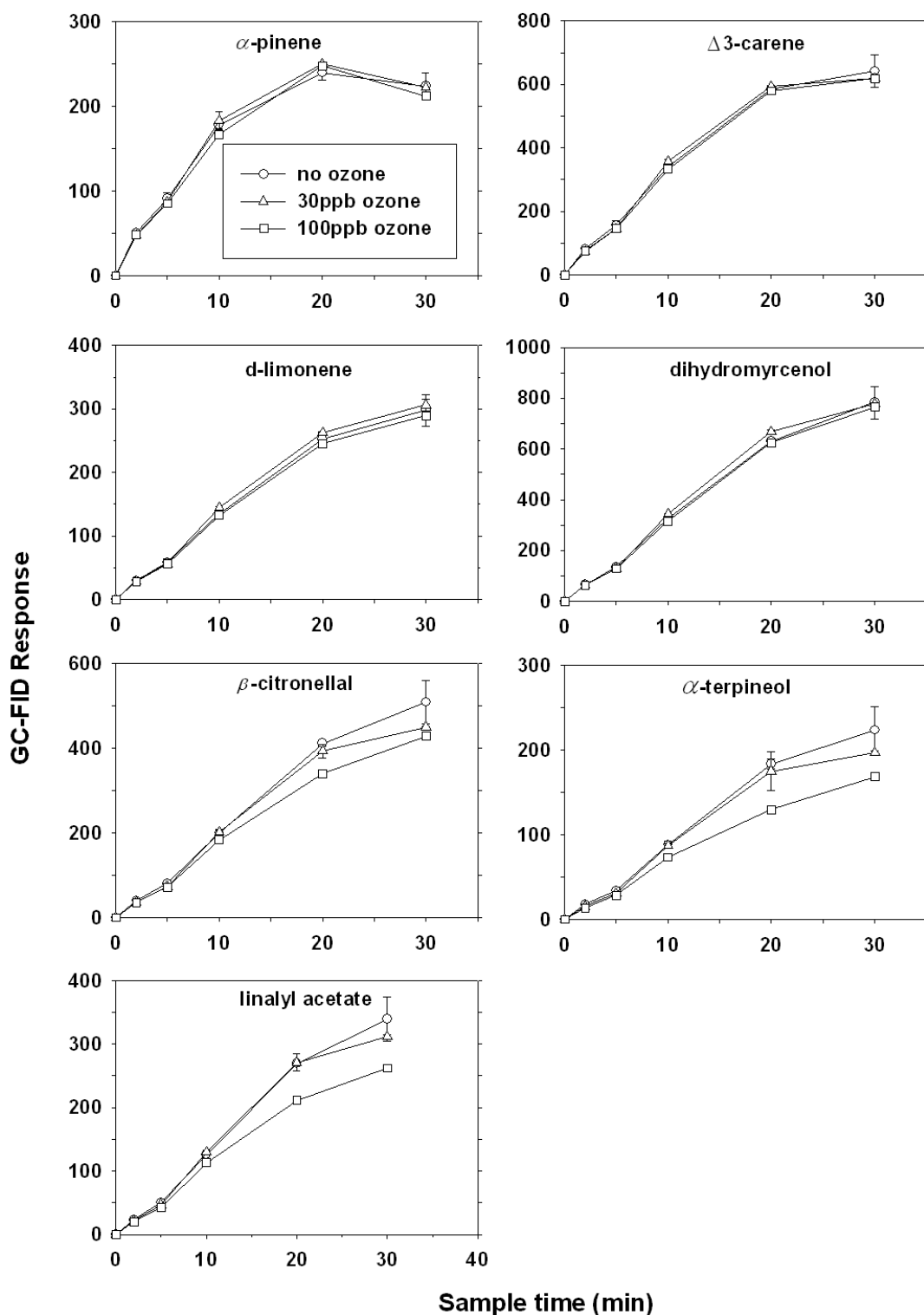
Figure 7. Normalized FID responses as a function of sampling time for individual terpenes in a gas mixture with ozone.
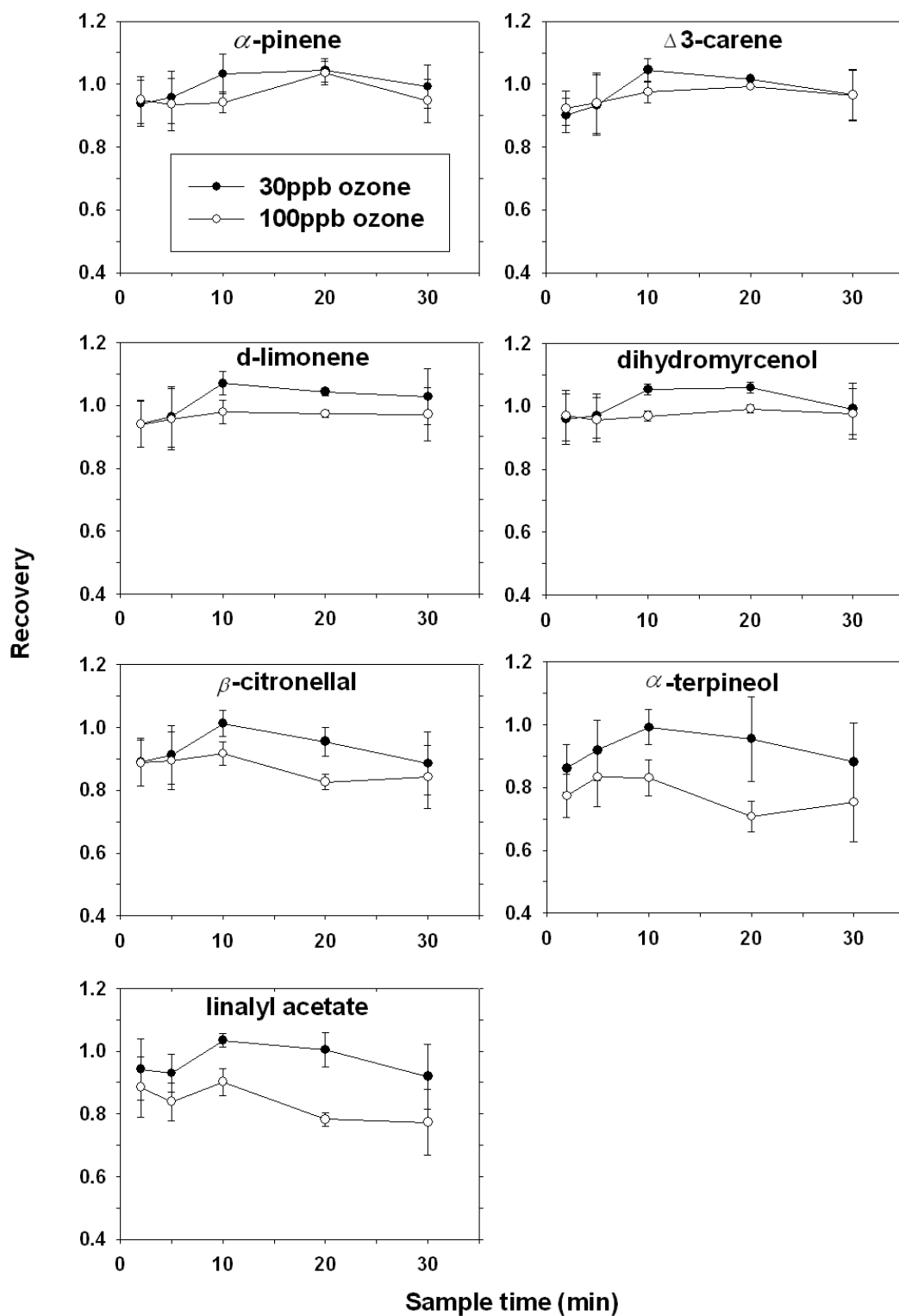
Figure 8. The recovery as a function of sampling time of individual terpenes in a gas mixture with ozone.

II. Surface Reaction Rate and Probability of Ozone and α-Terpineol on Polyvinyl Chloride,

Glass, and Latex Paint Surfaces: Laboratory Experiments and Modeling

(to be submitted to Environmental Science and Technology)

SHI SHU AND GLENN MORRISON*

Department of Civil, Architecture and Environmental Engineering, Missouri University of

Science and Technology

*Corresponding author phone: (573)341-7192; e-mail: gcm@mst.edu;

fax: (573)341-4729

Abstract

Low volatility terpenoids emitted from consumer products can react with ozone on surfaces and may significantly alter concentrations of ozone, terpenoids and reaction products in indoor air. We measured the reaction probability and a second-order surface-specific reaction rate for the ozonation of α-terpineol, a representative indoor terpenoid, adsorbed onto polyvinylchloride (PVC), glass, and latex paint coated spheres. The reaction probability ranged from $(0.38 \text{ to } 6.75) \times 10^{-5}$ and was sensitive to humidity, substrate and mass adsorbed. On average, ozone and α-terpineol are about 10 times more likely to react with each other on these surfaces than they are in the gas phase. The second-order surface-specific rate constant ranged from $(6.20 \text{ to } 33.1) \times 10^{-15}$ cm^4 s^{-1} $molecule^{-1}$ and was much less sensitive to conditions or substrate. Combined with surface areas and air exchange rates typical of indoor environments, the rate of heterogeneous ozonation of α-terpineol is predicted to be comparable to that for homogeneous ozonation.

Keywords

Introduction

Ozone reactions with organic compounds on indoor surfaces result in lower ozone and higher product concentrations in buildings. Unsaturated oils used as lubricants in the production of carpet yarn make carpet one of the most ozone-reactive surfaces in buildings (1). Cooking oils and cleaners leave organic residues that can make counters and floors as, or more, reactive than carpet (2,3). Skin oils on cabin surfaces and clothing were shown to be responsible for at least half of the ozone consumed during simulated aircraft experiments (4). These reactions generate a host of oxidized organic species including aldehydes, ketones, and carboxylic acids (1,2,4,5).

Volatile compounds may also increase surface reactivity, at least temporarily. Many studies have shown that homogeneous ozone reactions with terpenes and related compounds increase indoor concentrations of formaldehyde, irritants and aerosols (6). However, there are some indications that heterogeneous ozone-terpene reactions may also be important. Based on the results of ozone reactions with dried cleaner residues, Destaillats et al. (7) and Singer et al. (8) attributed ozone consumption and product formation, in part, to chemistry with unsaturated species remaining on surfaces. Oxidation of volatile terpenes on heat-exchanger surfaces was inferred from larger-than-anticipated conversion rates (9). Even Teflon surfaces may support ozone-terpene reactions (10,11).

The results of these studies are primarily qualitative, or provide relative reactivity information. While detailed models of indoor chemistry have been developed (12), they do not include individual heterogeneous reactions due to a lack of kinetic and yield data. Yet the impact of adsorbed organics could be substantial. The rate of ozone reactions with surface-bound, unsaturated, organics can be substantially higher than the heterogeneous reaction. For example, the reaction probability for cyclohexene, functionalized to ensure its attachment to a glass surface, was shown to be 200 times greater than for the gas phase reaction (13). However, it is not clear how these values can be used to predict conversion rates on real indoor surfaces.

Enhanced reaction rates and high surface loadings point to substantial surface reactivity. Based on a combination of adsorption isotherms and conversion rates, Springs and Morrison (14,15) observed that the *effective* reaction probability for ozone reacting with terpenes (Δ-carene and d-limonene) adsorbed to glass and polyvinylchloride (PVC) beads was 10-100 times greater than that for the homogeneous reaction. When combined with the observation that more than half of the mass of two volatile terpenes (d-limonene and α-pinene) partitioned to surfaces in a furnished room, conversion rates at surfaces may be even greater than in the gas-phase.

Since less volatile terpenoids, such as terpene alcohols, will partition to indoor surfaces to a greater degree than those studied by Springs and Morrison, we seek to quantify the impact that a terpene alcohol can have on ozone reaction rates with surfaces relevant to indoor

environments. Specifically, we quantify an area-specific second-order reaction rate coefficient, k_2, associated with the ozone/α-terpineol reaction on three surfaces relevant to indoor environments (glass, polyvinylchloride, and latex paint). This coefficient can be used to estimate the relative impact of heterogeneous ozone-terpene reactions on indoor air concentrations of both ozone and α-terpineol. Further, this quantitative analysis can improve existing indoor chemical models by directly relating indoor terpenoid concentrations with the resulting enhancement in surface conversion rates. We also quantify a minimum effective reaction probability associated with these reactions.

We have chosen as a representative reactant 1-methyl-4-isopropyl-1- cyclohexen-8-ol (α-terpineol), naturally occurring monoterpene alcohol (structure shown in Figure 1). It is extensively used in fragrances for bath preparations, soaps, detergents, polishes, and other household products (16) and was observed to be the highest emitting terpene alcohol from a general purpose cleaner (17). α-Terpineol has a low vapor pressure (~2.6 Pa at 25°C; estimated using EPI suite, 2010) (18) and is therefore likely to exhibit substantial sorptive partitioning at equilibrium (19,20). The bimolecular rate constant for the gas phase reaction between ozone and α-terpineol (21) is among the highest reported for related compounds of indoor interest.

Methods

Materials   α-Terpineol (≥96%, FCC, Kosher, FG) was purchased from Sigma Aldrich (St. Louis, MO, USA). Polyvinyl Chloride (PVC) beads were purchased from Engineering

Laboratories Inc. (Oakland, NJ, USA). The diameters and other parameters are found in Table

1. The soda lime glass beads were purchased at MO-SCI Specialty Products, L.L.C. (Rolla,

MO, USA). Latex paint (American Tradition®, color coding 4007-9A, sky blue, flat) was

applied to ceramic (zirconium silicate; Ceroglass Inc.) beads and cured for more than 4 years,

to provide Latex paint surface. 5 L Pyrex bottles with polypropylene plug-seal caps were

purchased from Fisher Scientific (Pittsburgh, PA, USA). A mini-nert valve with 1/8" male NPT,

purchased from VICI Precision Sampling (Baton Rouge, LA, USA), was customer-modified

and attached to each cap.

Analytical   Stainless steel sorption tubes packed with Tenax-TA (Markes,

 Llantrisant, UK) and Solid Phase Micro Extraction (SPME; 65 μm PDMS-DVB Coating

StableFlexTM; Supelco) were both used as sample preparation methods for conventional gas

chromatography with flame ionization detector (GC/FID) detection of α-terpineol. Tenax-TA

tubes were used to quantify the concentration of terpineol at the exhaust of each reactor. 4 liters

of exhaust gas were collected over 20 minutes for later thermal desorption and analysis by

GC-FID. Tenax tubes were also used to verify the mass of vapor-phase α-terpineol injected by

syringe into adsorption bottles. Tenax tubes were calibrated by applying a known mass of

α-terpineol, diluted in methanol, to sorbent, evaporating the solvent, and thermally desorbing

and injecting the terpineol into the GC-FID.

In bottles used to conduct α-terpineol adsorption experiments, SPME was used to

quantify the gas phase α-terpineol concentration. Because the fiber will only adsorb a small

amount of the analyte (usually tens or hundreds of nanograms), SPME is especially useful when there is only a small amount of analyte, or when the concentration is low. The SPME fiber was exposed to the gas for 5 min, and then put into a GC injection port 240°C for 5 min to desorb all the α-terpineol. The SPME fiber removes less than 1% of the total mass of α-terpineol in the sorption bottle. SPME was calibrated by comparison with Tenax-TA results of the same gas mixture.

An HP6890 GC-FID with an HP 5MS column was used to analyze samples collected on both Tenax-TA tubes and SPME fibers. The carrier gas flow rate was 20 cm^3 min^{-1}. The initial oven temperature of 100°C was increased to 250°C at a rate of 35°C min^{-1}. The method detection limit was 5 ppb for Tenax-TA tube analysis and 1 ppb for SPME analysis.

Adsorption Apparatus and Procedure   α-Terpineol adsorption experiments were carried out using a series of the 5 L Pyrex bottles with customer modified caps. The bottles and caps with valves were washed by methanol, rinsed by ultra high purity water and then dried at 80°C for at least 24 hours before each experiment. Adsorption experiments were carried out in a temperature controlled chamber at 25°C, and at three relative humidity conditions (20%, 50%, and 80%). To generate the desired humidity, each bottle was flushed with high purity nitrogen gas for 30 min at 1.0 L min^{-1}, The humidity was controlled by sparging a fraction of the flow through high purity water.. For each relative humidity condition, beads (PVC, glass, or painted) were added to separate Pyrex bottles, and two replicates were carried out at the same time. Two empty bottles were used as controls. The geometric surface

area of PVC, glass, and painted surface were 3071 cm^2, 4000 cm^2, and 1565 cm^2 respectively.

The inner surface area of each Pyrex bottle was estimated to be 1738 cm^2. To inject a small

amount of α-terpineol, headspace gas was drawn from a 1L Boston round bottle containing

undiluted α-terpineol (96%). This bottle was maintained at 25°C and the resulting headspace

concentration of $(2.0 \pm 0.2) \times 10^{-5}$ g L^{-1} was verified by Tenax-TA tube analysis. A 5 mL gastight

syringe was used to draw the α-terpineol gas from the 1L bottle and to inject it into the 5L

Pyrex bottles. After the gas was injected, bottles were rotated on a tumbler at 7 rpm for 10

hours to allow the α-terpineol to uniformly adsorb to bead and bottle surfaces. In separate

experiments, no change in concentration was observed after 8 hours; therefore, 10 hours was

considered sufficient time for equilibrium. SPME was then used to measure the concentration

of α-terpineol in each bottle . This procedure was repeated (injection, tumble, sample) until the

final concentration in the bottle was at least 60 ppb. Each combination of humidity,

concentration and surface was repeated at least once.

Ozone Reaction Apparatus and Procedure   The apparatus used to measure

ozone/α-terpineol reaction rates on surfaces is shown in Figure 2. A zero air generator

(Parker-Balston) supplied clean air to the system, and flow controllers (MKS) maintained the

flows at desired rates. A saturated α-terpineol water solution was continuously injected into the

gas flow with a syringe pump and the resulting concentration was verified using Tenax-TA tube

analysis. Ozone was generated and monitored using a Dasibi UV photometric ozone analyzer.

The humidity of the reactor stream was controlled by adjusting the ratio of dry and humidified

air flow rates. The humidifier and the reactor were maintained at 25°C in a temperature controlled chamber (shown by dashed line in Figure 2).

Two plug flow reactors were used in different phases of the experiment. A 25 cm long glass reactor with an inner diameter of 1.1cm inner diameter was used to measure second-order reaction rate coefficients and reaction probabilities. The total volume and (geometric surface area) were 20 cm^3 glass beads (800 cm^2) , 20 cm^3 PVC beads (473 cm^2), and 20 cm^3 painted beads (313 cm^2). A larger 50cm long Teflon reactor with an inner diameter of 1.8 cm was used to measure the background reactivity of the beads that was then used to determine the minimum ozone/α-terpineol reaction probability on the surface. For these experiments, the total volume and surface area of were 100 cm^3 glass beads (4000 cm^2), 120 cm^3 PVC beads (2838 cm^2), and 120 cm^3 painted beads (1878 cm^2).

Before each experiment, the beads were ultra-sonicated for 30 min in high purity water to clean the surface and dried in the oven at 50°C for at least 24 hours. The reactor was operated with both ozone and α-terpineol for 12 hours to allow a steady-state concentration profile to develop before concentrations were measured at the inlet and outlet. At the concentrations used in this research, a pseudo-first-order approach for determining reaction rates was not possible. Both the ozone and α-terpineol concentrations diminish together and it was necessary to maintain inlet concentrations that were of similar magnitude. Otherwise, one of the reactants tended to become depleted. Therefore, the mixing ratios of ozone and α-terpineol were within a

factor of four of one another for each experiment. Typical inlet concentration pairs of ozone :

α-terpineol (ppb) were 4:1, 8:3, and 4:2.

Data Analysis

Adsorption Analysis   The equilibrium surface concentration on the beads was

determined by balancing the known mass injected against the gas-phase mass (SPME), mass

collected on the bottle surface (from control experiments) and the remaining mass on the beads,

as shown in Equation (1).

$$M_{total} = A_{bottle} \cdot C_{s,bottle} + V_{gas} \cdot C_{gas} + A_{beads} \cdot C_{s,beads} \tag{1}$$

where M_{total} is the total mass of terpineol injected to each bottle (g), A_{bottle} and A_{beads} are

the surface area of bottle and beads (cm^3), respectively, $C_{s,bottle}$ and $C_{s,beads}$ is the

concentration of α-terpineol on the surface of the bottle and beads (µg cm^{-2}), respectively. V_{gas}

is the volume of gas in each bottle (cm^3), and C_{gas} is the gas phase concentration of

α-terpineol (µg cm^{-3}).

