

Chemical Kinetics of a Monoterpene with Ozone on a Model Indoor Surface

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ABSTRACT

The objective of this research is to quantify surface reaction rates of ozone with Δ^3 -carene on model indoor surfaces. The monoterpene Δ^3 -carene is commonly used in cleaners and other consumer products, and its reaction with ozone generates toxic products, including formaldehyde. To assess surface reaction kinetics, a diluted stream of Δ^3 -carene is introduced into a plug flow reactor filled with small beads that act as model surfaces. First, adsorption is quantified in the form of molar surface loading, by performing breakthrough experiments with the monoterpene in the absence of ozone. Second, the diluted monoterpene is introduced into the plug flow reactor along with ozone, and the amount of ozone consumed (with and without the terpene) is quantified. The ozone uptake rate is combined with adsorption information to determine a pseudo-first order reaction rate coefficient and ultimately an ozone-terpene reaction probability. To mimic typical indoor conditions, the temperature is varied from 20 to 30°C and the relative humidity is varied from 10% to 80%. In this paper, the results for the reaction of ozone with Δ^3 -carene on glass are reported. We show for the first time that ozone reacts with Δ^3 -carene on this surface and that the ozone-terpene reaction probability ranges from approximately 3.0×10^{-6} to 2.5×10^{-5} . These reaction probabilities are 10 to 80 times higher than that estimated for the gas-phase reaction. Thus, glass enhances (i.e. catalytically) ozone-terpene reaction rates.

INTRODUCTION

The release of volatile organic compounds (VOCs) inside homes and business can lead to illnesses ranging from sick-building syndrome to cancer. Early indoor air quality research focused on direct release of VOCs, or “primary emissions”. Yet many contaminants present in indoor air are a result not of primary emission, but of transformations of compounds to form new contaminants. Thus, researchers are beginning to investigate these “secondary” formation and release phenomena that are typically the result of chemical reactions in air, at interfaces or within bulk materials.

The focus of this research is on the surface reaction of ozone with the chemical family known as terpenoids. These chemicals are commonly found in cleaners (Nazaroff and Weschler¹), air fresheners (Sarwar et al³), and personal care products, such as perfumes

and lotions. These chemicals are commonly derived from natural sources such as limonene in orange peel and pinene from pine trees (*Kirk-Othmer*⁵). While very high concentrations of terpenes can cause health problems, the secondary emissions from the reaction between terpenes and ozone can lead to products which cause more serious health effects (Wolkoff et al⁶, Wolkoff et al⁷, and Clausen et al⁸), such as formaldehyde (Atkinson and Arey⁴). In addition to formaldehyde, other products of the reaction may include carboxylic acids, other aldehydes, and aerosols. Cometo-Muñiz et al⁹ found that carboxylic acids have low odor and respiratory irritancy thresholds and can be many times more irritating than their aldehyde counterparts. Aerosols have the potential to act as respiratory irritants (Wolkoff et al⁶, Wolkoff et al⁷, and Clausen et al⁸) and have effects similar to small particulate matter in terms of respiratory illnesses (USEPA¹¹).

Knowing the potential risks associated with the products of the ozone-terpene reactions, the center of attention became how fast are these products formed and how much. To date, the terpene-ozone reaction research has predominantly focused on what occurs in the gas phase. Nazaroff and Weschler¹ showed that α -pinene reacted rapidly with ozone in the gas phase, producing a second-order rate constant of $2.1 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$. Weschler and Shields⁹ found a pseudo-first order reaction rate constant of 0.15 h^{-1} for typical indoor ozone concentrations when reacted with limonene. Atkinson and Arey⁴ found that the formaldehyde from these reactions was formed with a yield of 0.15. In addition, as ozone concentrations increased, the formaldehyde concentration increased (Destailats et al¹² and Singer et al¹³).