The relationship between α-terpineol concentrations on the bead and bottle surfaces

and the gas phase α-terpineol concentration, was expressed by a Freundlich isotherm (best

general model for results obtained), as shown in Equation (2).

$$C_{s,beads\ or\ bottle} = K_{f,beads\ or\ bottle} \cdot C_{gas}^{n} \tag{2}$$

where C_S is the mass of adsorbed α-terpineol normalized by the surface area of beads (ng cm^{-2}),

and C_{gas} is the α-terpineol mixing ratio in gas phase (ppb). In each case, K_f and n are

derived from the nonlinear least-squares fit of the isotherms.

Area-Specific, Second-Order Reaction Rate Constant   To provide a useful parameter for evaluating the impact of indoor surface chemistry, we define the area-specific second-order reaction rate constant, k_2 (cm^4 molec^{-1} s^{-1})   associated with overlying gas-phase concentrations, C_{O3} and C_{terp}, by Equation (3).

$$rate\ (molecules\ s^{-1}) = k_2 C_{O3} C_{terp} (A/V) \tag{3}$$

where A/V is the surface-area to volume ratio (in the reactor or other system where mass-transfer does not limit transport and uptake of either reactant). This second-order rate constant can then be used directly in indoor air quality models to estimate reactant product fluxes at indoor surfaces.

To determine k_2, we modeled the reactor as a plug flow reactor (PFR). The concentration of both ozone and α-terpineol change with distance, z, along the bead-filled region of the reactor and can be characterized by two coupled equations (steady-state). For the glass beads experiment, the surface area of the glass reactor was included in the total surface area, based on the assumption that the reactor has the same adsorption and reactivity characteristics as the glass bead, as shown by Equation (4) and (5).

$$\frac{dC_{O3}}{dz} = -k_{2,glass} C_{O3}(z) C_{terp}(z) \left(\frac{A_{glass}}{V_{reactor} \cdot u}\right) \tag{4}$$

$$\frac{dC_{terp}}{dz} = -k_{2,glass} C_{O3}(z) C_{terp}(z) \left(\frac{A_{glass}}{V_{reactor} \cdot u}\right) \tag{5}$$

where $k_{2,glass}$ is the second-order surface reaction rate on glass surface (cm^{4}molecule^{-1}s^{-1}), A_{glass} is the surface area provided by glass beads and the reactor (cm^2), $V_{reactor}$ is the volume

of the bead-filled regions of the reactor (cm^3), u is the actual gas velocity in the packed bed (cm s^{-1}), and $C_{O3}(z)$ and $C_{O3}(z)$ are the ozone and α-terpineol concentration respectively (molecule cm^{-3}), since they are functions of position z. Since measurement of low-volatility terpenes by SPME or Tenax-TA is unreliable in the presence of ozone (2,22,23), the loss of α-terpineol is assumed to be equal to the ozone loss (1:1 stoichiometry) after accounting for background ozone removal by reactor surfaces.   Gas-phase conversion of reactants is negligible (<<1%) during the 0.6 s residence time of the reactor.

For the glass reactor filled with PVC or painted beads, two different surfaces are present. We use results from the glass bead experiments and include them in equations 6 and 7 to solve for k_2 specific to PVC and paint.

$$\frac{dC_{O3}}{dz} = -(k_{2,x}A_x + k_{2,glass}A_{reactor})C_{O3}(z)C_{terp}(z)(\frac{1}{V_{reactor} \cdot u}) \tag{6}$$

$$\frac{dC_{terp}}{dz} = -(k_{2,x}A_x + k_{2,glass}A_{reactor})C_{O3}(z)C_{terp}(z)(\frac{1}{V_{reactor} \cdot u}) \tag{7}$$

where the $k_{2,x}$ is the second-order surface reaction rate on either PVC or painted surface, A_x is the surface area provided by PVC or painted beads, $A_{reactor}$ is the surface area of the glass reactor. Equations 4 through 7 were solved numerically and the resulting values of k_2 were adjusted to provide a best fit to experimentally derived values of inlet and outlet concentrations.

Minimum Ozone/α-Terpineol Reaction Probability   Equation (8) was used to calculate the reaction probability of ozone with the bare surfaces.

$$\gamma_{surface} = (-ln\frac{C_{O3,in}}{C_{O3,out}})\frac{4\,V_{reactor}\,Q}{<v>A_{beads}\,L\,A\,\rho} \tag{8}$$

where $\gamma_{surface}$ is the reaction probability of ozone associated with the bare substrate (PVC, glass, paint), $C_{O3,in}$ and $C_{O3,in}$ are the inlet and outlet ozone concentration, Q is the total flow rate, $<v>$ is the Boltzmann velocity for ozone, which is 36,000cm s^{-1} in this case (24), L is the length of the bead-filled region of the reactor, A is the cross sectional area of the plug flow reactor, and ρ is the porosity of the bead bed. A higher mixing ratio of ozone (~850 ppb) was used to allow for a measurable difference between $C_{O3,in}$ and $C_{O3,out}$.

For the glass beads/glass reactor data, the combined (total) reaction probability, γ_{total} can be expressed as a linear combination of reactivity of two surface sites (bare glass, and an α-terpineol molecule adsorbed to glass) and as a function of the position in reactor, z, as shown in Equation (9).

$$\gamma_{total} = \gamma_{terp,glass}f_{terp,glass}(z) + \gamma_{glass}[1 - f_{terp,glass}(z)] \tag{9}$$

where the $f_{terp,glass}(z)$ is the fraction of the surface area covered with α-terpineol molecules, $\gamma_{terp,glass}$ is the reaction probability of α-terpineol adsorbed on glass surface, and γ_{glass} is the reaction probability of bare glass surface. The fractional coverage, $f_{terp,glass}$, is determined by applying measured isotherms, assuming single-molecular adsorption (no stacking) and smooth bead surfaces. Because beads are not smooth, and not all of the adsorbed α-terpineol will be available for reaction (in a pore or covered by other molecules), the reaction probability determined is the *minimum* reportable value.

For the PVC or painted beads experiments in the glass reactor, the total reaction probability, γ_{total} can also be expressed as a function of the position in reactor, z, as shown in Equation (10).

$$\gamma_{total} = F\left[\gamma_{terp,x}f_{terp,x}(z) + \gamma_x\left(1 - f_{terp,x}(z)\right)\right] + \tag{10}$$
$$(1-F)\left[\gamma_{terp,glass}f_{terp,reactor}(z) + \gamma_{glass}(1 - f_{terp,reactor}(z))\right]$$

where F is the fraction of PVC or painted surface area relative to the total area (PVC or painted surface area plus the surface area of reactor), $f_{terp,x}(z)$ and $f_{terp,reactor}(z)$ are the α-terpineol coverage on the PVC or painted surface and reactor respectively, $\gamma_{terp,x}$ and $\gamma_{terp,glass}$ are the reaction probability of α-terpineol adsorbed on PVC or painted surface and glass surface respectively, γ_P and γ_{glass} are the reaction probability of bare PVC or painted surface and glass surface respectively.

The total surface reaction probability is evaluated in a similar manner as in Equation (11) and (12), but must account for changes in both ozone and terpineol through the reactor.

$$\frac{dC_{O3}}{dz} = -\frac{\gamma_{total}(z) <v> A_{surface}}{4u} \frac{}{V_{reactor}} C_{O3}(z) \tag{11}$$

$$\frac{dC_{terp}}{dz} = -\frac{\gamma_{total}(z) <v> A_{surface}}{4u} \frac{}{V_{reactor}} C_{O3}(z) \tag{12}$$

where the $A_{surface}$ is the total area of beads and the reactor, and other parameters are defined previously.

Results and Discussion

α-Terpineol Adsorption   The α-terpineol adsorption isotherms are shown in

Figures 3 a, b and c. Freundlich parameters (Equation 2) are also shown in the figures. The

three different materials exhibit very different α-terpineol sorption characteristics. Glass and

paint sorb approximately ten times more α-terpineol than PVC under the same conditions. The

relative humidity more strongly influences α-terpineol adsorption on glass than on PVC or

paint. As the relative humidity increases, substantially less α-terpineol will adsorb to glass.

This may be because both water and α-terpineol are polar and they compete with each other for

adsorption sites on glass. Changes in relative humidity do not strongly influence adsorption on

PVC, perhaps because the surface is much less polar than glass. Interestingly, water appears to

increase the capacity of the painted surface for α-terpineol. This is consistent with the

observations of other studies which found that some polar VOCs adsorption on some building

materials will increase along with the relative humidity (25,26). In this case, surface water may

increase the polarity of the surface or even allow for α-terpineol, as a somewhat soluble

alcohol, to dissolve into water that has condensed in pores, as suggested by other works

(25,27). Overall, water appears to impact adsorption in very different ways on each of these

surfaces.

Area-Specific, Second-Order Reaction Rate Constant   Figure 4 shows the results

for the area-specific, second-order reaction rate constant, k_2. The value of k_2 ranges from 0.68

to 3.17×10^{-14} cm^{4}s^{-1}molecule^{-1}. This relatively small range is surprising given the very different

adsorption capacity of the three materials, and for the very different impact on capacity due to differences in humidity. For example, at 40 ppb α-terpineol and 50% RH, k_2 ranges from 0.8-2.2 $\times 10^{-14}$ cm^4 s^{-1} molecule^{-1}, but the adsorbed mass is nearly 30 times higher (per unit area) on the painted surface than on the PVC. Qualitatively, k_2, follows adsorbed mass concentration (paint > glass> PVC), but the differences are small and do not reflect the quantitative differences in adsorbed mass concentration. Even though RH can change adsorptive capacity by an order of magnitude on glass and paint, there is little impact on k_2. It appears that k_2 is only weakly influenced by the adsorbed mass, but instead is more strongly linked to the gas-phase concentration of α-terpineol. This suggests that the ozone reactivity is dependent on the interfacial activity of α-terpineol, rather than the amount adsorbed.

The assumption that reactant flux is first order in α-terpineol appears to be reasonable, for the narrow range of gas-phase concentrations studied. By comparing the resulting flux and k_2 with concentration at each humidity, the reaction order of α-terpineol is ~1 for most conditions and surfaces. To develop a more accurate reaction order, the concentration of both species should be expanded to include several orders of magnitude.

Minimum Reaction Probability Figure 5 shows the results for the minimum ozone/α-terpineol reaction probability, $\gamma_{O3,terp}$. Also shown for comparison is the gas-phase reaction probability (2.5×10^{-6}) based on the reported (21) gas-phase reaction rate constant in dry air. All measured values are higher than the gas-phase value. The highest (PVC, 50% RH) is about 25 times greater than that for the gas-phase reaction. The large range of values is

consistent with the observation that adsorption characteristics vary widely, but the surface

reactivity (characterized by k_2) does not.

Again, these values represent the *minimum* measurable value, not an absolute reaction

probability. The model used to calculate the ozone α-terpineol reaction probability on surfaces

was based on the assumption that the α-terpineol molecules form no more than a monolayer.

This assumption may be valid when the fractional coverage is very small. However, at the

indoor-relevant concentrations used here, the adsorbed α-terpineol molecules would cover ~

3% to ~ 30% of the geometric surface area. Thus, multi-layer "islands" of α-terpineol are

likely, and not all α-terpineol molecules are equally available for reaction with ozone. Physical

barriers to reaction, such as adsorption deep within pores, further reduce the reported reaction

probability. The highest reaction probability occurs for the lowest coverage (PVC), but even

this result is likely to be lower than the actual value.

The fact that ozone α-terpineol reaction probabilities on surfaces are larger than that in

gas phase is consistent with observations from other studies (14,15,28-30). Research on the

ozone reaction with vinyl-terminated self-assembled monolayers (SAMs) suggested that the

reaction follows the Langmuir-Hinshelwood mechanism (28,29,31,32).   Instead of a

gas-phase ozone molecule colliding and reacting with a surface species, ozone is thought to

first adsorb to the surface and then react. The difference between the gas and surface reaction

probabilities may simply be that the actual reaction mechanism differs from the assumed

mechanism used to calculate the reaction probability. Also, when a polar molecule like

α-terpineol is adsorbed, the carbon-carbon double bonds may become more available for reaction, due to less random molecular orientation of the molecules at the interface. (33,34). Surface orientation and double-bond location can significantly influence rates of ozone reactions with surface bound olefins (13).

Implications for Indoor Air Quality   The second-order surface rate constant, as defined in this research, can be used in combination with building parameters to estimate the relative importance of surface conversion rates and gas-phase conversion rates. When k_2 ($cm^4 s^{-1} molecule^{-1}$) is multiplied by the surface to volume ratio (cm^{-1}) of the indoor environment the result is directly comparable to the gas phase bimolecular second-order reaction rate coefficient ($cm^3 s^{-1} molecule^{-1}$). For residences, Singer et al. (2007) found the surface to volume ratio (S/V) to range from 0.029 to 0.046 cm^{-1}. In combination with the measured range for all materials in this study, $k_2 S/V$ is $(2\text{-}15) \times 10^{-16}$ $cm^3 s^{-1} molecule^{-1}$. Thus, in comparison with the bimolecular rate constant (3×10^{-16} $cm^3 s^{-1} molecule^{-1}$) (21), surface conversion occurs at rates roughly equal, or much higher than the gas phase reaction. It is striking that the range is relatively narrow despite the observation that the surface mass concentration of α-terpineol varies substantially for these different surfaces under the same conditions.

It is not advisable to rely too heavily on this extrapolation to indoor environments with "real surfaces". Surfaces can be coated with water, salts, particles and other organics that may influence the apparent surface reactivity of α-terpineol. The influence of "soiled" surfaces has

not yet been established. Further, the second-order rate coefficient, k_2, was developed based on the assumption that the background reactivity is negligible compared with the resulting ozone consumption by the ozone-terpineol reaction at the surface. However, brick and masonry surfaces have high ozone-reaction probabilities (35,36), even in the absence of adsorbed reactants. Surfaces such as carpet or kitchen counters are coated with oils (cooking, skin, etc.) that increase the background reactivity of those materials (1,2,5). In addition to being inconsistent with the underlying assumptions for k_2, highly reactive surfaces consume ozone at rates that can be limited by external mass transport, resulting in an ozone-depleted boundary layer. This in turn, would reduce the surface ozone-terpineol conversion rates relative to the gas-phase rates.   Low reactivity paint, vinyl and glass surfaces are likely to 1) be most consistent with the definition of k_2 and 2) be the most important locations for the reactions of sorbed reactants due to the lack of competition for ozone.

Allowing that surfaces significantly promote the ozone-terpene reaction rate, any differences in reaction products (gas-phase vs. surface reactions) may significantly impact product concentrations in air and on surfaces. By exposing a surface manually coated with α-terpineol, Ham and Wells (37) showed that unique products were formed on the surface and that the distribution of products differed from those identified in the gas-phase reaction (21). Further, surface reactions can also promote the formation of secondary organic aerosols (38), and the yields may differ substantially from those measured for the gas-phase reaction alone (39).

Acknowledgements

Literature Cited

(1)   Morrison, G.; Nazaroff, W. Ozone Interactions with Carpet: Secondary Emissions of Aldehydes. *Environ. Sci. Technol.* **2002**, *36*, 2185-2192.

(2)   Wang; Morrison Ozone-Initiated Secondary Emission Rates of Aldehydes from Indoor Surfaces in Four Homes. *Environ. Sci. Technol.* **2006**, *40*, 5263-5268.

(3)   Wang, H.; Morrison Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air* **2010**, *9999*.

(4)   Weschler, C.; Wisthaler, A.; Cowlin, S.; Tamás, G.; Strøm-Tejsen, P.; Hodgson, A.; Destaillats, H.; Herrington, J.; Zhang, J.; Nazaroff, W. Ozone-initiated chemistry in an occupied simulated aircraft cabin. *Environmental Science and Technology* **2007**, *41*, 6177-6184.

(5)   Coleman, B. K.; Destaillats, H.; Hodgson, A. T.; Nazaroff, W. W. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. *Atmospheric Environment* **2008**, *42*, 642-654.

(6)   Weschler, C. Chemical reactions among indoor pollutants: What we've learned in the new millennium. *Indoor Air, Supplement* **2004**, *14*, 184-194.

(7)   Destaillats; Singer, B. C.; Lee, S. K.; Gundel, L. A. Effect of Ozone on Nicotine Desorption from Model Surfaces: Evidence for Heterogeneous Chemistry. *Environmental Science and Technology* **2006**, *40*, 1799-1805.

(8) Singer; Coleman, B.; Destaillats, H.; Hodgson, A.; Lunden, M.; Weschler, C.; Nazaroff, W. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmospheric Environment* **2006**, *40*, 6696-6710.

(9)   Fick, J.; Pommer, L.; Åstrand, A.; Östin, R.; Nilsson, C.; Andersson, B. Ozonolysis of monoterpenes in mechanical ventilation systems. *Atmospheric Environment* **2005**, *39*, 6315-6325.

(10) Fick, J.; Pommer, L.; Nilsson, C.; Andersson, B. Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of α-pinene. *Atmospheric Environment* **2003**, *37*, 4087-4096.

(11) Pommer Oxidation of terpenes in indoor environments, Department of Chemistry, Umea University, 2003.

(12) Carslaw, N. A new detailed chemical model for indoor air pollution. *Atmospheric Environment* **2007**, *41*, 1164-1179.

(13) Stokes, G. Y.; Buchbinder, A. M.; Gibbs-Davis, J. M.; Scheidt, K. A.; Geiger, F. M. Heterogeneous Ozone Oxidation Reactions of 1-Pentene, Cyclopentene, Cyclohexene, and a Menthenol Derivative Studied by Sum Frequency Generation. *Journal of Physical Chemistry A* **2008**, *112*, 11688-11698.

(14) Springs, M.; Morrison Pittsburgh, PA, 2007.

(15) Springs, M.; Morrison Copenhagen, Denmark, 2008.

(16) Nazaroff; Weschler Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmospheric Environment* **2004**, *38*, 2841-2865.

(17) Singer; Destaillats, H.; Hodgson, A. T.; Nazaroff Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air* **2006**, *16*, 179-191.

(18) US EPA *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.00*; United States Environmental Protection Agency: Washington, DC, 2010.

(19) Singer, B. C.; Revzan, K. L.; Hotchi, T.; Hodgson, A. T.; Brown, N. J. Sorption of organic gases in a furnished room. *Atmospheric Environment* **2004**, *38*, 2483-2494.

(20) Singer, B. C.; Hodgson, A. T.; Hotchi, T.; Ming, K. Y.; Sextro, R. G.; Wood, E. E.; Brown, N. J. Sorption of organic gases in residential rooms. *Atmospheric Environment* **2007**, *41*, 3251-3265.

(21) Wells, J. R. Gas-Phase Chemistry of α-Terpineol with Ozone and OH Radical: Rate Constants and Products. *Environmental Science & Technology* **2005**, *39*, 6937-6943.

(22) Calogirou, A.; Larsen, B. R.; Brussol, C.; Duane, M.; Kotzias, D. Decomposition of Terpenes by Ozone during Sampling on Tenax. *Analytical Chemistry* **1996**, *68*, 1499-1506.

(23) Clausen, P.; Wolkoff, P. Degradation products of Tenax TA formed during sampling and thermal desorption analysis: Indicators of reactive species indoors. *Atmospheric Environment* **1997**, *31*, 715-725.

(24) Cano-Ruiz, J.; Kong, D.; Balas, R.; Nazaroff, W. Removal of reactive gases at indoor surfaces: Combining mass transport and surface kinetics. *Atmospheric Environment - Part A General Topics* **1993**, *27 A*, 2039-2050.

(25) Won, D.; Corsi, R.; Rynes, M. New indoor carpet as an adsorptive reservoir for volatile organic compounds. *Environmental Science and Technology* **2000**, *34*, 4193-4198.

(26) Won, D.; Corsi, R. L.; Rynes, M. Sorptive Interactions between VOCs and Indoor Materials. *Indoor Air* **2001**, *11*, 246.

(27) Huang, H.; Haghighat, F.; Blondeau, P. Volatile organic compound (VOC) adsorption on material: influence of gas phase concentration, relative humidity and VOC type. *Indoor Air* **2006**, *16*, 236-247.

(28) Moise, T.; Rudich, Y. Reactive uptake of ozone by proxies for organic aerosols: Surface versus bulk processes. *Journal of Geophysical Research D: Atmospheres* **2000**, *105*, 14667-14676.

(29) Moise, T.; Rudich, Y. Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products. *Journal of Physical Chemistry A* **2002**, *106*, 6469-6476.

(30) Voges, A. B.; Stokes, G. Y.; Gibbs-Davis, J. M.; Lettan, R. B.; Bertin, P. A.; Pike, R. C.; Nguyen, S. T.; Scheidt, K. A.; Geiger, F. M. Insights into Heterogeneous Atmospheric Oxidation Chemistry: Development of a Tailor-Made Synthetic Model for Studying Tropospheric Surface Chemistry. *The Journal of Physical Chemistry C* **2007**, *111*, 1567-1578.