With the extensive amount of research on the gas-phase reactions, the question was raised about what happens on the surface level and how the impacts of these reactions compare to those in the gas phase. While looking at gas-phase reactions, Pommer¹⁴ and Fick¹⁵ found the experimental reactivity between terpenes and ozone much higher than predicted, possibly due to reactions on the surfaces used in the experiments. Fick et al.¹⁶ also encountered similar results during experiments in real mechanical ventilation systems with a greater decrease in concentration of terpenes between the upstream and downstream sampling locations. Destailats et al.¹⁷ tested for secondary pollutants created when common household products were exposed to ozone and observed the deposition rate of ozone remained at a relatively high level even after gas-phase terpenes concentrations had dropped to low levels by ventilation. This indicated that terpenes remained on the surface, enhancing ozone reactivity with that surface.

The broad goal of this research is to characterize how terpene-ozone reactions on indoor surfaces influence indoor air quality. The specific objective is to measure the surface-specific reaction probability of ozone with a common terpene (Δ^3 carene) adsorbed to a glass surface, under a range of temperature and humidity conditions. This fundamental information will be used to better understand how this class of reactions occur on common indoor surfaces. For example, we seek to answer questions regarding 1) the probability of a reaction occurring when an ozone molecule encounters a terpene molecule adsorbed to a surface, 2) whether there is any catalytic effect, i.e. does the ozone-terpene reaction occur faster than anticipated in the gas phase, 3) whether there is any impact of temperature and humidity on the rate of these reactions, and 4) whether

indoor surfaces significantly enhance overall conversion rates of these reactions compared to gas-phase reactions alone.

MATERIALS AND METHODS

Overview

To measure the rate of ozone-terpene surface reactions, we used a laboratory reactor filled with beads of a material that acts as a “model” indoor surface. Real indoor surfaces are more difficult to work with because they tend to be inhomogeneous, true surface areas are difficult to characterize, and external mass transport to the surface is difficult to control. Alternatively, reaction rates are readily measured on small spheres packed into a plug-flow style reactor. Although the measured rates are not associated with “real” indoor surfaces, they are indicative of reaction rate enhancement on surfaces in general.

Two general types of experiments were performed: 1) quantification of the surface coverage (adsorption) of Δ^3 carene and 2) measurement of the rate of ozone uptake on the surface. The purpose of the adsorption experiments was to quantify the extent of adsorption of the terpene to the model surface. Using the data from these experiments, a molar surface loading was determined. This parameter characterizes the surface coverage of terpene and allows us to calculate the frequency with which ozone strikes the adsorbed terpene. The ozone uptake experiments were used to determine the rate at which ozone is consumed on a model surface saturated (at equilibrium) with terpenes. The results of these experiments are combined to obtain a surface-specific ozone-terpene reaction probability. Both types of experiments were performed over a range of temperatures and humidity levels that are typical of indoor environments.

Materials

For the adsorption experiments, glass beads, approximately one millimeter in diameter, were used to represent a typical household surface. Prior to the experiment, the beads were sonicated in distilled water to remove any contamination and then dried in a 100°C oven for several hours. After drying, the beads were placed in the reactor (described below).

Compressed breathing air was conditioned and humidified to simulate various indoor conditions. For this set of experiments, Δ^3 -carene (Sigma-Aldrich) was used as the representative terpene. This chemical is commonly found in household cleaners. Ozone was generated by passing breathing air over an ultraviolet lamp.

The Δ^3 -carene was introduced into the system as a gas mixture. This was prepared by injecting 87 μL of Δ^3 -carene into a 1.8 L gas cylinder and then slowly adding ultrapure nitrogen until the total pressure in the tank pressure reached 100 psi (690 kPa). For QA/QC purposes, three 9 mL samples of the gas were pulled from the system at the point where the gas exits the reactor and combines with the bypass stream, analyzed on a TD/GC/MS, and compared to standards with a known concentration. A control gas for the adsorption experiment was developed using 20 mL of methane gas to a 1.8 L gas

cylinder and then slowly introducing ultrapure nitrogen until the tank pressure reached 100 psi.