(31) McIntire, T. M.; Scott Lea, A.; Gaspar, D. J.; Jaitly, N.; Dubowski, Y.; Li, Q.; Finlayson-Pitts, B. J. Unusual aggregates from the oxidation of alkene self-assembled monolayers: a previously unrecognized mechanism for SAM ozonolysis? *Phys. Chem. Chem. Phys.* **2005**, *7*, 3605.

(32) Stokes, G.; Chen, E.; Walter, S.; Geiger, F. Two reactivity modes in the heterogeneous cyclohexene ozonolysis under tropospherically relevant ozone-rich and ozone-limited conditions. *Journal of Physical Chemistry A* **2009**, *113*, 8985-8993.

(33) Heinz, T.; Tom, H.; Shen, Y. Determination of molecular orientation of monolayer adsorbates by optical second-harmonic generation. *Physical Review A* **1983**, *28*, 1883-1885.

(34) Buchbinder, A.; Weitz, E.; Geiger, F. Pentane, hexane, cyclopentane, cyclohexane, 1-hexene, 1-pentene, cis-2-pentene, cyclohexene, and cyclopentene at vapor/α-alumina and liquid/α-alumina interfaces studied by broadband sum frequency generation. *Journal of Physical Chemistry C* **2010**, *114*, 554-566.

(35) Usher, C.; Michel, A.; Stec, D.; Grassian, V. Laboratory studies of ozone uptake on processed mineral dust. *Atmospheric Environment* **2003**, *37*, 5337-5347.

(36) Grøntoft, T.; Raychaudhuri, M. Compilation of tables of surface deposition velocities for O3, NO2 and SO2 to a range of indoor surfaces. *Atmospheric Environment* **2004**, *38*, 533-544.

(37) Ham, J. E.; Wells Surface chemistry reactions of α-terpineol [(R)-2-(4-methyl-3-cyclohexenyl)isopropanol] with ozone and air on a glass and a vinyl tile. *Indoor Air* **2008**, *18*, 394-407.

(38) Waring Indoor Secondary Organic Aerosol Formation: Influence of Particle Controls, Mixtures, and Surfaces, University of Texas at Austin: Austin, TX, **2009**.

(39) Waring; Siegel; Morrison; Corsi Orlando, FL, **2008**.

Table 1. Parameters of PVC, glass, and painted beads

Beads	Diameter (mm)	Porosity when packed**	Geometric surface area normalized by density ($cm^2\,g^{-1}$)
PVC	1.6 (0.008)*	0.37	25.90 (1.3)
Glass	0.9 (0.1)	0.40	27.18 (3.0)
Painted	2.3 (0.4)	0.40	7.58 (1.3)

* Numbers in parenthesis are uncertainty.

** Porosity are determined gravimetrically.
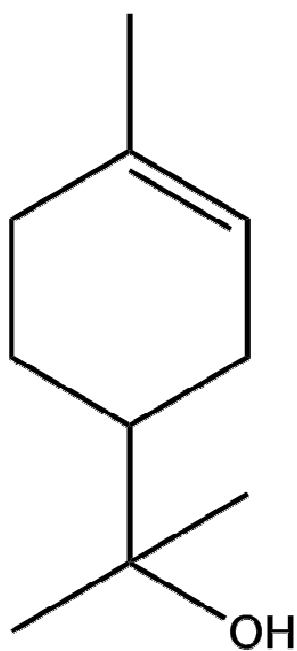
Figure 1. α-Terpineol (1-Methyl-4-isopropyl-1-cyclohexen-8-ol).
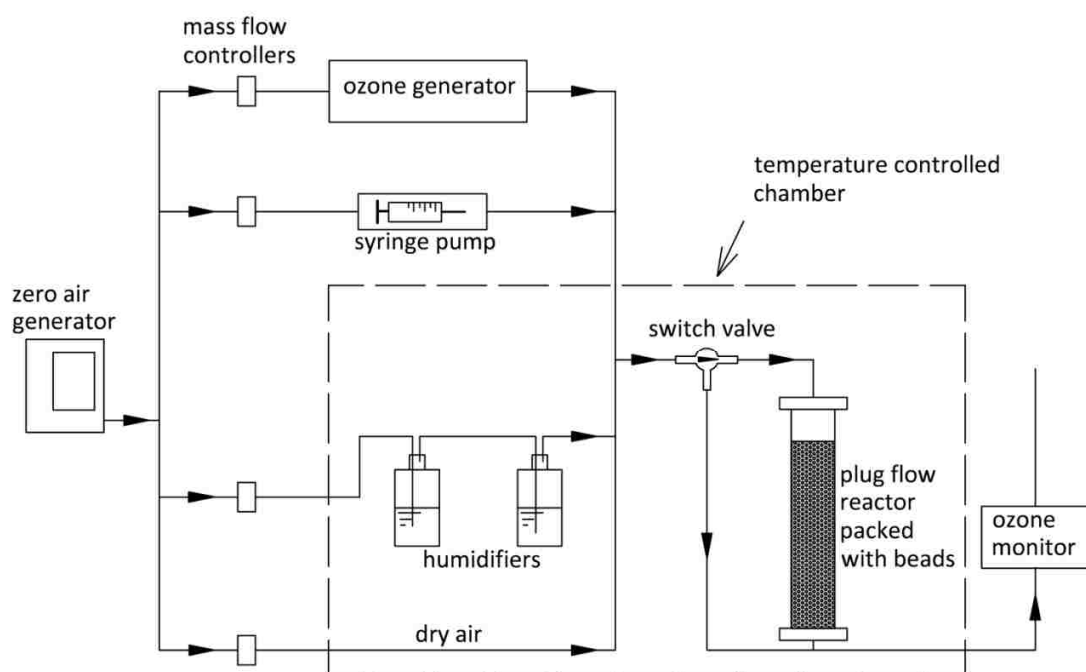
Figure 2. Packed bed, plug-flow reactor apparatus used to measure the second-order reaction rate coefficient, k_2, and the reaction probability.
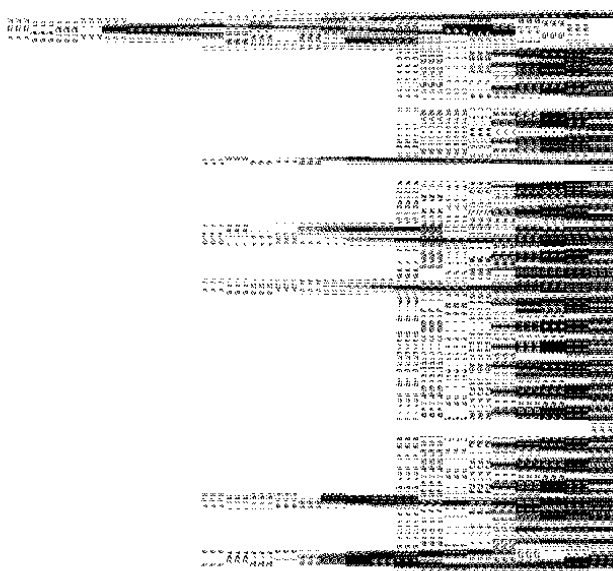
Figure 3. Adsorption isotherms for α-terpineol on glass (a), PVC (b) and paint (c). Results were fit to a Freundlich isotherm.
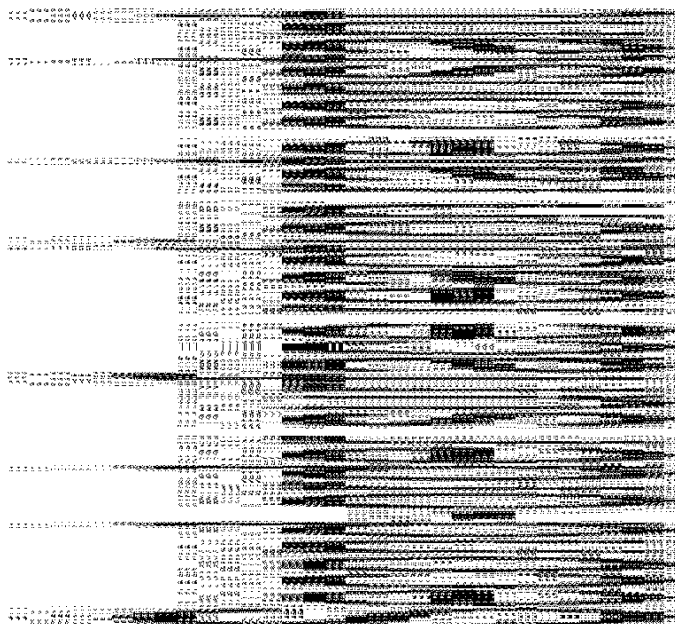
Figure 4. Area-specific, second-order surface reaction rate constant, k_2, for α-terpineol on glass, PVC and paint. The data points are slightly offset horizontally for clarity and to avoid overlapping symbols.
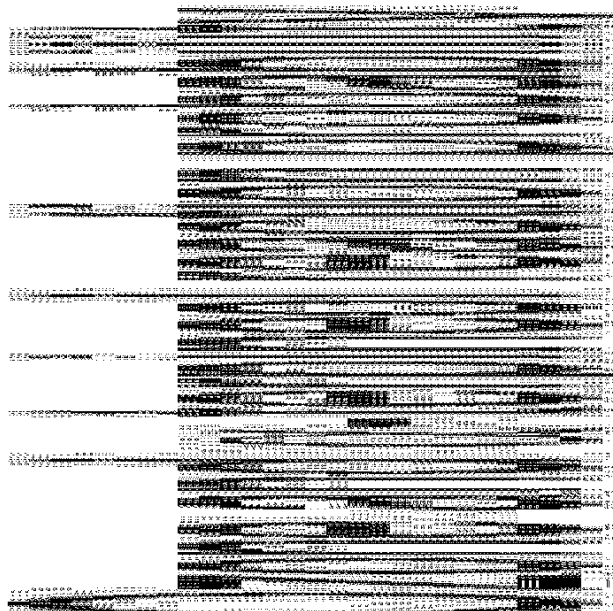
Figure 5. The ozone-α-terpineol reaction probability on PVC, glass and painted surfaces under different relative humidity conditions. The data points are slightly offset horizontally for clarity and to avoid overlapping symbols

III. Surface reaction rate and probability of ozone and dihydromyrcenol measured in a bench scale reactor and room-sized chamber

(to be submitted to Atmospheric Environment)

SHI SHU AND GLENN C. MORRISON*

Department of Civil, Agriculture and Environmental Engineering, Missouri University of

Science and Technology, Rolla, MO, 65401 USA

Email : ssfdb@mst.edu , gcm@mst.edu

*Corresponding author, phone: (573)-341-7192, email: gcm@mst.edu,

fax: (573)-341-4729

Abstract

Low volatility terpenoids emitted from consumer products can react with ozone on surfaces and may significantly alter concentrations of ozone, terpenoids and reaction products in indoor air. We measured the reaction probability and a second-order surface-specific reaction rate for the ozonation of dihydromyrcenol, a representative indoor terpenoid, adsorbed onto polyvinylchloride (PVC), glass, and latex paint coated spheres. The reaction probability ranged from (0.06 to 8.97) $\times 10^{-5}$ and was very sensitive to humidity, substrate and mass adsorbed. On average 1.28×10^{-5}, ozone and dihydromyrcenol are at about 10 times more likely to react with each other on these surfaces than they are in the gas phase. The second-order

surface-specific rate constant ranged from (0.32 to 7.05) $\times 10^{-15}$ cm^4 s^{-1} molecule^{-1}and was much less sensitive to conditions or substrate. We also measured the ozone deposition velocity due to adsorbed DHM on painted drywall in a room-sized chamber. The resulting rate coefficient, (0.42 - 1.6) $\times 10^{-15}$ cm^4 molecule$^-$1 s^{-1}), was consistent with that derived from bench-scale experiments for paint under similar conditions.

Keywords

indoor air, ozone, dihydromyrcenol, surface reactions, kinetics

1. Introduction

Reactions among pollutants in buildings alter indoor air compositions and thus influence exposure of occupants to reactants and products. Ozone, a component of urban smog, reacts with organic compounds both in the gas phase (homogeneous) and on indoor surfaces (heterogeneous). These reactions can result in lower ozone and higher product concentrations in buildings. Homogeneous reactions of ozone with nitrogen oxides and terpenes have been thoroughly studied in both ambient and indoor chemistry literature (Hoffmann et al. 1997; Calogirou, Larsen, and Kotzias 1999; Hakola et al. 1994; Atkinson and Arey 2003; Yu et al. 1999). However, heterogeneous ozone chemistry remains poorly understood, especially for the surfaces and compounds unique to indoor environments.

These heterogeneous reactions may be of equal or even greater importance, compared with gas-phase reactions in buildings. During a simulated aircraft experiment, more than half of ozone was consumed on cabin surfaces and clothing, (Weschler et al. 2007). Based on the

results of ozone reactions with dried cleaner residues, Destaillats et al. (Destaillats et al. 2006)

and Singer et al. (Singer et al. 2006) attributed ozone consumption and product formation, in

part, to chemistry with unsaturated species remaining on surfaces.   Oxidation of volatile

terpenes on heat-exchanger surfaces was inferred from larger-than-anticipated conversion rates

(Fick et al. 2005). Even Teflon surfaces may support ozone-terpene reactions (Fick et al. 2003;

Pommer 2003). Unsaturated oils (Morrison and Nazaroff 2002; Wang and Morrison 2006;

Wang and Morrison 2010; Weschler et al. 2007; Wisthaler and Weschler 2009), terpenes

(Springs and Morrison 2007; Springs and Morrison 2008) and other compounds coat, or adsorb

onto, building surfaces and increase the apparent ozone reactivity of these surface (Wang and

G.C. Morrison 2006). Like the gas phase reaction, ozone reactions with terpenes on surfaces

can also produce irritants and aerosols (Weschler 2004; Waring 2009). These reactions

generate a host of oxidized organic species including aldehydes, ketones, and carboxylic acids

(Morrison and Nazaroff 2002; Wang and Morrison 2006; Weschler et al. 2007; Ham and Wells

2008; Coleman et al. 2008). However, these studies are primarily qualitative, or provide

relative reactivity information.

It is important to quantify rates of reactions on indoor surfaces. Existing studies

directed to chemistry on atmospheric aerosols have shown that the reaction probability of

ozone with surface-bound organic compounds tend to be much higher than the reaction

probability of the equivalent gas phase reaction (Dubowski et al. 2004; Voges et al. 2007a;

Stokes et al. 2008). In combination with the large surface area-to-volume ratio found in

buildings, enhanced surface reactivity can cause surface chemistry to dominate homogeneous conversion indoors. In spite of its importance, existing indoor air quality models do not yet include individual heterogeneous reactions due to a lack of kinetic and product yield data.

The kinetics of some surface reactions relevant to indoor environments have been measured. Springs and Morrison (Springs and Glenn Morrison 2007) found that the surface-specific reaction probabilities of Δ-carene and d-limonene were 10-100 times greater than those in the gas phase. Because of its likely ubiquity on indoor surfaces, the kinetics of the ozone squalene surface reaction has been measured by two groups. A reaction probability of $(45 \pm 14) \times 10^{-5}$ (Wells, Morrison, and Coleman 2008) and a pseudo-first-order rate constant of 1.22×10^{-5} s^{-1} (Petrick and Dubowski 2009) were determined. Shu and Morrison defined and quantified a second-order surface reaction rate coefficient for ozone and α-terpineol, which can be directly incorporated into indoor air quality models (Shu and Glenn Morrison 2009). Their results suggested that more than half of the ozone reacts with α-terpineol on surfaces rather than in building air.

In this research, we measure heterogeneous ozone kinetic rate constants for 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol), a naturally occurring monoterpene alcohol (structure shown in Figure 1). Similar to α-terpineol, it is extensively used in fragrances for bath preparations, soaps, detergents, polishes, and other household products (Nazaroff and Weschler 2004; Colombo et al. 1991) and was observed to be one of the primary terpene alcohols emitted from a general purpose cleaner (Singer et al. 2006). Dihydromyrcenol also

has a low vapor pressure (~16.5 Pa at 25°C) (US EPA 2010) and is therefore likely to exhibit

substantial sorptive partitioning at equilibrium (Singer et al. 2004; Singer et al. 2007). Because

of its small bimolecular (gas-phase) rate constant, 2×10^{-18} cm^3 molecule^{-1} s^{-1} (Forester, Ham,

and Wells 2006), its gas-phase conversion tends to be negligible compared with much more

reactive terpenes and terpenoids such as limonene and α-terpineol. However, Ham et al.

observed, qualitatively, that the reaction rate was much higher on a dihydromyrcenol coated

vinyl tile, than in the gas phase, based on the rate of product emissions (Ham and Wells 2009).

Thus, we seek to quantify this surface rate and estimate how indoor surfaces influence

overall conversion of dihydromyrcenol. Specifically, we quantify an area-specific

second-order reaction rate coefficient, k_2, associated with the ozone/ dihydromyrcenol reaction

on three surfaces relevant to indoor environments (glass, polyvinylchloride, and latex paint).

This coefficient can be used to estimate the relative impact of heterogeneous ozone-terpene

reactions on indoor air concentrations of both ozone and dihydromyrcenol. Further, this

quantitative analysis can improve existing indoor chemical models by directly relating indoor

terpenoid concentrations with the resulting enhancement in surface conversion rates. We also

quantify a minimum effective reaction probability associated with these reactions.

2. Methods

2.1 Materials

Dihydromyrcenol (99%) was purchased from Sigma Aldrich (St. Louis, MO, USA).

The Polyvinyl Chloride (PVC) beads were purchased from Engineering Laboratories Inc.

(Oakland, NJ, USA). The soda lime glass beads were purchased from MO-SCI Specialty Products, L.L.C. (Rolla, MO, USA). Latex paint (American Tradition®, color coding 4007-9A, sky blue, flat) was applied to ceramic (zirconium silicate) beads and cured for more than 4 years, to generate a dry latex paint surface. Bead diameters and other parameters are found in Table 1. 5 L Pyrex bottles with autoclavable polypropylene plug-seal caps were purchased from Fisher Scientific (Pittsburgh, PA, USA). A mini-nert valve with a 1/8 inch male NPT connection, purchased from VICI Precision Sampling (Baton Rouge, LA, USA), was customer-modified and attached to each cap. For the 8.2 m^3 chamber experiments, drywall was painted with white satin latex paint (Sherwin Williams), installed in the ventilated chamber and allowed to cure for ~ 3 years.

2.2   Analytical

Stainless steel sorption tubes packed with Tenax-TA (Markes, Llantrisant, UK) and Solid Phase Micro Extraction (SPME; 65 μm PDMS-DVB Coating StableFlexTM; Supelco) were both used as sample preparation methods for conventional gas chromatography with flame ionization detector (GC/FID) detection of dihydromyrcenol. Tenax-TA tubes were used to quantify the concentration of dihydromyrcenol at the exhaust of each reactor. 4 liters of exhaust gas were collected over 20 min for later thermal desorption and analysis by GC-FID. Tenax tubes were also used to verify the mass of vapor-phase dihydromyrcenol injected by syringe into adsorption bottles. Tenax tubes were calibrated by applying a known mass of

dihydromyrcenol, diluted in methanol, to sorbent, evaporating the solvent, and thermally

desorbing and injecting the dihydromyrcenol into the GC-FID.

In bottles used to conduct dihydromyrcenol adsorption experiments, SPME was used

to quantify the gas phase dihydromyrcenol concentration. Because the fiber will only adsorb a

small amount of the analyte (usually tens or hundreds of nanograms), SPME is especially

useful when there is only a small amount of analyte, or when the concentration is low. The

SPME fiber was exposed to the gas for 5 min, and then inserted into a GC injection port 240°C

for 5 min to desorb all the dihydromyrcenol. The SPME fiber removes less than 1% of the total

mass of dihydromyrcenol in the sorption bottle. SPME was calibrated by comparison with

Tenax-TA results of the same gas mixture.

An HP6890 GC-FID with an HP 5MS column was used to analyze samples collected

on both Tenax-TA tubes and SPME fibers. The carrier gas flow rate was 20 cm^3 min^{-1}. The

initial oven temperature of 100°C was increased to 250°C at a rate of 35°C min^{-1}. The method

detection limit was 5 ppb for Tenax-TA tube analysis and 1 ppb for SPME analysis.

2.3   Adsorption apparatus and procedure

Dihydromyrcenol adsorption experiments were carried out using a series of the 5 L

Pyrex bottles with customer modified caps as described above. The bottles and caps with

valves were washed with methanol, rinsed with ultra high purity water and then dried at 80°C

for at least 24 hours before each experiment. Adsorption experiments were carried out in a

temperature controlled chamber at 25°C, and at three relative humidity conditions (20%, 50%,

and 80%). To generate the desired humidity, each bottle was flushed with high purity nitrogen gas for 30 min at 1.0 L min^{-1}. The humidity was controlled by sparging a fraction of the dry nitrogen flow through high purity water. For each relative humidity condition, beads (PVC, glass, or painted) were added to separate Pyrex bottles, and two replicates were carried out at the same time. Two empty bottles were used as controls. The geometric surface area of PVC, glass, and painted surface were 3070 cm^2, 4000 cm^2, and 3120 cm^2 respectively. The inner surface area of each Pyrex bottle was estimated to be 1740 cm^2. To inject a small amount of dihydromyrcenol, headspace gas was drawn from a 1 L Boston round bottle containing ~5 g pure dihydromyrcenol liquid. This bottle was maintained at 25°C and the resulting headspace concentration of 1.18 mg L^{-1} (181 ppm) was verified by Tenax-TA tube analysis. A 5 mL gastight syringe was used to draw the dihydromyrcenol gas from the 1 L bottle and to inject it into the 5 L Pyrex bottles. After the gas was injected, bottles were rotated on a tumbler at 7 rpm for 10 hours to allow the dihydromyrcenol to uniformly adsorb to bead and bottle surfaces. Time required to achieve equilibrium was verified in separate experiments. SPME was use to measure the concentration of dihydromyrcenol in each bottle after 10 hours. Each combination of humidity, concentration and surface was repeated at least once.

2.4 Plug flow reactor apparatus and procedure

The plug flow reactor (PFR) system used to measure ozone/ dihydromyrcenol reaction rates on surfaces is shown in Figure 2. A zero air generator (Parker-Balston) supplied clean air to the system, and flow controllers (MKS) maintained the flows at desired rates. Diffusion

tubes (VICI Metronics, Poulsbo, Washington) filled with pure dihydromyrcenol liquid were used to continuously add dihydromyrcenol into the gas flow and the resulting concentration was verified using Tenax-TA tube analysis. Ozone was generated and monitored using a Dasibi (Glendale, CA) UV photometric ozone analyzer. The humidity of the reactor stream was controlled by adjusting the ratio of dry and humidified air flow rates. The water bubbler and the reactor were maintained at 25°C in a temperature controlled chamber (shown by dashed line in Figure 2).

A 50-cm long Teflon reactor with an inner diameter of 1.8 cm was used. The total volume and (surface area) were: 100 cm^3 glass beads (4000 cm^2); 120 cm^3 PVC beads (2840 cm^2); and 120 cm^3 painted beads (1880 cm^2). The surface area of the Teflon reactor was 283 cm^2.

Before each experiment, the beads were ultra-sonicated for 30 min in high purity water to clean the surface and dried in the oven at 50°C for at least 24 hours. Both ozone and dihydromyrcenol were delivered to the reactor for 12 hours to allow a steady-state concentration profile to develop in the reactor before concentrations were measured at the inlet and outlet. Because dihydromyrcenol reacts with ozone, both the ozone and dihydromyrcenol concentrations are reduced at the reactor exhaust. Under our experimental conditions, it is possible to completely deplete a reactant if the other is introduced at a significantly higher molar concentration. Typical inlet concentration pairs of ozone: dihydromyrcenol (ppb) were 10:4, 10:3, and 10:2.

2.5   Chamber experiment apparatus and procedure

A diagram of the 8.2 m^3 chamber used to measure ozone dihydromyrcenol surface conversion rates is shown in Fig 3. The chamber (2.03 m $\times$ 2.06 m $\times$ 1.96 m) was equipped with painted drywall on all surfaces including the floor. The chamber was ventilated with laboratory room air that was filtered through activated carbon. The air exchange rate was maintained at 0.6 $\pm$ 0.05 h^{-1} and was measured by monitoring the decay of methane trace gas with a stand-alone flame ionization detector (FID). A small fan was placed in the chamber to ensure that the air in the chamber was well mixed. Ozone generation and dihydromyrcenol injection methods were the similar to those used in the PFR system, except larger diameter diffusion tubes for dihydromyrcenol were used. Using an automated set of Teflon valves, the ozone analyzer collected samples from either the gas inlet duct or center of the chamber. The ozone and dihydromyrcenol were injected ~1.5 m upstream from the supply register for the chamber, resulting in a mixing residence time of ~ 40 seconds. The ozone concentration was (3.2 $\pm$ 0.1) $\times 10^{12}$ molecule cm^{-3} (~ 120 $\pm$ 4 ppb), and dihydromyrcenol concentration range were ~ 0.06 - 5.4$\times 10^{12}$ molecule cm^{-3} (~ 2 - 200 ppb), respectively. Considering that the gas phase reaction of ozone and dihydromyrcenol is very slow (2 $\times 10^{-18}$ cm^3 molecule^{-1} s^{-1}), homogeneous conversion in the duct was negligible compared with that in the chamber. The temperature and relative humidity (RH) inside the chamber were monitored with a thermistor and RH transducer (VAISALA ™, Boulder, CO). The temperature and RH conditions were those of the laboratory and not independently controlled. Thus, the temperature was (22.5 $\pm$

1.0)°C. Because these experiments were performed in winter, the relative humidity was generally low and ranged from 8% - 40%; 85 % of the time, the RH ranged between 20% - 40%.

Following an air exchange rate measurement, the ozone concentration was raised to ~ 2 ppm and maintained there for 12 hours to quench ozone-reactive sites and decrease the background reactivity. The ozone injection rate was then reduced and ozone allowed achieving a new steady state inlet value equal to ~120 ppb. The ozone concentration was allowed to decay to ~ 0 ppb prior to starting a dihydromyrcenol reactivity experiment. This experiment proceeded as follows: First, dihydromyrcenol was introduced to chamber. After ~ 5 hours, SPME was used to quantify the dihydromyrcenol concentration in the chamber. Then ozone was introduced, SPME was again used to quantify the dihydromyrcenol concentration in chamber again after the ozone concentration had stabilized.

3. Data analysis

3.1   Adsorption

To determine the dihydromyrcenol-specific ozone reaction probability on the surface, we require a measure of the surface coverage of dihydromyrcenol under a range of concentrations in the PFR experiments. The equilibrium surface concentration on the beads was determined by balancing the known mass injected against the gas-phase mass (SPME), mass collected on the bottle surface (from control experiments) and the remaining mass on the beads, as shown in Equation (1).

$$M_{total} = A_{bottle}C_{s,bottle} + V_{gas}C_{gas} + A_{beads}C_{s,beads} \tag{1}$$

where M_{total} is the total mass of dihydromyrcenol injected to each bottle (g), A_{bottle} and

A_{beads} are the surface area of bottle and beads (cm^2), respectively, $C_{s,bottle}$ and $C_{s,beads}$ is

the concentration of dihydromyrcenol on the surface of the bottle and beads (g cm^{-2}),

respectively. V_{gas} is the volume of gas in each bottle (cm^3), and C_{gas} is the gas phase

concentration of dihydromyrcenol (g cm^{-3}).

The relationship between dihydromyrcenol concentrations on the bead and bottle

surfaces and the gas phase dihydromyrcenol concentration, was expressed by a Freundlich

isotherm (best general model for results obtained), as shown in Equation (2).

$$C_{s,beads\ or\ bottle} = K_{f,beads\ or\ bottle} \cdot C_{gas}^{n} \tag{2}$$

where C_S and C_{gas} are in units of (ng cm^{-2}) and (ppb) respectively. In each case, K_f and n

are derived from the nonlinear least-squares fit of the isotherms.

3.2   Area-specific, second-order reaction rate constant

To provide a useful parameter for evaluating the impact of indoor surface chemistry,

we define an area-specific second-order reaction rate constant, k_2 (cm^4 molec^{-1} s^{-1}) associated

with overlying gas-phase concentrations, C_{O3} and C_{DHM}, by Equation (3).

$$rate\ (molecules\ s^{-1}) = k_2 C_{O3} C_{DHM} (A/V) \tag{3}$$

where (A/V) is the surface-area to volume ratio (in the reactor or other system where

mass-transfer does not limit transport and uptake of either reactant). This is the rate of the

ozone-dihydromyrcenol reaction, not necessarily the total rate of ozone or dihydromyrcenol

loss and does not account for background removal of ozone. In our system, background ozone

removal was negligible compared with that due to its reaction with dihydromyrcenol, when

dihydromyrcenol was present. This second-order rate constant can be used directly in indoor

air quality models to estimate reactant and product fluxes at indoor surfaces.

To determine k_2, we modeled the reactor as a plug flow reactor (PFR). The

concentration of both ozone and dihydromyrcenol change with distance, z, along the

bead-filled region of the reactor and can be characterized by two coupled equations

(steady-state). Adsorption and reaction on the surface of the Teflon reactor (283 cm^2) is

negligible compared with that taking place on the beads. A mass balance on the PFR at

steady-state results in the following equations for the concentration of ozone and

dihydromyrcenol, both of which are functions of distance (z) down the reactor:

$$\frac{dC_{O3}}{dz} = -k_2 C_{O3} C_{DHM} \left(\frac{A_{beads}}{V_{reactor} \cdot u} \right) \tag{4}$$

$$\frac{dC_{DHM}}{dz} = -k_2 C_{O3} C_{DHM} \left(\frac{A_{beads}}{V_{reactor} \cdot u} \right) \tag{5}$$

where $V_{reactor}$ is the volume of the bead-filled regions of the reactor , u is the average gas

velocity in the reactor. The loss of dihydromyrcenol is assumed to be equal to the ozone loss

(1:1 stoichiometry) after accounting for background ozone removal by reactor surfaces.

Gas-phase conversion of ozone or dihydromyrcenol is negligible during the <4 s residence

time of the reactor.

Equations 4 and 5 were solved numerically and the resulting values of k_2 were adjusted to provide a best fit to experimentally derived values of inlet and outlet concentrations.

3.3   Minimum ozone/dihydromyrcenol reaction probability

Equation (6) was used to calculate the reaction probability of ozone with bare surfaces (background reactivity) (Morrison and Nazaroff 2000).

$$\gamma_{surface} = (-ln \frac{C_{O3,in}}{C_{O3,out}}) \frac{4 \, V_{reactor} \, Q}{<v> A_{beads} \, L \, A \, \rho} \tag{6}$$

where $\gamma_{surface}$ is the reaction probability of ozone associated with the bare substrate (PVC, glass, and paint), $C_{O3,in}$ and $C_{O3,out}$ are the inlet and outlet ozone concentration, Q is the total flow rate, $<v>$ is the Boltzmann velocity for ozone, which is 360 m s^{-1} in this case (Cano-Ruiz et al. 1993), L is the length of the bead-filled region of the reactor, A is the cross sectional area of the plug flow reactor, and ρ is the porosity of the bead bed. At typical operating concentrations ($\sim$ 120 ppb), there was no measurable difference in the inlet and outlet ozone concentrations, indicating negligible background reactivity. A relatively high mixing ratio of ozone   ($\sim$ 850 ppb) was required to generate a measurable difference the inlet and outlet.

The combined (total) reaction probability, γ_{total}, is assumed to be a linear combination of the reactivity of adsorbed dihydromyrcenol and exposed surface sites. Because dihydromyrcenol is consumed by its reaction with ozone, the ozone and dihydromyrcenol concentrations vary along the length of the reactor. Thus, the surface coverage is not uniform throughout the reactor and is a function of the position in reactor, as shown in Equation (7).

$$\gamma_{total} = \gamma_{O3,DHM} f_{DHM,beads,z} + \gamma_{beads}[1 - f_{DHM,beads,z}] \tag{7}$$

where the $f_{DHM,beads,z}$ is the fraction of the surface area covered with dihydromyrcenol

molecules at position z, $\gamma_{O3,DHM}$ is the reaction probability of adsorbed dihydromyrcenol. The

fractional coverage, $f_{DHM,beads,z}$, is determined by applying measured isotherms, assuming

single-molecular adsorption (no stacking) and smooth bead surfaces. Because beads are not

smooth, and not all of the adsorbed dihydromyrcenol will be equally available for reaction (e.g.

in a pore or covered by other molecules), the reaction probability determined is the *minimum*

reportable value.

The total surface reaction probability is evaluated in a similar manner as in Equation (8) and (9),

but must account for changes in both ozone and dihydromyrcenol through the reactor.

$$\frac{dC_{O3}}{dz} = -\frac{\gamma_{total}(z) <v>}{4u} \frac{A_{beads}}{V_{reactor}} C_{O3}(z) \tag{8}$$

$$\frac{dC_{DHM}}{dz} = -\frac{\gamma_{total}(z) <v>}{4u} \frac{A_{beads}}{V_{reactor}} C_{O3}(z) \tag{9}$$

3.4   Ozone deposition velocity on drywall in 8.2 m³ chamber

In the presence of ozone alone, the background deposition velocity of the painted

drywall was quantified by applying a mass balance on ozone as shown in Equation (10).

$$QC_{O3,in} = v_{d,bkg} A C_{O3,out} + QC_{O3,out} \tag{10}$$

where the $v_{d,bkg}$ is the background ozone deposition velocity (m s⁻¹), and the A is the surface

area of the painted drywall in the chamber (24.40 m²). Q is the volumetric flow rate through

the chamber (m^3 h^{-1}). $C_{O3,in}$ and $C_{O3,out}$ are ozone inlet and outlet concentration, measured at the supply and the center of the chamber respectively.

In the presence of both ozone and dihydromyrcenol, the mass balance equation on ozone results in Equation (11).

$$QC_{O3,in} = \left((v_{d,bkg} + v_{d,DHM})A + Q + k_{gas}C_{DHM,out}V\right)C_{O3,out} \tag{11}$$

where the k_{gas} is the ozone-dihydromyrcenol gas phase reaction rate constant, which is 2 ×10^{-18} cm^3 s^{-1} molecule^{-1} (Forester, Ham, and Wells 2006), V is the volume of chamber (8.2 m^3), $v_{d,DHM}$ is the ozone deposition velocity associated with dihydromyrcenol adsorbed on drywall. In developing Equation (11), it is assumed that the fractional coverage, f, of dihydromyrcenol is small, and that $v_{d,bkg}$ is not significantly reduced by adsorption of dihydromyrcenol that obscures surface sites. Thus, any observed change in ozone uptake by surfaces is due to reactions with adsorbed dihydromyrcenol. We evaluate this assumption in the Results and Discussion section.

4. Results and discussion

4.1 Dihydromyrcenol adsorption

The dihydromyrcenol adsorption isotherms are shown in Figures 4 a, b and c along with Freundlich parameters (in Equation 2).

Glass and paint adsorb approximately ten times more dihydromyrcenol than PVC under the same conditions. The relative humidity influences dihydromyrcenol adsorption on glass more than on PVC or paint. As the relative humidity increases, much less

dihydromyrcenol will adsorb to the glass surface. These trends are consistent with the results of

α-terpineol adsorption on these surfaces (Shu and Morrison, in preparation). This may be due

to competition between water and dihydromyrcenol for adsorption sites on glass. On PVC,

dihydromyrcenol does not appear to compete with water under these conditions.

4.2   Area-specific, second-order reaction rate constant

Figure 5 shows the results for the area-specific, second-order reaction rate constant, k_2,

for all surfaces and conditions. The value of k_2 ranges from approximately $(0.5 - 7.0) \times 10^{-15}$

$cm^4 s^{-1}$ molecule^{-1}. This relatively small range is surprising given the very different surface

concentrations of dihydromyrcenol on the three materials, and for the very different impact on

surface concentration due to differences in humidity. Considering the medium concentration

and 50% RH condition, the range of k_2 on glass surface $(0.5 - 2.5 \times 10^{-15}$ $cm^4 s^{-1}$ molecule^{-1})

coincides closely with the range of k_2 on PVC surface ($0.5 - 5.0 \times 10^{-15}$ $cm^4 s^{-1}$ molecule^{-1}).

However, the adsorbed mass is nearly 5 times higher (per unit area) on glass than on PVC.

Even though RH can strongly influence the adsorptive capacity significantly on glass and paint,

there is little impact on k_2. It appears that k_2 is only weakly influenced by the adsorbed mass,

but instead is more strongly linked to the gas-phase concentration of dihydromyrcenol. This

phenomenon was also observed for α-terpineol (reference) and suggests that the ozone

reactivity is dependent on the interfacial activity of dihydromyrcenol, rather than the mass

adsorbed.

The assumption that reactant flux is first order in dihydromyrcenol appears to be poor for

range of gas-phase concentrations studied. By comparing the resulting flux and k_2 with

concentration at each humidity, the reaction order of dihydromyrcenol ranges from -1 to 0.5.

However, the k_2 values can be used to estimate the magnitude of surface the surface reaction

and compare with other loss mechanisms for indoor conditions similar to those in these

experiments. To develop a more accurate reaction order, the concentration of both species

should be expanded to include several orders of magnitude.

4.3   Minimum reaction probability

Figure 6 shows the results for the minimum ozone/dihydromyrcenol reaction

probability, $\gamma_{O3,DHM}$. Also shown for comparison is the gas-phase reaction probability ($2.5 \times$

10^{-6}) based on the reported gas phase reaction rate constant in dry air (Forester, Ham, and Wells

2006). All measured values are higher than the gas-phase value. The highest (PVC, 50% RH) is

about 25 times greater than that for the gas-phase reaction. The large of values are consistent

with the observation that adsorption characteristics vary widely, but the surface reactivity

(characterized by k_2) does not.

Again, these values represent the *minimum* measurable value, not an absolute reaction

probability. The model used to calculate the ozone dihydromyrcenol reaction probability on

surfaces was based on the assumption that the dihydromyrcenol molecules form no more than a

monolayer. This assumption may be valid when the fractional coverage is very small. However,

at the "indoor relevant" concentrations used here, the adsorbed dihydromyrcenol molecules

would cover ~3% to ~30% of the surface area. Thus, multi-layer "islands" of dihydromyrcenol

may form, and not all dihydromyrcenol molecules will be equally available for reaction with ozone. Physical barriers to reaction, such as adsorption deep within pores, further reduce the reported reaction probability. Consistent with this mechanism, the highest reaction probability occurs for the lowest coverage (PVC).

The fact that ozone dihydromyrcenol reaction probabilities on surfaces are larger than that in gas phase is consistent with observation from other studies. For example, Springs and Morrison determined the ozone reaction probability of surface-bound Δ-carene ranged from 3.0×10^{-6} to 2.5×10^{-5}, which is 10 to 80 times higher as the reaction probability in gas phase (Springs and Morrison 2007; Springs and Morrison 2008). Voges et al. also found that the a terpene-functionalized glass surface has ozone reaction probability of $\sim 10^{-5}$, which is as 20 times high as the gas phase reaction probability (Voges et al. 2007b). Although the enhancement of reaction probability is obvious, the reason behind this enhancement of reaction probability is not clear yet. One possible explanation for this higher ozone reactivity with adsorbed species is that when dihydromyrcenol molecules adsorbed on surfaces, the carbon-carbon double bonds became more available to the ozone, due to spontaneous polarization (Derjaguin and Shulepov 1979; GY Stokes et al. 2009) of dihydromyrcenol molecules. Further research is needed to investigate the surface chemistry at molecule level.

4.4   Ozone deposition on drywall in chamber

Figure 7 shows the ozone deposition velocity measured in the room-sized chamber experiments. The background ozone deposition velocity and reaction probability ranged from

0.072 to 0.077 m h^{-1} and (0.22 - 0.24) $\times$ 10^{-6} respectively. These values are in the low range of other reported values (Wang and Morrison 2006; Wang and Morrison 2010; Klenø et al. 2001), perhaps because the drywall surface was maintained in a clean laboratory chamber with little possibility of being coated with oils and other reactive compounds typical of occupied indoor environments. As the steady-state dihydromyrcenol mixing ratio was increased, the ozone deposition velocity associated with dihydromyrcenol adsorbed on drywall, $v_{d,DHM}$, increased accordingly (by Equation 12). For a dihydromyrcenol mixing ratio of ~ 170 ppb, $v_{d,DHM}$ is approximately equal to $v_{d,bkg}$.

An effective surface rate coefficient can be gleaned from these data and compared with those from the PFR experiment for painted beads. The combined parameter $k_{2,surf}C_{DHM}$ in Equation 3 and as measured in the PFR experiments most closely corresponds to $v_{d,DHM}$ in the 8.2 m^3 chamber experiments. Thus the chamber based $k_{2,surf}$ values range from (0.42 - 1.6) $\times$ 10^{-15} cm^4 molecule^{-}1 s^{-1}. For painted beads at low humidity, $k_{2,surf}$ ranged from (1.5 - 2.5) $\times$ 10^{-15} cm^4 molecule^{-}1 s^{-1}. On average, the values from either system are within a factor of 2 of one another. PFR experimental results over all conditions and surfaces ranged over a factor of 10 and include the low end of the large chamber values. Some differences between the PFR and chamber results could be due to differences in materials and conditions: 1) the drywall could not be cleaned and oven dried, 2) the composition of paint film on drywall and beads were not identical since they are of a different brand, color, and age, 3) the humidity and temperature in

the chamber were not identical to that in the PFR. In spite of these differences, the results

between experimental systems are in good agreement.