Systems

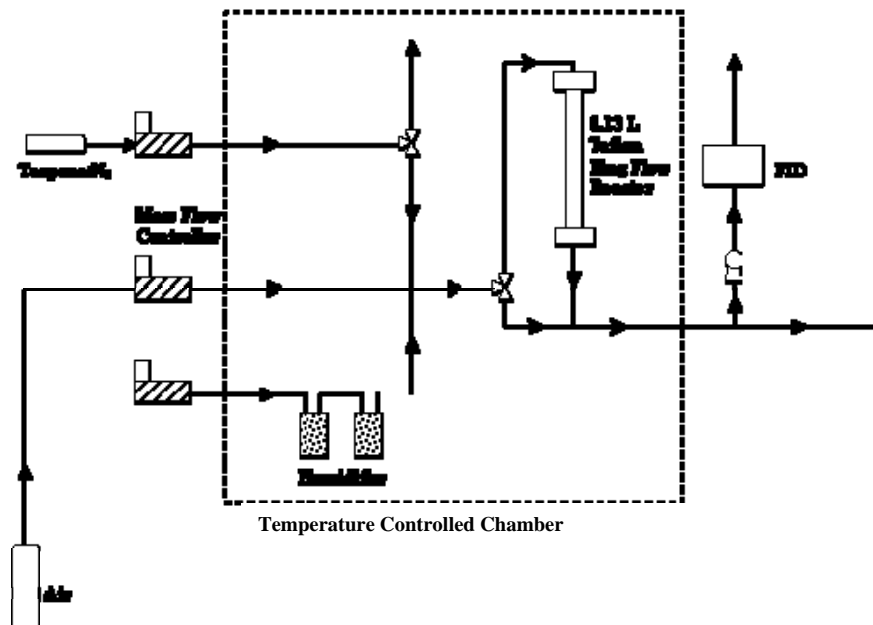
The experiments described in this paper take place in a Teflon plug flow reactor. The reactor is approximately 1.8 cm in diameter and 50 cm in length. The reactor is filled to the top with glass beads, and occupies ~ 50% of the reactor volume.

A temperature chamber housed the reactor along with three solenoid valves to control the delivery of the ozone and terpene along with the option to bypass the reactor. The temperature of the chamber was varied between 20°C and 30°C. Two gas sparging bottles were also located inside the chamber. These bottles allowed the humidity of the compressed air to vary between 10% and 80%.

For the adsorption experiments, 1,000 cc/min humidified, temperature controlled air was mixed with a terpene before being introduced to the reactor. This flowrate provides enough air for the FID while making sure there is still enough excess air to prevent outside air from being pulled into the system. As shown in Figure 1, a cylinder supplied compressed air to the system. The air was split between two mass flow controllers to achieve various levels of humidity. One controller delivered dry air to the system while the second controller supplied air to the gas sparging bottles in order to humidify the air. The two air streams were rejoined prior to entering the reactor. A third mass flow controller delivered air from an additional gas cylinder containing one ppm terpene in ultrapure nitrogen at a rate of 10 cc/min. This gas stream was controlled by one of the three solenoid valves located inside of the temperature chamber. The valve allowed the terpene to enter the system just prior the humidified clean air stream entering the reactor or to bypass the system completely. The air streams entered a second solenoid valve that either allowed the air stream to enter or bypass the reactor.

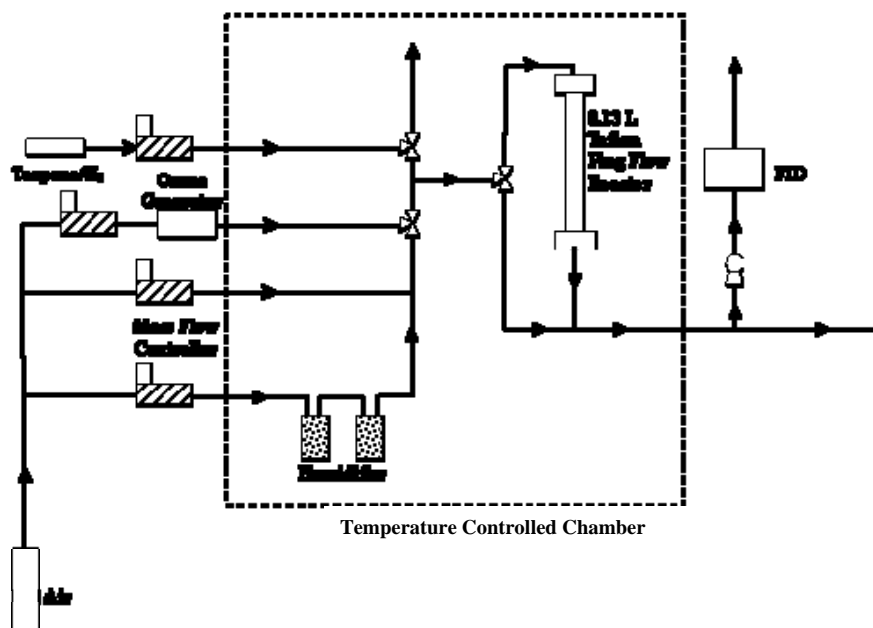
The reactor bypass line rejoined the system immediately following the reactor. A portion of the air stream was carried by a small pump to a flame ionization detector (FID) at a rate of 400 cc/min, where the signal was used to represent the terpene concentration. The rest of the reactor exhaust air stream was vented to a fume hood.