4.5   Implications for indoor air quality

When multiplied with the surface to volume ratio (cm^{-1}), $k_{2,surf}$, can be used just as

the gas phase bimolecular second-order reaction rate coefficient to define removal rates of

ozone or dihydromyrcenol in mass-balance models of indoor air. Thus, they can be compared

directly when considering the relative conversion rates taking place in the gas-phase and on

surfaces. For a typical indoor surface to volume ratio of 0.03 cm^{-1}(Hodgson, Ming, and Singer

2004), the effective bimolecular rate coefficient due to surface reactions is (0.4 - 2) $\times 10^{-16}$ cm^3

s^{-1}molecule^{-1}. This is 20 - 100 times greater than the gas phase bimolecular rate coefficient (2

$\times 10^{-18}$ cm^3 s^{-1} molecule^{-1} (Forester, Ham, and Wells 2006). Thus the ozonation rate of

dihydromyrcenol in buildings is overwhelmingly dominated by surface chemistry, not

gas-phase chemistry.

It is not yet possible to extrapolate these and other recent findings to predict the

reactivity and behavior of all alkenes in buildings. Some generalizations may be appropriate,

however. Low volatility compounds will sorb more strongly than more volatile compounds,

and thus are likely to have more influence over the area-averaged reactivity of indoor surfaces.

Stokes et al. (Stokes et al. 2009) showed that the reaction probabilities for surface-linked

compounds do not correlate with the type of alkene attached to the surface or its corresponding

gas-phase reaction rates. In fact 1) there was an anti-correlation with gas-phase reaction

probabilities, 2) surface reaction probabilities are much larger than their gas-phase counterparts, and 3) there appears to be a "flattening" of reactivity. For gas-phase reaction probabilities that span 3 orders of magnitude, the corresponding surface-specific reaction probabilities only span 2 orders of magnitude. We also observe this flattening with the α-terpineol (Shu and Morrison, in preparation) and dihydromyrcenol reaction probabilities. Surface-specific reaction probabilities for alkenes measured to date tend to be $> 10^{-5}$. The highest "minimum" value from this research for dihydromyrcenol was $\sim 8 \times 10^{-5}$, which is likely to be closer to the "real" reaction probabilities for this sorbed compound. Intriguingly, the area-averaged reaction probability in buildings tends to be $\sim 10^{-5}$ (Cano-Ruiz et al. 1993) even though measurements of individual surfaces can range from 10^{-8} (clean glass) to $>10^{-4}$ for brick. Nazaroff et al. (William W. Nazaroff, Gadgil, and Charles J. Weschler 1993) suggested that surface soiling/coatings may be responsible for the narrow range of area-averaged ozone deposition velocities observed in buildings. Similarly, reactivity flattening, and substantial surface reaction probabilities (even for otherwise low-reactivity compounds in the gas phase) suggest that adsorbed volatile and semi-volatile alkenes may be responsible for much of the ozone uptake in buildings.

Acknowledgements

Jonathan McKinney, graduate student in Chemical Engineering Department of Missouri

University of Science and Technology, for their many valuable contributions.

References

Atkinson, R., and J. Arey. 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. *Atmospheric Environment* 37, no. 2.

Calogirou, A., B.R. Larsen, and D. Kotzias. 1999. Gas-phase terpene oxidation products: A review. *Atmospheric Environment* 33, no. 9: 1423-1439.

Cano-Ruiz, J.A., D. Kong, R.B. Balas, and W.W. Nazaroff. 1993. Removal of reactive gases at indoor surfaces: Combining mass transport and surface kinetics. *Atmospheric Environment - Part A General Topics* 27 A, no. 13: 2039-2050.

Coleman, B.K., Destaillats, H., Hodgson, A.T., and Nazaroff. W. 2008. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. *Atmospheric Environment* 42, no. 4: 642-654.

Colombo, A., Bortoli, M., Knoppel, H., Schauenburg, H., and Vissers, H. 1991. Small Chamber Tests and Headspace Analysis of Volatile Organic Compounds Emitted from Household Products. *Indoor Air* 1, no. 1 (3): 13-21.

Derjaguin, B.V, and Shulepov, Y.V. 1979. Spontaneous polarization of an adsorption monolayer of polar molecules. *Surface Science* 81, no. 1: 149-163.

Destaillats, H., Singer, B.C., Lee, S.K., and Gundel, L.A. 2006. Effect of Ozone on Nicotine Desorption from Model Surfaces: Evidence for Heterogeneous Chemistry. *Environmental Science and Technology* 40, no. 6: 1799-1805.

Dubowski, Y., Vieceli, J., Tobias, D.J., Gomez, A., Lin, A., Nizkorodov, S.A., McIntire, T.M., and Finlayson-Pitts, B.J. 2004. Interaction of gas-phase ozone at 296 K with unsaturated self-assembled monolayers: A new look at an old system. *Journal of Physical Chemistry A* 108, no. 47: 10473-10485.

Fick, J., Pommer, L., Åstrand, A., Östin, R., Nilsson, C., and Andersson, B. 2005. Ozonolysis of monoterpenes in mechanical ventilation systems. *Atmospheric Environment* 39, no. 34 (November): 6315-6325.

Fick, J., Pommer, L., Nilsson, C., and Andersson, B. 2003. Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of α-pinene. *Atmospheric Environment* 37, no. 29: 4087-4096.

Forester, C.D., Ham, J., and Wells. J.R. 2006. Gas-phase chemistry of dihydromyrcenol with ozone and OH radical: Rate constants and products. *International Journal of Chemical Kinetics* 38, no. 7: 451-463.

Hakola, H., Arey, J., Aschmann,. S.M., and Atkinson, R. 1994. Product formation from the gas-phase reactions of OH radicals and O3 with a series of monoterpenes. *Journal of Atmospheric Chemistry* 18, no. 1: 75-102.

Ham, J.E. and Wells, J.R. 2009. Surface chemistry of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone on silanized glass, glass, and vinyl flooring tiles. *Atmospheric Environment* 43, 4023-4032.

Ham, J. E., and Wells. J.R. 2008. Surface chemistry reactions of a-terpineol [(R)-2-(4-methyl-3-cyclohexenyl)isopropanol] with ozone and air on a glass and a vinyl tile. *Indoor Air* 18, no. 5: 394-407.

Hodgson, A.T., Ming, K.Y., and Singer, B.C. 2004. *Quantifying Object and Material Surface Areas in Residences*. Lawrence Berkeley National Laboratory.

Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D. R., Flagan, C.,   and Seinfeld, J.H. 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *Journal of Atmospheric Chemistry* 26, no. 2: 189-222.

Klenø, J. G., Clausen, P.A., Weschler, C.J.,   and Wolkoff, P. 2001. Determination of Ozone Removal Rates by Selected Building Products Using the FLEC Emission Cell. *Environmental Science & Technology* 35, no. 12 (June 1): 2548-2553.

Morrison, G.C. and Nazaroff. W.W. 2000. The Rate of Ozone Uptake on Carpets: Experimental Studies. *Environmental Science & Technology* 34, no. 23 (December 1): 4963-4968.

Morrison, G.C. and Nazaroff. W.W. 2002. Ozone Interactions with Carpet: Secondary Emissions of Aldehydes. *Environmental Science & Technology* 36, no. 10 : 2185-2192.

Nazaroff, W.W. and Weschler, C.J. 2004. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmospheric Environment* 38, no. 18 : 2841-2865.

Nazaroff, W.W., Gadgil, A.J., and Weschler, C.J. 1993. Critique of the use of deposition velocity in modeling indoor air quality. *ASTM Special Technical Publication*, 81-104.

Petrick, L. and Dubowski, Y. 2009. Heterogeneous oxidation of squalene film by ozone under various indoor conditions. *Indoor Air* 19, no. 5 (10): 381-391.

Pommer, L. 2003. Oxidation of terpenes in indoor environments. Department of Chemistry, Umea University.

Shu, S, and Morrison, G.C. Surface reaction rate of ozone and alpha-terpineol on polyvinylchloride and glass. In . Syracuse, New York, September 13.

Singer, B.C., Coleman, B.K., Destaillats, H., Hodgson, A.T., Lunden, M.M., Weschler, C.J., and Nazaroff, W.W. 2006. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmospheric Environment* 40, no. 35: 6696-6710.

Singer, B.C., Destaillats, H., Hodgson, A. T., and Nazaroff, W.W. 2006. Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air* 16, no. 3: 179-191.

Singer, B.C., Hodgson, A.T., Hotchi, T., Ming, K.Y., Sextro, R.G., Wood, E.E., and Brown, N.J. 2007. Sorption of organic gases in residential rooms. *Atmospheric Environment* 41, no. 15 : 3251-3265.

Singer, B.C., Revzan, K.L., Hotchi, T., Hodgson, A.T., and Brown, N.J. 2004. Sorption of organic gases in a furnished room. *Atmospheric Environment* 38, no. 16 : 2483-2494.

Springs, M. and Morrison, G.C. 2007. Chemical Kinetics of a Monoterpene with Ozone on a Model Indoor Surface. In . Pittsburgh, PA.

Springs, M. and Morrison, G.C.. 2008. Reaction probability between terpenes and ozone on model indoor surfaces. In . Copenhagen, Denmark.

Stokes, Avram M. Buchbinder, Julianne M. Gibbs-Davis, Karl A. Scheidt, and Franz M. Geiger. 2008. Heterogeneous Ozone Oxidation Reactions of 1-Pentene, Cyclopentene, Cyclohexene, and a Menthenol Derivative Studied by Sum Frequency Generation. *Journal of Physical Chemistry A* 112, no. 46 (November 20): 11688-11698. doi:10.1021/jp803277s.

Stokes, G.Y., Chen, E.H., Walter, S.T., and Geiger. F.M. 2009. Two reactivity modes in the heterogeneous cyclohexene ozonolysis under tropospherically relevant ozone-rich and ozone-limited conditions. *Journal of Physical Chemistry A* 113, no. 31: 8985-8993.

Stokes, G.Y, Buchbinder, A.M., Gibbs-Davis, J.M., Scheidt, K.A., and Geiger, F.M. 2009. Chemically diverse environmental interfaces and their reactions with ozone studied by sum frequency generation. *Vibrational Spectroscopy* 50, no. 1 : 86-98.

US EPA. 2010. *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.00*. Washington, DC: United States Environmental Protection Agency.

Voges, A.B., Stokes, G.Y., Gibbs-Davis, J.M., Lettan, R.B., Bertin, P.A., Pike, R.C., Nguyen, S.T., Scheidt, K.A., and Geiger, F.M. 2007a. Insights into Heterogeneous Atmospheric Oxidation Chemistry: Development of a Tailor-Made Synthetic Model for Studying Tropospheric Surface Chemistry. *The Journal of Physical Chemistry C* 111, no. 4 : 1567-1578.

Wang, H. and Morrison, G.C. 2006. Ozone-Initiated Secondary Emission Rates of Aldehydes from Indoor Surfaces in Four Homes. *Environmental Science & Technology* 40, no. 17 : 5263-5268.

Wang, H. and Morrison, G.C. 2010. Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air* 23, no. 3, 224-234.

Waring. 2009. Indoor Secondary Organic Aerosol Formation: Influence of Particle Controls, Mixtures, and Surfaces. Austin, TX: University of Texas at Austin, August.

Wells, J.R., Morrison, G.C., and Coleman, B.K. 2008. Kinetics and reaction products of ozone and surface-bound squalene. *Journal of ASTM International* 5, no. 7.

Weschler, C.J. 2004. Chemical reactions among indoor pollutants: What we've learned in the new millennium. *Indoor Air, Supplement* 14, no. 7: 184-194.

Weschler, C.J., Wisthaler, A., Cowlin, S., Tamás, G., Strøm-Tejsen, P., Hodgson, A.T., Destaillats, H., Herrington, J., Zhang, J., and Nazaroff, W.W. 2007. Ozone-initiated chemistry in an occupied simulated aircraft cabin. *Environmental Science and Technology* 41, no. 17: 6177-6184.

Wisthaler, A., and Weschler C.J. 2009. Atmospheric Chemistry Special Feature: Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *Proceedings of the National Academy of Sciences* (8).

Yu, J., Cocker, D.R., Griffin, R.J., Flagan, R.C., and Seinfeld, J.H. 1999. Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. *Journal of Atmospheric Chemistry* 34, no. 2 : 207-258.

Table 1. Parameters of PVC, glass, and painted beads

Beads	Diameter (mm)	Porosity when packed	Geometric surface area normalized by density ($cm^2\ g^{-1}$)
PVC	1.6 (0.008)	0.37	25.90 (1.3)
Glass	0.9 (0.1)	0.40	27.18 (3.0)
Painted	2.3 (0.4)	0.40	7.58 (1.3)

Figure 1.   Dihydromyrcenol (2.6-Dimethyl-7-octen-2-ol).
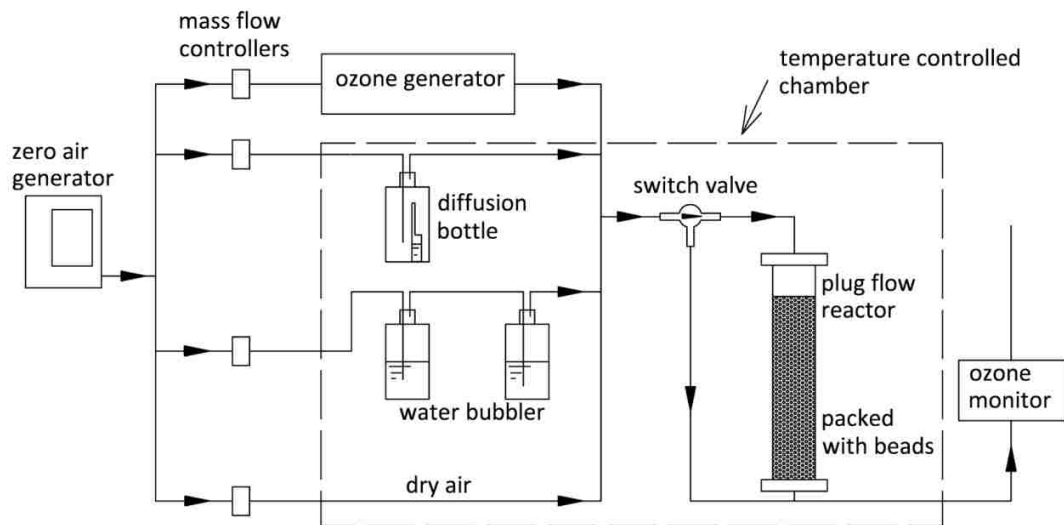
Figure 2. Plug flow reactor apparatus used to measure the area-specific rate of ozone reactions with dihydromyrcenol on bead surfaces.
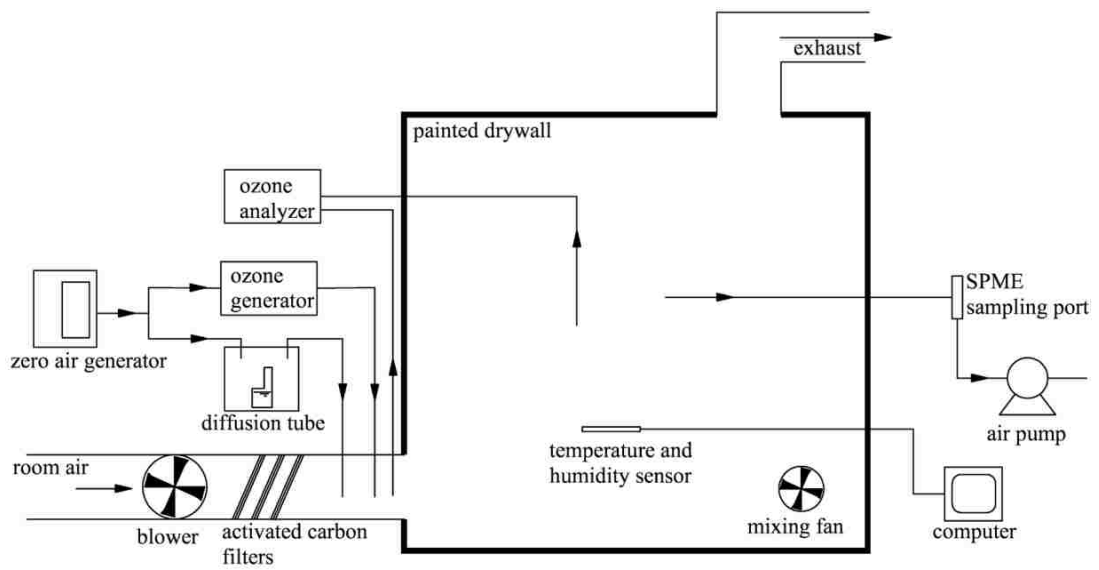
Figure 3. Room-sized chamber used to measure the ozone deposition velocity associated with dihydromyrcenol adsorbed on drywall.
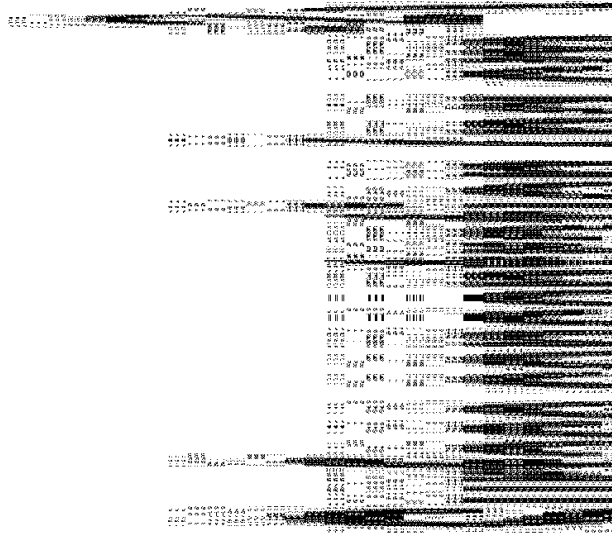
Figure 4.   Freundlich isotherms of dihydromyrcenol adsorption on (a) PVC, (b) glass and (c) paint.
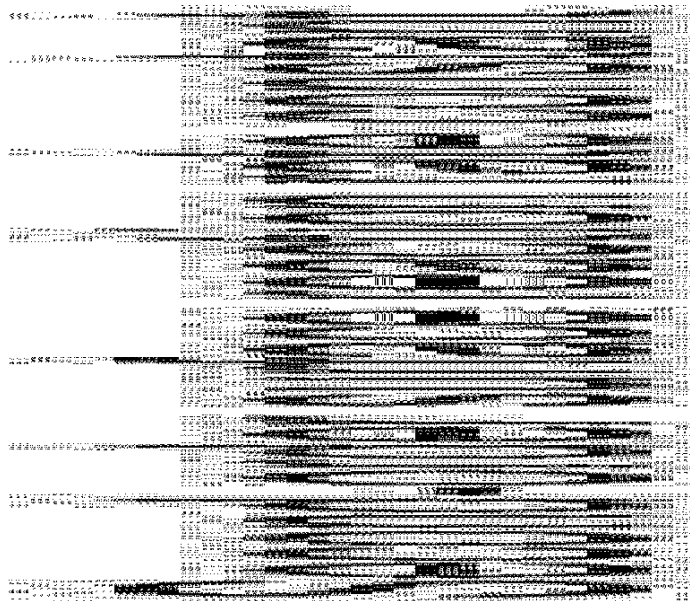
Figure 5. Area-specific, second-order surface reaction rate constant, k_2, of dihydromyrcenol on glass, PVC and paint. *The series were horizontally set off slightly to avoid overlapping symbols.
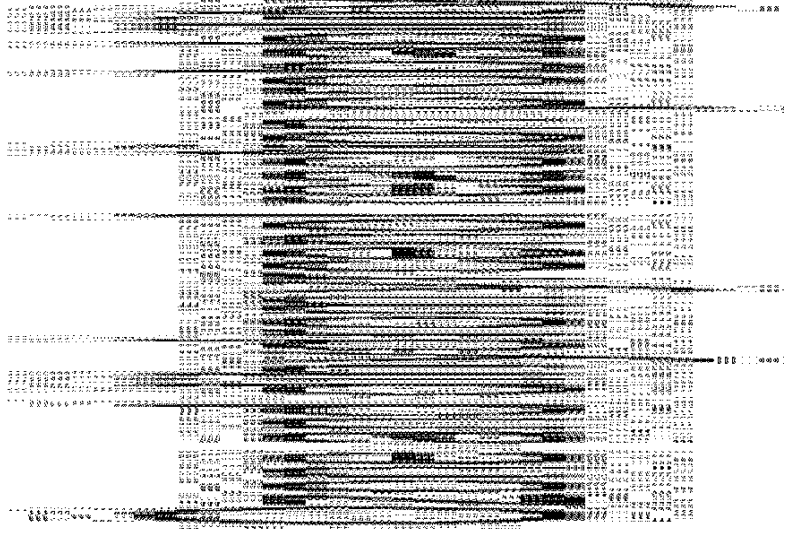
Figure 6. Ozone dihydromyrcenol reaction probability on PVC, glass and painted surfaces under different relative humidity conditions. *The series were horizontally set off slightly to avoid overlapping symbols.
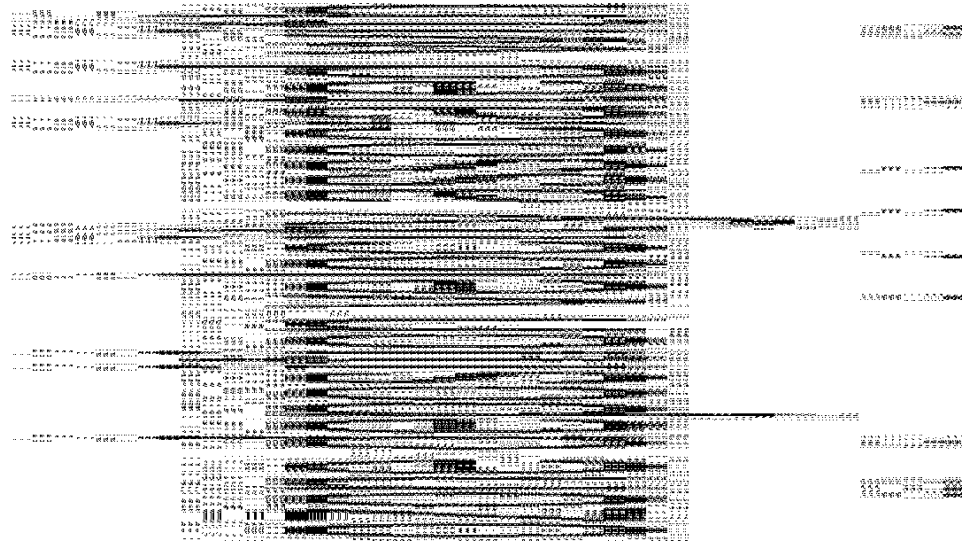
Figure 7. Ozone deposition velocity associated with dihydromyrcenol adsorbed on drywall, quantified by room-sized chamber experiments.