Figure 1. Experimental apparatus for measuring terpene adsorption on a model surface.



A similar set-up was used for the ozone experiments, as shown in Figure 2. For these experiments, 2,000 cc/min of compressed air was introduced into the system and divided to achieve the desired relative humidity levels. Since the ozone analyzer itself uses 1,000 cc/min, 2,000 cc/min is used to ensure the analyzer as well as the FID have enough air while having enough excess air to prevent outside air from being pulled into the system. A fourth mass flow controller controlled the flow of compressed air over an ultraviolet light to deliver 15 cc/min of ozone containing air. An additional solenoid valve controlled the injection of ozone into the system at the point the two other air streams merged. After passing through the reactor, 400 cc/min of the air was pumped to the FID and approximately 1,000 cc/min was delivered to an ozone analyzer.

Figure 2. Experimental apparatus for measuring ozone loss on a model surface when a terpene is introduced into the system.



Methods

Adsorption Experiments

In the adsorption experiments, the compressed air was divided between the two mass flow controllers. The division varied in order to achieve the desired level of humidity (10%, 50%, or 80%). Both air streams traveled into the temperature chamber where both streams were conditioned to 20°C, 25°C, or 30°C, the wet air stream was humidified, and the two air streams were combined again.

An initial hour-long experiment consisted of introducing the terpene gas stream into the system at a rate of 10 cc/min, while bypassing the reactor. The initial concentration of terpene used in the experiment is approximately 1.0 ppm. The solenoid valve delivering the terpene was turned on for fifteen minutes and then turned off for fifteen minutes. This sequence was repeated a second time. The purpose of this experiment was to develop a baseline reading to compare to the reactor data.

Following the initial experiment, the terpenes were introduced into the system while the air stream passed through the reactor. The same time and switch sequence used in the baseline experiment was repeated for the reactor experiment. Four hours of data were obtained.

The adsorption data obtained from the experiment was used to calculate the molar surface loading. The molar surface loading characterizes the moles of terpene adsorbed per unit

surface area at a specific gas-phase terpene concentration. The moles of terpene remaining on the surface are estimated by finding the difference between the integrated molar rate exiting the reactor in the absence of adsorption and the integrated molar rate exiting the reactor with adsorption. Equation 1 shows the molar surface loading calculation.

Equation 1. Calculation to determine molar surface loading.

$$\text{molar surface loading} = \frac{QC_o}{A \cdot MW} \left[\int_0^t C'_{meth}(t) dt - \int_0^t C'_{terp}(t) dt \right]$$

Where

Q = flow rate, adjusted for temperature (cc/min)

C_o = inlet concentration of terpene (μg/m³)

A = bead surface area (m²)

MW = molecular weight of terpene (g/mol)