IV. Gaseous and surface products of the heterogeneous reaction of ozone with

dihydromyrcenol and α-terpineol on glass

(to be submitted to Indoor Air)

SHI SHU AND GLENN C. MORRISON*

Department of Civil, Agriculture, and Environmental Engineering, Missouri University of

Science and Technology, Rolla, MO, 65401 USA

Email : ssfdb@mst.edu , gcm@mst.edu

*Corresponding author, phone: (573)-341-7192, email: gcm@mst.edu, fax: (573)-341-4729

Abstract

To better understand the effects of ozone/terpene surface reactions on indoor

environmental quality, the products of ozone reactions with surface-bound α-terpineol and

dihydromyrcenol were investigated. The positively identified surface ozone/dihydromyrcenol

reaction products from surface extraction samples include glyoxal while the identified product

in gas phase is formaldehyde. For surface ozone/α-terpineol reaction, positively identified

products from surface extraction sample are glyoxal and methylglyoxal. These have been

identified as being irritants with the potential to cause occupational asthma. Large aggregates,

0.5 - 10 μm in diameter, also formed on the glass surface. These aggregates are likely formed

by polymerization reactions initiated by hydroxyl or other radicals generated by the

ozone-terpenoid reaction. Therefore, some fraction of the ozonated terpenoids are converted to

very-low volatility species which remain on the surface and may change the chemical characteristics of that surface over time.

Keywords

ozone, surface reaction, α-terpineol, dihydromyrcenol, carbonyl

Introduction

The terpene is a category of hydrocarbons built up from isoprene sub-units. They are naturally emitted from flowers and plants and usually can be found in essential oils and resins (Kesselmeier and Staudt 1999). Strictly speaking, terpenoid is a modified terpene, wherein methyl groups are moved or removed, or oxygen functionality is added (IUPAC 1978). However, as is common practice, the terms terpene and terpenoid are used interchangeably throughout this paper. Terpenes are emitted in large quantities into the atmosphere (Isidorov, Zenkevich, and Ioffe 1985) and participate in atmospheric chemistry. For example, these emissions from trees result in higher secondary organic aerosol concentrations above forests (Tunved et al. 2006). Many terpenes contain carbon-carbon double bonds which react readily with ozone. These important atmospheric reactions have been studied for many years (Yu et al. 1999; Atkinson and Arey 2003).

Large quantity of terpenes is produced by chemical synthesis each year. For d-limonene alone, the worldwide annual production was ~ 70 million kg in 2009 (Kerton 2009). Because many terpenes have a pleasant odor, they have been extensively used as fragrance compounds in household products, including but not limited to perfume, soap, shampoo,

detergents, air fresheners, candles, and cosmetics. As a result, indoor terpene concentrations tend to be much higher than outdoors and can be the dominant components of indoor VOCs (Singer et al. 2006; Nazaroff and Weschler 2004). Many individual terpenes and terpene alcohols, such as α-pinene, Δ-carene, citronellal, citronellol, α-terpineol, dihydromyrcenol, limonene, linalool, have been identified in indoor air. However, the variety is likely to be much greater given the 100's to 1000's of kinds of terpenes included in fragrances. Some terpenes that dominate indoor measurements include limonene and α-pinene (Nazaroff and Weschler 2004) . These are used as "top-notes" and are the first compounds to evaporate and develop the fragrance desired by the manufacturer (McDaniel and McDaniel 2010). Others emit somewhat more slowly and provide a longer-lasting experience. For example, α-terpineol is a major component of pine oil (Nazaroff and Weschler 2004), and has been found in liquid cleaner/disinfectant, liquid floor detergent (Colombo et al. 1991) and air fresheners (Salthammer and Uhde 2009). Dihydromyrcenol is one of the principal components of lavender (Nazaroff and Weschler 2004) and has been found in liquid floor detergent (Colombo et al. 1991).

The gas phase rates and products of the reaction between ozone and many terpenes have been studied. Important volatile terpenes such as limonene and α-pinene have been studied intensively (Wainman et al. 2000; Fan et al. 2003; Sack et al. 1992; Clausen et al. 2001). However, only recently has the chemistry of indoor-relevant terpenes such as citronellal, dihydromyrcenol, α-terpineol, geraniol, ionone, benzyl alcohol, and linalyl acetate been

studied (Fick et al. 2002; Forester, Ham, and Wells 2006; Forester, Ham, and Wells 2007; Ham, Proper, and Wells 2006; Harrison, Ham, and Wells 2007; Wells 2005; Harrison and Wells 2009).

Even less is known about the reactions that take place on surfaces. Products were identified for the reaction of ozone with α-terpineol and dihydromyrcenol that had been directly applied to glass and vinyl tiles in a methanol solution (Ham and Wells 2008; Ham and Wells 2009). It was found that some products generated on the surface were different from those identified gas phase reaction products. In addition to residue from activities such as cleaning (direct application), volatilized compounds will also adsorb and accumulate on all other indoor surfaces. In recent kinetic studies, adsorbed terpenes can significantly enhance the ozone reactivity of surfaces, and overall terpene conversion indoors may be dominated by surface instead of gas-phase reactions (Shu and Morrison, in preparation). Thus, the redistribution of terpenes to all surfaces in a building influences the chemistry in several ways: increasing surface area for reaction to take place, enhancing rates via heterogeneous mechanisms and altering the product yield compared with the gas-phase reaction.

In this research we identify the products resulting from ozone reactions with adsorbed terpenes at indoor-relevant concentrations. There are several major differences between directly applied terpenes and those that naturally adsorb to indoor surfaces. In (9,10), the spraying method resulted in surface concentrations of α-terpineol and dihydromyrcenol on the order of tens of ug cm^{-2}. Adsorption isotherms of these same species (Shu and Morrison, in

preparation), indicate that for a relatively high gas phase concentration (100 ppb), the resulting surface concentrations of these two species on glass are at least 3 orders of magnitude lower (tens of ng cm^{-2}). When the surface concentration is on the order of tens of ug cm^{-2}, the terpene molecules will be in close association or even form a relatively thick coating. At low concentrations, the terpenoids are more likely to be isolated on widely separated surface sites. Even for equivalent surface concentrations, the deposition of terpene molecules onto the surfaces in a solution may alter the surface itself such that terpene-site interactions differ from those resulting from gas-phase adsorption. To better understand the reaction products resulting from ozone reactions with adsorbed terpenes, we used a plug flow reactor packed with glass beads. Ozone was allowed to react with terpenes that had adsorbed to the glass surface. Gas-phase and surface products were identified.

Experiments

Materials

The terpenes used in this research were α-terpineol (96% pure) and dihydromyrcenol (99% pure), which were obtained from Sigma Aldrich (St. Louis, MO). Glass beads with 0.9 ± 0.1 mm diameter were purchased from MO-SCI Specialty Products (Rolla, MO). To more reliably assign chromatographic peaks, several pure standards of possible products, as suggested by the MS library search results and previous studies, were also purchased from Sigma Aldrich (St. Louis, MO). These were derivatized through the impinge sample train and

analyzed as described below. The standard compounds included 2-butanone, 2-pentanone, formaldehyde, acetone, glyoxal, glycolaldehyde, and methyl glyoxal.

For analysis of surface aggregates, pre-cleaned glass microscope slides and petri dishes were purchased from Fisher Scientific (Pittsburg, PA). The detergent, liqui -Nox, was purchased from ALCONOX (White Plains, NY). Other organic solvents, optima grade hexane and the reagent grade methanol, were purchased from Sigma Aldrich (St. Louis, MO).

Flow reactor

A plug flow reactor (PFR) system, which has been described in detail elsewhere (Shu and G. Morrison, 2009), was used in this experiment. Briefly, a 25 cm long × 1.1 cm inner diameter glass tube was packed with glass beads. Clean air was directed to the reactor flowing at 2.0 L min^{-1}. Water, ozone and the terpenoid were added to the stream to achieve 50% relative humidity (RH), ~ 150 ppb ozone and ~ 55 ppb α-terpineol (or ~ 70 ppb dihydromyrcenol) at the inlet of the reactor.

Multiple negative control experiments were performed to ensure that the products identified were from reactions taking place on the glass, not other sources. The experimental design and the samples taken are shown in Table 1. All the experiments took place at 50% RH and 25°C.

Analysis of reactants

Ozone was measured at the inlet and outlet of the PFR using a photometric ozone analyzer (Dasibi, Glendale, CA). The concentrations of terpenes were verified using a

solid-phase microextraction technique described in detail elsewhere (Shu and Morrison 2010).

This method was specifically designed to quantify reactive terpenes in the presence of ozone.

Analysis of gas phase products

Based on previous studies (Forester, Ham, and Wells 2006; Ham and Wells 2008), we

anticipated that a large fraction of volatile gas-phase products would be carbonyl and

dicarbonyl compounds and specifically sought to identify these species. A 22 mL threaded

midget impinger filled with 15 mL mixture of 25% MilliQ water in optima grade methanol

(Sigma Aldrich, St. Louis, MO) was used to collect gas from the outlet of the PFR. The gas

flow to the impinger was 1.3 L min^{-1}. To prevent ozone reacting with terpenes in the impinge

solution, a clean Supelco LpDNPH ozone scrubber was used to remove ozone between the

PFR outlet and the impinger inlet. Separate control experiments were performed to verify that

product formation that may take place within the ozone scrubber itself did not interfere with the

measurement.   However, the scrubber could remove some of the products by adsorption. The

total sampling time was 6 hours and the volume of solvent remaining in the impinger was ~ 4

mL. After sampling, the solvent was transferred to an amber glass vial and 250 μL 23mM

O-(2,3,4,5,6-pentalfluorobenzyl) hydroxylamine (PFBHA) water solution was added and

allowed to react (derivatize) for 24 hours. Derivatized compounds were concentrated directly

from solution for 2 hours onto a Supelco StableFlex^{TM} solid phase microextraction (SPME)

fiber (65 μm PDMS-DVB coating, manual holder). The SPME fiber was injected into the inlet

of an Agilent 6890 Gas Chromatography system coupled with Agilent 5793 Mass Selective

Detector. The carrier gas, helium, was set at a constant flow rate of 0.7 mL/min through an Agilent HP 5MS capillary column (0.25 mm $\times$ 30 m $\times$ 0.25µm). The oven was set to 40°C initially, held for 6 min, and then increased at a rate of 10°C to 260°C, and held for 3 min. The total run time was 31 min.

After impinger sampling, the glass beads (25 cm^3) were transferred to a 40 mL glass vial and 10 mL of solvent (the same water methanol mixture used in impinger) was added. 10 mL solvent is the minimum volume required to just immerse the glass beads. The vial was ultra-sonicated for 10 min at room temperature to allow the solvent to extract the compounds adsorbed on the glass beads. 4 mL of the solution was transferred to an amber glass vial and 250 µL of the 23mM PFBHA water solution was added for 24 hour derivatization. The same SPME sampling method and GC/MS method used for gas phase carbonyl identification were used to analyze the surface extract samples.

Surface aggregates

To identify the formation of aggregates on glass, slides were exposed to the ozone/terpene mixture and imaged in a scanning electron microscope (SEM). The microscope slides were first cut into about 2 cm $\times$ 3 cm pieces and further cleaned as follows: 1) sonicated in ultra high purity water with a few drops of Liqui-Nox for 15 minutes, and rinsed with MilliQ water thoroughly, 2) sonicated in optimal grade hexane for 15 minutes and rinsed with hexane, 3) sonicated in reagent grade methanol for 15 minutes and rinsed with hexane. After these steps,

the slides were dried in a sealed 10L stainless steel chamber, through which 0.2 L min^{-1} high

purity N_2 flowed.

Slides were exposed to a mixture of ozone and terpene (α-terpineol or

dihydromyrcenol) in a 250 mL glass flask acting as a flow through reactor. The ozone and

α-terpineol mixing ratios were 86 ± 4 ppb and 50 ± 2 ppb respectively, measured at the outlet.

For the dihydromyrcenol experiment, the mixing ratios were 108 ± 5 ppb ozone and 123 ± 3

ppb dihydromyrcenol. Experimental conditions were 50% RH and 25°C. After 20 hours of

exposure, the slides were immediately transported to the SEM in sealed petri dishes. Cut pieces

of cleaned slides were used as controls.

Prior to SEM analysis, the slides were coated with Au/Pd for 1 minute. After coating,

images of each slide were taken using a Hitachi s 4700 field emission scanning electron

microscopy (FESEM).

Results and discussion

Products in outlet gas

Ozone/dihydromyrcenol   Only formaldehyde, with an o-xime retention time

of 12.68 min, was observed as product in the outlet gas. The peak area of the formaldehyde

oxime from the surface reaction sample (Exp. # 8) was about twice that from the gas phase

reaction control sample (Exp. #6).

Ozone/α-terpineol   From the outlet flow sample, only one peak (23.01 min) was determined to be associated with the surface ozone α-terpineol reaction. Major EI ions associated with this compound include 196 (100), 181(87), 167 (50), and 99 (44). This peak is not positively identified.

Products extracted from glass surface

Ozone/dihydromyrcenol   PFBHA oxime derivatives positively identified with pure standards were observed at 16.58 min, 16.62 min, 17.70 min, 24.74 min, and 24.85 min residence times. Based on a MS library search and comparison with retention times from derivatized standards, the 16.58 min and 16.62 min oxime were assigned to 2-butanone, the 17.70 min o-xime was assigned to 2-pentanone, and the 24.74 min and 24.85 min peak were assigned to glyoxal. Two peaks for each derivative are consistent with two stereo-isomers produced by the derivatization reaction; a second peak for the 2-pentanone oxime overlapped with major peak at 17.57 min. Small peaks were observed at these retention times in the blank samples, but the peak areas from samples were at least 5 times larger. The glyoxal is an expected product because it has been observed in both gas phase and surface ozone dihydromyrcenol reactions (Forester, Ham, and Wells 2006; Ham and Wells 2009). The two ketones are not anticipated products of this chemistry nor have they been observed by other researchers.

PFBHA oxime derivatives that were not positively identified by pure standards include peaks at 15.40 min, 17.23 min, 17.57 min and 21.12 min. The peak at 15. 4 min was not

identified. The 17.23 min o-xime peak is suggested by the MS library to be trimethylacetaldehyde (86% match) or 3-methyl-2-butanone (67% match). Based on the EI pattern reported by Ham and Wells (Ham and Wells 2009) and the observed retention time, the peak at 17.57 min may be 2-methyl butanal. The peak at 21.12 min has not yet been identified.

Ozone/α-terpineol   PFBHA oxime derivatives positively identified with pure standards were observed at 24.74 min (glyoxal) and 24.90 min (methylglyoxal) residence times. The glyoxal peak from ozone α-terpineol surface reaction (Exp. #7) was ~ 7 times larger than those observed in blank samples. These differences indicate that the presence of glass surface enhanced the formation of glyoxal and methylglyoxal significantly. Interestingly, only methylglyoxal was reported as a product of gas phase ozone α-terpineol reaction (Wells 2005), but not observed in a surface ozone/α-terpineol reaction (Ham and Wells 2008). This difference might be due to the much smaller surface concentration of the terpenoid used in the present study.

PFBHA oxime derivatives that were not positively identified by pure standards include peaks at 23.56 min, 24.69 min, 24.98 and 25.02 min. The peaks at 23.56 min and 24.69 min have not yet been identified. The peaks at 24.97 and 25.02 have major EI ions as follows: 181 (100), 195 (67-91), 167 (40), 117 (32), and 99 (34).The EI pattern and the maximum m/z observed = 364, suggests 3-(1-hydroxy-1-methylethyl) -6-methylcyclohex- 2-en-1-one), or an isomer very similar to that proposed by Ham and Wells et al. (Ham and Wells 2009), is formed.

Aggregates on glass surface

On the slides exposed to ozone and terpenes, aggregates of 0.5 to 10 µm in at least one dimension were observed, for both α-terpineol and dihydromyrcenol experiments. SEM images of select aggregates are shown in Figure 1. Most of the aggregates have a diameter of 1 - 2 µm, for both α-terpineol and dihydromyrcenol exposed slides. On the ~ 6 cm^2 area of a slide, approximately 10 aggregates > 1 µm were observed for both compounds. The unexposed glass slide (control) is free of particles larger than 0.1 µm in any dimension.

The shape, size, and morphology appear to be very similar to the aggregates been observed by McIntire et al. (McIntire et al. 2005) resulting from ozone reactions with vinyl-terminated 3- and 8-carbon self-assembled monolayers. Besides those particle-like aggregates, some aggregates of film-like shape as shown in Figure 1 (a) were also observed.

The formation of these aggregates is likely due to polymerization of heterogeneous surface reaction products. Ozone-alkene reactions produce a primary ozonide, which can then decompose to an aldehyde / ketone and a Criegee Intermediate (CI) (Criegee 1975). The CI can react with an aldehyde to produce a semi-stable secondary ozonide or decompose to generate hydroxyl or other radicals, which can initiate polymerization (Odian 2004). As McIntire et al. pointed out in the vinyl-terminated SAMs study (McIntire et al. 2005), many studies support the hypothesis that CI will react with adjacent unreacted C=C double bonds (Katrib et al. 2004; Hearn and Smith 2004; Hearn and Smith 2005; Tobias et al. 2000; Docherty et al. 2005; Ziemann 2003). In present experiment, the orientation, local density, and arrangement of the

molecules are not known, but it is possible that unsaturations are adjacent. According to the adsorption isotherm of α-terpineol and dihydromyrcenol on glass (Shu and Morrison, in preparation), the surface coverage of α-terpineol and dihydromyrcenol under the present experimental conditions were 143% and 16%, respectively. Therefore, islands or multiple layers of terpenoids may develop and radical reactions with adjacent unsaturated molecules are possible. Differences in the number, shape, size and microstructure, might be explained by differences in terpenoid structure and/or the fact that α-terpineol was present at a much higher surface concentration. For example, larger aggregates appeared to form during the terpineol reactions. However a larger number of smaller aggregates were observed for dihydromyrcenol which may suggest that a larger number of "islands" formed at the lower surface density. In the future, surface composition analysis methods, such as Auger Electron Spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), could be applied to better understand the composition of aggregates.

Implications for indoor air quality

The surface ozone/terpene reactions produced products similar to that of gas phase reactions, including irritants and sensitizers such as glyoxal and methylglyoxal (Anderson et al. 2007). Formaldehyde, which is a carcinogen, was also found in the gas phase as a product of the surface reaction. While the yield of these products was not determined, surface ozonation rates of terpenes are predicted to dominate gas-phase conversion rates in buildings (Shu and

Morrison, 2009). Thus, the surface reactions may contribute substantially to indoor concentrations of observed dicarbonyls.

Due to the prevalence of ozone and terpenoids in buildings, this research suggests that indoor surfaces are likely to be covered with polymeric aggregates. These can affect pollutant and water uptake at surfaces and influence the polarity and surface tension of indoor surfaces.

Acknowledgements

References

Anderson, S.E., Wells, J.R., Fedorowicz, A., Butterworth, L.F., Meade, B.J. and Munson, A.E. (2007) Evaluation of the contact and respiratory sensitization potential of volatile organic compounds generated by simulated Indoor air chemistry. *Toxicological Sciences* 97, no. 2: 355-363.

Atkinson, R., and Arey, J. (2003) Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. *Atmospheric Environment* 37, no. 2.

Clausen, P.A., Wilkins, C.K., Wolkoff, P. and Nielsen, G.D. (2001) Chemical and biological evaluation of a reaction mixture of R-(+)-limonene/ozone: Formation of strong airway irritants. *Environment International* 26, no. 7 : 511-522.

Colombo, A., Bortoli, M., Knoppel, H., Schauenburg, H., and Vissers. H. (1991) Small Chamber Tests and Headspace Analysis of Volatile Organic Compounds Emitted from Household Products. *Indoor Air* 1, no. 1 (3): 13-21.

Criegee, R. (1975) Mechanism of Ozonolysis. *Angewandte Chemie International Edition in English* 14, no. 11 (11): 745-752.

Docherty, K.S., Wu, W., Lim, Y.B., and Ziemann, P.J. (2005) Contributions of Organic Peroxides to Secondary Aerosol Formed from Reactions of Monoterpenes with Ozone. *Environmental Science & Technology* 39, no. 11 : 4049-4059.

Fan, Z., Lioy, P., Weschler, C.J., Fiedler, N., Kipen, H., and Zhang, J. (2003) Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions. *Environmental Science and Technology* 37, no. 9: 1811-1821.

Fick, J., Pommer, L., Andersson, B., and Nilsson, C. (2002) A study of the gas-phase ozonolysis of terpenes: the impact of radicals formed during the reaction. *Atmospheric Environment* 36, no. 20 : 3299-3308.

Forester, C.D., Ham, J.E., and Wells, J.R. (2006) Gas-phase chemistry of dihydromyrcenol with ozone and OH radical: Rate constants and products. *International Journal of Chemical Kinetics* 38, no. 7: 451-463.

Forester, C.D., Ham, J.E., and Wells, J.R. (2007) Geraniol (2,6-dimethyl-2,6-octadien- 8-ol) reactions with ozone and OH radical: Rate constants and gas-phase products. *Atmospheric Environment* 41, no. 6: 1188-1199.

Forester, C.D., Ham, J.E., and Wells, J.R. (2006) Gas-phase chemistry of dihydromyrcenol with ozone and OH radical: Rate constants and products. *International Journal of Chemical Kinetics* 38, no. 7: 451-463.

Forester, C.D., Ham, J.E., and Wells, J.R. (2007) [beta]-Ionone reactions with ozone and OH radical: Rate constants and gas-phase products. *Atmospheric Environment* 41, no. 38 (December): 8758-8771.

Ham, J.E., Proper, S.P., and Wells, J.R. (2006) Gas-phase chemistry of citronellol with ozone and OH radical: Rate constants and products. *Atmospheric Environment* 40, no. 4: 726-735.

Ham, J.E. and Wells, J.R., (2009) Surface chemistry of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone on silanized glass, glass, and vinyl flooring tiles. June 22.

Ham, J.E., and Wells, J.R. (2008) Surface chemistry reactions of a-terpineol [(R)-2-(4-methyl-3-cyclohexenyl) isopropanol] with ozone and air on a glass and a vinyl tile. *Indoor Air* 18, no. 5: 394-407.

Ham, J.E., and Wells, J.R. (2009) Surface chemistry of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone on silanized glass, glass, and vinyl flooring tiles. *Atmospheric Environment* 43 : 4023-4032

Harrison, J.C., Ham, J.E. and Wells, J.R. (2007) Citronellal reactions with ozone and OH radical: Rate constants and gas-phase products detected using PFBHA derivatization. *Atmospheric Environment* 41, no. 21: 4482-4491.

Harrison, J.C., and Wells, J.R. (2009) Gas-phase chemistry of benzyl alcohol: Reaction rate constants and products with OH radical and ozone. *Atmospheric Environment* 43, no. 4: 798-804.

Hearn, J.D., and Smith, G.D. (2004) Kinetics and Product Studies for Ozonolysis Reactions of Organic Particles Using Aerosol CIMS†. *The Journal of Physical Chemistry A* 108, no. 45 (November 1): 10019-10029.

Hearn, J.D., and Smith, G.D. (2005) Measuring rates of reaction in supercooled organic particles with implications for atmospheric aerosol. *Physical Chemistry Chemical Physics* 7, no. 13: 2549-2551.

Isidorov, V.A., Zenkevich, I.G. and Ioffe, B.V. (1985) Volatile organic compounds in the atmosphere of forests. *Atmospheric Environment - Part A General Topics* 19, no. 1: 1-8.

IUPAC. (1978) *Biochemical nomenclature and related documents*. The Biochemical Society.

Katrib, Y., Martin, S.T., Hung, H., Rudich, Y., Zhang, H., Slowik, J.G., Davidovits, P., Jayne, J.T., and Worsnop, D.R (2004) Products and Mechanisms of Ozone Reactions with Oleic Acid for Aerosol Particles Having Core–Shell Morphologies. *The Journal of Physical Chemistry A* 108, no. 32: 6686-6695.

Kerton, F.M. (2009) *Alternative solvents for green chemistry*. Royal Society of Chemistry,

Kesselmeier, J. and Staudt, M. (1999) Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry* 33, no. 1: 23-88.

McDaniel, R.S., and McDaniel, K.J. (2010) *Soap Maker's Workshop: The Art and Craft of Natural Homemade Soap*. Krause Publications Craft

McIntire, T.M., Lea, A.S., Gaspar, D.J., Jaitly, N., Dubowski, Y., Li, Q., and Finlayson-Pitts, B.J. (2005) Unusual aggregates from the oxidation of alkene self-assembled monolayers: a previously unrecognized mechanism for SAM ozonolysis? *Physical Chemistry Chemical Physics* 7, no. 20: 3605.

Nazaroff, W.W. and Weschler. C.J. (2004) Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmospheric Environment* 38, no. 18: 2841-2865.

Odian, G.G. (2004) *Principles of polymerization*. John Wiley and Sons.

Sack, T.M., Steele, D.H., Hammerstrom, K., and Remmers, J. (1992) A survey of household products for volatile organic compounds. *Atmospheric Environment - Part A General Topics* 26 A, no. 6: 1063-1070.

Salthammer, T., and Uhde, E. (2009) *Organic Indoor Air Pollutants: Occurrence, Measurement, Evaluation*. Wiley-VCH.

Shu, S., and Morrison. G.C.. (2010) Dynamic solid phase microextraction sampling for reactive terpenes in the presence of ozone. *Talanta* 82, no. 5: 1884-1891.

Shu, S, and Morrison, G.C. (2009) Surface reaction rate of ozone and alpha-terpineol on polyvinylchloride and glass. In . Syracuse, New York, September 13.

Singer, B.C., Destaillats, H., Hodgson, A. T., and Nazaroff, W.W. (2006) Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air* 16, no. 3: 179-191.

Tobias, H.J., Docherty, K.S., Beving, D.E., and Ziemann, P.J. (2000) Effect of Relative Humidity on the Chemical Composition of Secondary Organic Aerosol Formed from Reactions of 1-Tetradecene and O3. *Environmental Science and Technology* 34, no. 11: 2116-2125.

Tunved, P., Hansson, H.C., Kerminen, V.M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P.P., Komppula, M., and Kulmala, M. (2006) High natural aerosol loading over boreal forests. *Science* 312, no. 5771: 261-263.

Wainman, T., Zhang, J., Weschler, C.J., and Lioy, P.J. (2000) Ozone and limonene in indoor air: A source of submicron particle exposure. *Environmental Health Perspectives* 108, no. 12: 1139-1145.

Wells, J.R. (2005) Gas-Phase Chemistry of α-Terpineol with Ozone and OH Radical: Rate Constants and Products. *Environmental Science and Technology* 39, no. 18: 6937-6943.

Yu, J, Cocker, D.R., Griffin, R.J., Flagan, R.C., and Seinfeld, J.H. (1999) Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. *Journal of Atmospheric Chemistry* 34, no. 2 : 207-258.

Ziemann, P.J. (2003) Formation of Alkoxyhydroperoxy Aldehydes and Cyclic Peroxyhemiacetals from Reactions of Cyclic Alkenes with O3 in the Presence of Alcohols. *The Journal of Physical Chemistry A* 107, no. 12 : 2048-2060.

Table 1. Experiments

#	Experiment	Gas	Beads in reactor	Purpose	Samples gas	beads
1	air blank	air only	Yes	air and beads background	Yes	Yes
2	ozone blank	air, ozone	Yes	ozone background	Yes	Yes
3	α-terpineol blank	air, α-Terpineol	Yes	check impurity of α-terpineol	Yes	Yes
4	Dihydromyrcenol blank	air, dihydromyrcenol	Yes	check impurity in DHM,	Yes	Yes
5	ozone/α-terpineol control	air, α-terpineol, ozone	No	gas phase reaction control	Yes	No
6	ozone/dihydromyrcenol control	air, dihydromyrcenol, ozone	No	gas phase reaction control	Yes	No
7	ozone/α-terpineol surface reaction	air, α-terpineol, ozone	Yes	surface reaction	Yes	Yes
8	Ozone/dihydromyrcenol surface reaction	air, dihydromyrcenol, ozone	Yes	surface reaction	Yes	Yes
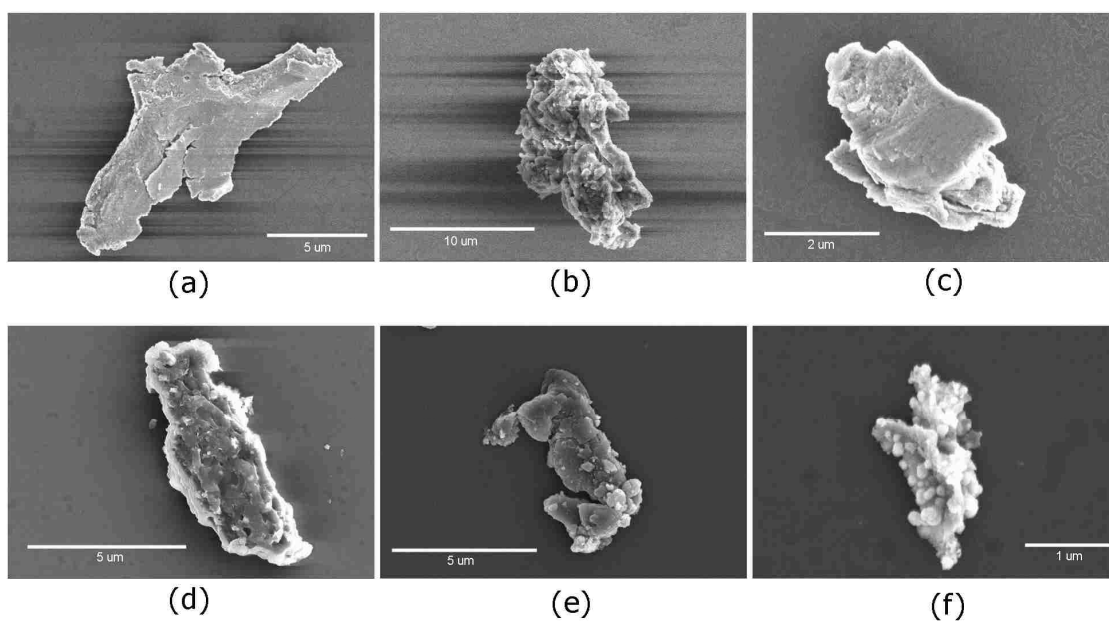
Figure 1. Aggregates found under SEM on glass slides exposed to α-terpineol (a, b, c) and dihydromyrcenol (d, e, f).

SECTION

4. CONCLUSIONS

The primary results of this work are presented in three manuscripts for publication in peer-reviewed journals. Conclusions from this work have been reported in each paper, respectively, and are reported here as they relate to the objectives.

Objective 1: to develop a reliable analytical method to quantify ozone reactive terpenes, for single compound and also terpene mixtures, in the samples where ozone is present.

This objective is met and the results are shown in paper I. The results can be concluded as following:

1. Solid Phase Microextraction (SPME) sampling in a dynamic sampler is demonstrated to be an accurate analytical method which can minimize the interference from ozone reacting with the analytes, both for single terpenes sample and for terpene mixture sample.

2. This method works even better when there are multiple reactive compounds in the sample, because reactive compounds can compete with each other for ozone and, potentially, improve recovery for individual compounds by spreading out reactive losses across all adsorbed species.

3. For the eight compounds studied in the presence of ozone, the MDL ranged from 1.6 – 5.8 ppb for a 5 minute sampling time, and the presence of 30 or 100 ppb ozone does not affect the MDL significantly.

Objective 2: to quantify the adsorption, surface reaction rates, and surface reaction probability of ozone with terpenes (α-terpineol and dihydromyrcenol) adsorbed on different indoor materials, under different relative humidity conditions.

This objective is met and the results are shown in paper II and paper III. The conclusion can be summarized as following:

1. Much more α-terpineol and dihydromyrcenol adsorbs to glass than to PVC or latex paint. The relative humidity affects adsorption on glass more than on PVC or paint. Adsorbed mass decreases as the relative humidity increases, potentially because of the competition for adsorption sites between water and terpene molecules.

2. All of the surfaces, when loaded with α-terpineol or dihydromyrcenol, consume ozone at a higher rate than without terpenes.

3. The quantified second-order surface reaction rate coefficients are not affected by the relative humidity.

Objective 3: to compare the surface bound reaction probability with reported values of the gas-phase reaction probability;

This objective is met and the results are shown in paper II and paper III. The conclusion can be summarized as following:

1. For both α-terpineol and dihydromyrcenol, all values of measured surface ozone reaction probability are greater than their gas phase ozone reaction probability, which are calculated based on reported gas phase bimolecular rate constant.

Objective 4: to investigate to what extent the ozone surface reaction alters the concentration of indoor VOCs, ozone, and their reaction products,

This objective is met and the results are shown in paper II and paper III. The conclusion can be summarized as following:

1. By extrapolating the measured second-order surface reaction rate to indoor environments at typical conditions, for α-terpineol, the surface conversion occurs at rates that are ~ 1 – 5 times the gas phase reaction rate.

2. By extrapolating the measured second-order surface reaction rate to indoor environments of typical conditions, for dihydromyrcenol, the surface conversion occurs at rates that are ~ 20 – 100 times the gas phase reaction.

Objective 5: to identify some of the heterogeneous reaction products.

This objective is met and the results are shown in paper IV. The conclusion can be summarized as following:

1. In outlet gas samples, formaldehyde was the only identified product of surface ozone/dihydromyrcenol reaction, while no product was identified for surface ozone/α-terpineol reaction.

2. In surface extraction samples, 2-butanone, 2-pentanone, and glyoxal were identified as products of surface ozone/dihydromyrcenol reaction, while glyoxal and methylglyoxal were identified as products of surface ozone/α-terpineol reaction

3. Aggregates of 0.5 to 10 µm in at least one dimension were formed on glass as the result of surface ozone reactions with both dihydromyrcenol and α-terpineol.

5. SIGNIFICANCE AND IMPACTS

In the atmospheric chemistry field, most ozone surface chemistry studies have focused on the ozone reaction with self-assembled monolayers of vinyl-terminated carbon compounds on silicon or carbon substrates. These surfaces mimic atmospheric aerosols. Ozone reactions can affect the hydrophobicity of these particles and thus modify the potential of these particles to act as cloud and ice nuclei. These studies have mostly been performed under strictly controlled laboratory conditions. Ozone-surface chemistry is also of interest for indoor air quality studies, but the specific surfaces and compounds of interest are quite different. Few studies have investigated the role of surface chemistry on controlling the composition of indoor air. This research is the first to quantify the surface reaction kinetics of ozone and terpenes. The results allow us to qualitatively and quantitatively evaluate the relative importance of surface and gas-phase reactions. Methods developed in this research can be extended to quantify surface reaction kinetics of reactants other than those studied in this research (other terpenoids, other oxidants such as nitrogen oxides, etc.). Further, the results directly improve our understanding of aerosol chemistry, even in "ambient" air. The central result of this research, that heterogeneous terpenoid chemistry is as, or more, important than homogeneous chemistry, demonstrates that existing models of indoor air are missing this important mechanism. This appears to be especially important when the compounds involved are not very reactive in gas phase.

6. FUTURE RESEARCH

In this work, two terpene alcohols and three indoor surface materials have been studied. To draw more comprehensive conclusions, a greater number of compounds, including alcohols, carboxylic acids and other organic compounds, of higher and lower volatility, should be evaluated, individually and in mixtures, on a wider variety of surface materials. Temperature effects on the ozone/terpene surface reaction kinetics also need to be investigated.

To begin to understand this chemistry and extrapolate to the vast number of compounds present in buildings, the mechanism of the ozone terpene surface reaction should be studied at the molecular level. Certain surface chemistry analysis methods, such as Fourier Transform Infrared Spectrometry (FTIR), Sum-frequency Generation (SFG), ellipsometry, and so on, can be used to investigate the molecular orientation when species are adsorbed on surfaces and to track the reaction.

The products of heterogeneous ozone-terpene reactions need to be studied more completely as well. The reactions produce reaction products that are unstable and therefore difficult to identify and quantify.

APPENDIX A.

PFR DIMENSIONLESS NUMBERS CALCULATIONS

The mass transfer of ozone to the beads surface was limited by the surface uptake rate (or reaction rate), not the mass transfer from gas phase to the beads surface. This can be verified by determining the Sherwood number in the PFR. The Sherwood number (Sh) is correlated with Reynolds number (Re) and Schmidt number (Sc), as expressed in Equation (A.1)(Wakao and Kagei 1982).

$$Sh = 2 + 1.1Sc^{\frac{1}{3}}Re^{0.6} \tag{A.1}$$

Reynolds number (Re) and Schmidt number (Sc) can be calculated by Equation (A.2) and (A.3).

$$Re = \frac{\rho \, v \, D_p}{\mu \, \varepsilon} \tag{A.2}$$

$$Sc = \frac{\mu}{\rho \, D} \tag{A.3}$$

where ρ is density of air (1.18×10^{-6} kg cm^{-3}), μ is dynamic viscosity of air (1.983×10^{-7} kg cm^{-1} s^{-1}), v is superficial velocity (41.7 cm s^{-1}), which equals to the flow rate divided by the cross-sectional area of the reactor, ε is porosity of packed bed (unitless), D_p is the diameter of spherical particles (cm), and D is the diffusivity of ozone in air, which is 0.14 cm^2 s^{-1}.

The transport limited deposition velocity, v_t, can be calculated from Sherwood number, by using Equation (A.4).

$$v_t = \frac{Sh \times D}{D_p} \tag{A.4}$$

The deposition of ozone is a two-steps process, so that the deposition velocity, v_d, could be either transport limited or reaction limited, as shown in Equation (A.5).

$$v_d = \left(\frac{1}{v_t} + \frac{4}{\gamma_{total} <v>}\right)^{-1} \tag{A.5}$$

If $\frac{1}{v_t} \gg \frac{4}{\gamma_{total} <v>}$, the ozone deposition on surface is transport limited, and if $\frac{1}{v_t} \ll \frac{4}{\gamma_{total} <v>}$, then it is reaction limited process.

The values of these parameters and the calculated dimensionless numbers are shown in Table A.1. The Sherwood numbers showed that under the operation conditions, the mass transfer by convection is at least 15 times high as the mass transfer diffusion. The Sherwood number is sufficiently large, and the dominant resistance is the surface uptake by reaction. The values of $\frac{1}{v_t}$ are in the range of (4.1 - 6.6) $\times 10^{-2}$ s cm^{-1}. The experiment data showed that the total reaction probability of terpene loaded surface, γ_{total}, is no more than 10^{-5}, which means that the minimum of $\frac{4}{\gamma_{total} <v>}$ is no less than 11 s cm^{-1}. Based on aforementioned criteria, conclusion can be drawn that the ozone mass transfer in PFR at operation conditions is a reaction limited process.

Table A.1 Parameters and dimensionless numbers of PFR at operation conditions

	D_P	ε	Re	Sc	Sh	v_t
	cm	-	-	-	-	cm/s
PVC	0.16	0.40	100	1.20	20.45	17.89
Glass	0.09	0.37	61	1.20	15.69	24.41
Painted	0.23	0.40	143	1.20	24.94	15.18

APPENDIX B.

DISCUSSION ON BET SURFACE AREA

For bare surface, the background ozone reaction probability is calculated from the inlet and outlet ozone concentration, by using Equation (B.1).

$$\gamma_{background} = \frac{4Q V_{reactor}}{L\, A_{cross}\, \rho A_{beads} <v>}\left(-ln\frac{C_{out}}{C_{in}}\right) \tag{B.1}$$

where Q is flow rate through PFR (cm^{3}s^{-1}), $V_{reactor}$ is the volume of PFR (cm^3), L is length of PFR (cm), A_{cross} is the cross-sectional area of PFR (cm^2), ρ is the porosity of packed bed (unitless), $<v>$ is the Boltzmann velocity, which is 3.60×10^4 cm s^{-1} for ozone at 293k.

The surface ozone terpene reaction probability is calculated by Equation (B.2) to (B.4).

$$\gamma_{terp} = \frac{\gamma_{total} - \gamma_{background}(1 - f_{terp})}{f_{terp}} = \left(\frac{\gamma_{total} - \gamma_{background}}{f_{terp}}\right) + \gamma_{background} \tag{B.2}$$

$$\frac{dC_{O3}}{dz} = -\frac{\gamma_{total}(z) <v>}{4u}\frac{A_{surface}}{V_{reactor}}C_{O3}(z) \tag{B.3}$$

$$\frac{dC_{DHM}}{dz} = -\frac{\gamma_{total}(z) <v>}{4u}\frac{A_{surface}}{V_{reactor}}C_{O3}(z) \tag{B.4}$$

For a specific kind of bead, the BET surface area can be expressed is proportional to their geometrical surface, which as shown in Equation (B.5).

$$A_{surface}^{BET} = cA_{surface} \tag{B.5}$$

where c is a constant, estimated to be in the range from 1.5 to 10 for PVC, glass, and painted beads.

So, when BET surface area was used in the calculation of reaction probability, the new results can be expressed as:

$$\gamma_{background}^{BET} = \frac{1}{c}\gamma_{background} \tag{B.6}$$

$$\gamma_{total}^{BET} = \frac{1}{c}\gamma_{total} \tag{B.7}$$

$$f_{terp}^{BET} = \frac{1}{c}f_{terp} \tag{B.8}$$

So we can get:

$$\gamma_{terp}^{BET} = \frac{\gamma_{total}^{BET} - \gamma_{background}^{BET}(1 - f_{terp}^{BET})}{f_{terp}^{BET}} = \frac{\frac{1}{c}\gamma_{total} - \frac{1}{c}\gamma_{background}(1 - \frac{1}{c}f_{terp})}{\frac{1}{c}f_{terp}} \tag{B.9}$$
$$= \left(\frac{\gamma_{total} - \gamma_{background}}{f_{terp}}\right) + \frac{1}{c}\gamma_{background}$$

If we compare Equation (B.9) to Equation (B.2), we will see that the γ_{terp}^{BET} will be very close to γ_{terp}, because the $\gamma_{background}$ (in the order of 10^{-7}) is very small compared to the γ_{total}, which is in the order of 10^{-5}. This is why the ozone terpene reaction probability results would be almost the same not matter if BET surface area or geometric surface area was used in the calculation.

APPENDIX C.

MATLAB CODES ON CD-ROM

1. INTRODUCTION

Included with this dissertation is a CD-ROM, which contains the MATLAB CODES

(.m files) to numerically solve the plug flow reactor models, in order to calculate the

second-order surface reaction rate coefficients and the surface ozone-terpene reaction

probabilities. All the MATLAB CODES have been developed using MATLAB R2008a.

2. CONTENTS

DHMProbabilityCalGlass.m

DHMProbabilityCalPVC.m

DHMrateCalGlass.m

DHMrateCalPVC.m

TerpProbabilityCalGlass.m

TerpProbabilityCalPVC.m

TerprateCalGlass.m

TerprateCalPVC.m

BIBLIOGRAPHY

Anderson, S.E., Wells, J.R, Fedorowicz, A.,, Butterworth, L.F., Meade, B.J., and Munson. A.E., Evaluation of the contact and respiratory sensitization potential of volatile organic compounds generated by simulated Indoor air chemistry. Toxicological Sciences 2007, 97, no. 2: 355-363.

Atkinson, R.. Atmospheric chemistry of VOCs and NO(x). Atmospheric Environment 2000, 34, no. 12: 2063-2101.

Atkinson, R., and Arey. J. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. Atmospheric Environment 2003, 37, no. 2.

Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M., and Dominici, F. Ozone and short-term mortality in 95 US urban communities, 1987-2000. Journal of the American Medical Association 2004, 292, no. 19: 2372-2378.

Boeniger, M.F. Use of ozone generating devices to improve indoor air quality. American Industrial Hygiene Association Journal 1995, 56, no. 6: 590-598.

Britigan, N., Alshawa, A., and Nizkorodov, S.A. Quantification of ozone levels in indoor environments generated by ionization and ozonolysis air purifiers. Journal of the Air and Waste Management Association 2006, 56, no. 5: 601-610.

Calogirou, A., Larsen, B.R., and Kotzias, D. Gas-phase terpene oxidation products: A review. Atmospheric Environment 1999, 33, no. 9: 1423-1439.

Cano-Ruiz, J.A., Kong, D., Balas, R.B., and Nazaroff, W.W. Removal of reactive gases at indoor surfaces: Combining mass transport and surface kinetics. Atmospheric Environment - Part A General Topics 1993, 27 A, no. 13: 2039-2050.

Carslaw, N. A new detailed chemical model for indoor air pollution. Atmospheric Environment 2007, 41, no. 6: 1164-1179.

Chauhan, A.J., Krishna, M.T., Frew, A.J., and Holgate, S.T. Exposure to nitrogen dioxide (NO2) and respiratory disease risk. Reviews on Environmental Health 1998, 13, no. 1: 73-90.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J. et al. Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene. Science 2004, 303, no. 5661 : 1173-1176.

Coleman, B.K., Destaillats, H., Hodgson, A.T., and Nazaroff, W.W. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. Atmospheric Environment 2008, 42, no. 4: 642-654.

Colombo, A., Bortoli, M., Knoppel, K., Schauenburg, H., and Vissers, H. Small Chamber Tests and Headspace Analysis of Volatile Organic Compounds Emitted from Household Products. Indoor Air 1991, 1, no. 1 (3): 13-21.

Delfino, R.J. Epidemiologic evidence for asthma and exposure to air toxics: linkages between occupational, indoor, and community air pollution research. Environmental Health Perspectives 2002, 110, no. 4 : 573-589.

Doyle, M., Sexton, K.G., Jeffries, H., and Jaspers, I. Atmospheric photochemical transformations enhance 1,3-butadiene-induced inflammatory responses in human epithelial cells: The role of ozone and other photochemical degradation products. Chemico-Biological Interactions 2007, 166, no. 1: 163-169.

Dubowski, Y. Vieceli, J., Tobias, D.J., Gomez, A., Lin, A., Nizkorodov, S.A., McIntire, T.M., and Finlayson-Pitts, B.J. Interaction of gas-phase ozone at 296 K with unsaturated self-assembled monolayers: A new look at an old system. Journal of Physical Chemistry A 2004, 108, no. 47: 10473-10485.

Faiz, A., Weaver, C.S., and Walsh, M.P., Air pollution from motor vehicles: standards and technologies for controlling emissions. World Bank Publications 1996.

Forester, C.D., Ham, J.E. and Wells, J.R. Gas-phase chemistry of dihydromyrcenol with ozone and OH radical: Rate constants and products. International Journal of Chemical Kinetics 2006, 38, no. 7: 451-463.

Forester, C.D., Ham, J.E. and Wells, J.R. Geraniol (2,6-dimethyl-2,6- octadien-8-ol) reactions with ozone and OH radical: Rate constants and gas-phase products. Atmospheric Environment 2007, 41, no. 6: 1188-1199.

Forester, C.D. and Wells, J.R. Yields of Carbonyl Products from Gas-Phase Reactions of Fragrance Compounds with OH Radical and Ozone. Environmental Science and Technology 2009, 43, no. 10 : 3561-3568.

Galizia, A., and Kinney, P.L. Long-term residence in areas of high ozone: Associations with respiratory health in a nationwide sample of nonsmoking young adults. Environmental Health Perspectives 1999, 107, no. 8: 675-679.

Haghighat, F. and Huang. H. Integrated IAQ model for prediction of VOC emissions from building material. Building and Environment 2003, 38, no. 8 : 1007-1017.

Ham, J.E., Proper, S.P., and Wells, J.R. Gas-phase chemistry of citronellol with ozone and OH radical: Rate constants and products. Atmospheric Environment 2006, 40, no. 4: 726-735.

Ham, J.E. and Wells, J.R. Surface chemistry of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone on silanized glass, glass, and vinyl flooring tiles. Atmospheric Environment 2009, 43, no. 26 : 4023-4032

Ham, J. E., and Wells, J.R. Surface chemistry reactions of a-terpineol [(R)-2-(4-methyl-3-cyclohexenyl)isopropanol] with ozone and air on a glass and a vinyl tile. Indoor Air 2008, 18, no. 5: 394-407.

Harrison, J.C., and Wells, J.R.. Gas-phase chemistry of benzyl alcohol: Reaction rate constants and products with OH radical and ozone. Atmospheric Environment 2009, 43, no. 4: 798-804.

Hoang, C., Kinney, P., and Corsi. R. Ozone removal by green building materials. Building and Environment 2009, 44, no. 8: 1627-1633.

Huang, H., Haghighat, F., and Blondeau, P., Volatile organic compound (VOC) adsorption on material: influence of gas phase concentration, relative humidity and VOC type. Indoor Air 2006,16, no. 3 : 236-247.

Hubbell, B.J., Hallberg, A., McCubbin, D.R., and Post, E. Health-related benefits of attaining the 8-hr ozone standard. Environmental Health Perspectives   2005, 113, no. 1: 73-82.

Isidorov, V.A., Zenkevich, I.G., and Ioffe, B.V. Volatile organic compounds in the atmosphere of forests. Atmospheric Environment - Part A General Topics 1985, 19, no. 1: 1-8.

IUPAC. Biochemical nomenclature and related documents. The Biochemical Society. 1978.

Jerrett, M., Burnett, R.T., Arden Pope III, C., Ito, K., Thurston, G., Krewski, D., Shi, Y. Calle, E., and Thun, M. Long-term ozone exposure and mortality. New England Journal of Medicine 2009, 360, no. 11: 1085-1095.

Jørgensen, R.B. Sorption of VOCs on material surfaces as the deciding factor when choosing a ventilation strategy. Building and Environment 2007, 42, no. 5: 1913-1920.

Kasper, M., Roehlecke, C., Witt, M., Fehrenbach, H., Hofer, A., Miyata, T., Weigert, C., Funk, R.H.W., and Schleicher, E.D. Induction of apoptosis by glyoxal in human embryonic lung epithelial cell line L132. American Journal of Respiratory Cell and Molecular Biology 2000, 23, no. 4: 485-491.

Kerton, F. M. Alternative solvents for green chemistry. Royal Society of Chemistry, 2009.

Kesselmeier, J. and Staudt, M. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. Journal of Atmospheric Chemistry 1999, 33, no. 1: 23-88.

Khamaganov, V.G., and Hites, R.A., Rate Constants for the Gas-Phase Reactions of Ozone with Isoprene, α- and β-Pinene, and Limonene as a Function of Temperature. The Journal of Physical Chemistry A 2001, 105, no. 5: 815-822.

Kinney, P.L. The pulmonary effects of outdoor ozone and particle air pollution. Seminars in Respiratory and Critical Care Medicine 1999, 20, no. 6: 601-607.

Kissel, J.C. Potential impact of deliberately introduced ozone on indoor air quality. Journal of exposure analysis and environmental epidemiology 1993, 3, no. 2: 155-164.

Klenø, J.G., Clausen, P.A., Weschler, C.J., and Wolkoff, P. Determination of Ozone Removal Rates by Selected Building Products Using the FLEC Emission Cell. Environmental Science and Technology 2001, 35, no. 12 (June 1): 2548-2553.

Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., and Engelmann, W.H. The National Human Activity Pattern Survey (NHAPS): A resource for assessing exposure to environmental pollutants. Journal of Exposure Analysis and Environmental Epidemiology 2001, 11, no. 3: 231-252.

Kreiss, K., Gomaa, A., Kullman, G., Fedan, K., Simoes, E.J., and Enright, P.L. Clinical bronchiolitis obliterans in workers at a microwave-popcorn plant. New England Journal of Medicine 2002., 347, no. 5: 330-338.

Lelieveld, J., and Dentener, F.J. What controls tropospheric ozone? Journal of Geophysical Research D: Atmospheres 2000, 105, no. 3: 3531-3551.

McDaniel, R.S., and McDaniel, J.K., Soap Maker's Workshop: The Art and Craft of Natural Homemade Soap. Krause Publications Craft, 2010.

McIntire, A. Lea, S., Gaspar, D.J., Jaitly, N., Dubowski, Y., Li, Q., and Finlayson-Pitts, B.J. Unusual aggregates from the oxidation of alkene self-assembled monolayers: a previously unrecognized mechanism for SAM ozonolysis? Physical Chemistry Chemical Physics 2005, 7, no. 20: 3605.

McIntire, T.M., Ryder, O., and Finlayson-Pitts, B.J. Secondary ozonide formation from the ozone oxidation of unsaturated self-assembled monolayers on zinc selenide attenuated total reflectance crystals. Journal of Physical Chemistry C 2009., 113, no. 25: 11060-11065.

McNaught, A.D., and Wilkinson, A. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Oxford: Blackwell Scientific Publications. 1997.

Mendell, M.J., Fisk, W.J., Kreiss, K., Levin, H., Alexander, D., Cain, W.S., Girman, J.R., et al. Improving the health of workers in indoor environments: Priority research needs for a National Occupational Research Agenda. American Journal of Public Health 2002, 92, no. 9: 1430-1440.

Morrison, G.C., and Nazaroff, W.W., Ozone Interactions with Carpet: Secondary Emissions of Aldehydes. Environmental Science and Technology 2002, 36, no. 10 : 2185-2192.

Morrison, G.C. Interfacial chemistry in indoor environments. Environmental Science and Technology 2008, 42, no. 10: 3495-3499.

Nazaroff, W.W. and Weschler. C.J., Cleaning products and air fresheners: exposure to primary and secondary air pollutants. Atmospheric Environment 2004, 38, no. 18 : 2841-2865.

Nazaroff, W.W., Weschler, C.J., and Corsi, R. Indoor air chemistry and physics. Atmospheric Environment 2003, 37, no. 39: 5451-5453.

Nyberg, F., and Pershagen, G., Epidemiologie studies on ozone. Scandinavian Journal of Work, Environment and Health 1996, 22, no. 3: 72-98.

Reiss, R., Ryan, P.B., Koutrakis, P., and Tibbetts, S.J., Ozone reactive chemistry on interior latex paint. Environmental Science and Technology 1995, 29, no. 8: 1906-1912.

Rohr, A.C., Weschler, C.J., Koutrakis, P., and Spengler, J.D., Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting. Aerosol Science and Technology   2003, 37, no. 1: 65-78.

Salthammer, T, and Uhde, E. Organic Indoor Air Pollutants: Occurrence, Measurement, Evaluation. Wiley-VCH, 2009.

Sarwar, G., Olson, D.A., Corsi, R.L., and Weschler, C.J., Indoor Fine Particles: The Role of Terpene Emissions from Consumer Products. Journal of the Air and Waste Management Association 2004, 54, no. 3: 367-377.

Schwartz, J., Dockery, D.W., and Neas, L.M. Is daily mortality associated specifically with fine particles? Journal of the Air and Waste Management Association 1996, 46, no. 10: 927-939.

Seinfeld, J.H., and Pandis, S.N. Atmospheric chemistry and physics: from air pollution to climate change. Wiley. 2006.

Sexton, K.G., Jeffries, H.E., Jang, M., Kamens, R.M., Doyle, M., Voicu, I., and Jaspers, I. Photochemical products in urban mixtures enhance inflammatory responses in lung cells. Inhalation Toxicology 2004, 16, no. 1: 107-114.

Singer, B.C., Destaillats, H., Hodgson, A. T., and Nazaroff, W.W. Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. Indoor Air 2006, 16, no. 3: 179-191.

Singer, B.C., Hodgson, A.T., Hotchi, T., Ming, K.Y., Sextro, R.G., Wood, E.E., and Brown, N.J. Sorption of organic gases in residential rooms. Atmospheric Environment   2007, 41, no. 15 : 3251-3265.

Spengler, J.D., Samet, J.M., and McCarthy, J.F. Indoor air quality handbook. McGraw-Hill Professional. 2001.

Springs, M. and Morrison, G.C. Reaction probability between terpenes and ozone on model indoor surfaces, Indoor Air 2008 Conference, Copenhagen, Denmark

Springs, M. and Morrison, G.C. Reactions rates of ozone and terpenes adsorbed to modeled indoor surfaces. (submitted to Indoor Air)

Stokes, G.Y., Buchbinder, A.M., Gibbs-Davis, J.M., Scheidt, K.A., and Geiger, F.M.. Heterogeneous Ozone Oxidation Reactions of 1-Pentene, Cyclopentene, Cyclohexene, and a Menthenol Derivative Studied by Sum Frequency Generation. Journal of Physical Chemistry A 2008112, no. 46: 11688-11698.

Stokes, G.Y., Chen, E.H., Walter, S.T., and Geiger. F.M. Two reactivity modes in the heterogeneous cyclohexene ozonolysis under tropospherically relevant ozone-rich and ozone-limited conditions. Journal of Physical Chemistry A 2009, 113, no. 31: 8985-8993.

Stokes, G.Y., Chen, E.H., Buchbinder, A.M., Paxton, W.F., Keeley, A., and Geiger, F.M. Atmospheric heterogeneous stereochemistry. Journal of the American Chemical Society 2009, 131, no. 38: 13733-13737.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Maso, M.D., Lihavainen, H., Viisanen, Y., Aalto, P.P., Komppula, M., and Kulmala, M. High natural aerosol loading over boreal forests. Science 2006, 312, no. 5771: 261-263.

Voges, A.B., Stokes, G.Y., Gibbs-Davis, J.M., Lettan, R.B., Bertin, P.A., Pike, R.C., Nguyen, S.T., Scheidt, K.A., and Geiger, F.M. Insights into Heterogeneous Atmospheric Oxidation Chemistry:⬜ Development of a Tailor-Made Synthetic Model for Studying Tropospheric Surface Chemistry. The Journal of Physical Chemistry C 2007, 111, no. 4 : 1567-1578.

Wang, H., and Morrison, G.C. Ozone-Initiated Secondary Emission Rates of Aldehydes from Indoor Surfaces in Four Homes. Environmental Science and Technology 2006, 40, no. 17 (September 1): 5263-5268.

Wang, H., and Morrison, G.C. Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. Indoor Air 2010, no. 3 : 224-234.

Waring, M. Siegel, J., Morrison, G.C., and Corsi. R.L. Indoor secondary organic aerosol formation due to ozone/terpene surface reactions. In . Orlando, FL. 2008.

Wells. J.R., Gas-Phase Chemistry of α-Terpineol with Ozone and OH Radical: Rate Constants and Products. Environmental Science and Technology 2005, 39, no. 18: 6937-6943.

Weschler. C.J. Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. Environmental Health Perspectives 2006, 114, no. 10: 1489-1496.

Weschler, C.J., Shields, H.C., and Naik, D.V., Indoor ozone exposures. Journal of the Air and Waste Management Association 1989, 39, no. 12: 1562-1568.

Weschler, C.J., Wisthaler, A., Cowlin, S., Tamás, G., Strøm-Tejsen, P., Hodgson, A.T., Destaillats, H., Herrington, J., Zhang, J., and Nazaroff, W.W. Ozone-initiated chemistry in an occupied simulated aircraft cabin. Environmental Science and Technology 2007, 41, no. 17: 6177-6184.

Wisthaler, A, and Weschler. C.J. Atmospheric Chemistry Special Feature: Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. Proceedings of the National Academy of Sciences (8). 2009.

Won, D., Corsi R.L., and Rynes, M. New indoor carpet as an adsorptive reservoir for volatile organic compounds. Environmental Science and Technology 2000, 34, no. 19: 4193-4198.

Xu, Y, and Little J.C. Predicting Emissions of SVOCs from Polymeric Materials and Their Interaction with Airborne Particles. Environmental Science and Technology 2006, 40, no. 2 : 456-461.

Yan, W., Zhang, Y., and Wang, X. Simulation of VOC emissions from building materials by using the state-space method. Building and Environment 2009, 44, no. 3 : 471-478.

Yu, J., Cocker, D.R., Griffin, R.J., Flagan, R.C., and Seinfeld, J.H. Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. Journal of Atmospheric Chemistry 1999, 34, no. 2 : 207-258.

VITA

Shi Shu was born on July 5th, 1980, in Changsha, Hunan Province, China. In 2002 and 2005, he received his bachelor's and master's degree in Environmental Engineering from Hunan University, Changsha, China. respectively. He worked for one year as an Environmental Engineer in Southwest Electric Power Design Institute, Chengdu, China, after graduation. In June 2006, he started his Ph.D study in Civil Engineering in Missouri University of Science and Technology (University of Missouri-Rolla by then), Rolla, MO, USA.