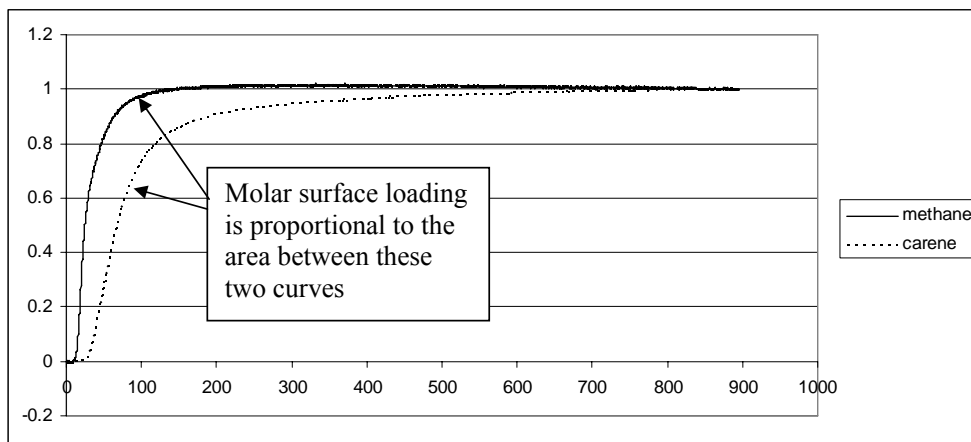
C'_{meth}(t) = normalized methane concentration at time t (mol/m³)

C'_{terp}(t) = normalized terpene concentration at time t (mol/m³)

For this calculation, the dynamic concentration results from 5 to 8 experiments (for both methane and terpene) were normalized and then combined to generate an average dynamic, normalized concentration curve. Normalization was performed by dividing each concentration reading by the average of the last nine steady-state concentration values. This procedure reduces experimental/instrumental noise and generates a molar surface loading with more precision.

Figure 3 shows the molar surface loading for data obtained at 20°C and 10% relative humidity. The area between the lines represents the amount of terpene which adsorbed to the bead surface.

Figure 3. An example of the derivation of the molar surface loading from an experiment performed at 20°C and 10% relative humidity. The area between the methane (non-adsorbing) curve and carene curve is proportional to the molar surface loading of the terpene.



Ozone Uptake Experiments

In the ozone experiments, approximately 2,000 cc/min of compressed air was divided between the two mass flow controllers. The division varied in order to achieve the desired level of humidity (10%, 50%, or 80%). Both air streams traveled into the temperature chamber where both streams were heated to 20°C, 25°C, or 30°C, the wet air stream was humidified, and the two air streams were combined again.

An initial experiment was run for 20 minutes where ozone was introduced into the system at a rate of 15 cc/min but the air stream bypassed the reactor. The typical initial ozone concentration used for these experiments was approximately 220 ppb. This established a baseline concentration for ozone.

Following the baseline experiment, the ozone-laden air stream was passed through the reactor and the concentration was allowed to stabilize. Once the ozone concentration stabilized, the terpene solenoid valve was turned on for 20 minutes to add terpenes to the system and then turned off for 20 minutes. This sequence was repeated for a total of 16 experiments.

After the reactor experiments were completed, the terpene solenoid was turned off and the ozone air stream was allowed to bypass the reactor for an additional 20 minute experiment.

The data obtained from the ozone experiments was used to determine the reaction probability of a bare surface and then for a terpene-laden surface. These values were then used to calculate the ozone-terpene reaction probability. The following derivation explains how this parameter is derived.

Even though the reaction between ozone and Δ^3 carene is second-order, a pseudo-first order reaction is assumed since the concentration of terpenes is significantly larger than the concentration of ozone. (a reference to the “method of excess” would be appropriate here). Therefore, a standard pseudo-first order reaction equation for a linear plug-flow reactor starts the calculations (Equation 2a)¹⁸. The integration of Equation 2a from 0 to the length of the reactor, L, and from the initial concentration, C_o, to the concentration at length L, C_L, yields the next step in the calculations, Equation 2b.

Comment [JJ1]: Add reference?

In order to proceed, Equation 2b must be updated to reflect information that is readily available. The pseudo-first order reaction rate, k, takes into consideration all deposition which occurs on the surface, shown in Equation 2c as a product of the deposition velocity and the surface area to volume ratio. Equation 2d shows the equation for the deposition velocity. And finally, Equation 2e shows the equation for the mean velocity through the reactor. Equations 2c through 2e are plugged into Equation 2b and then rearranged in Equation 3 to obtain a useful equation for calculating the reaction probability. For the system used in this experiment, v_t, the gas-phase mass-transfer coefficient was assumed to be small and neglected.

Equation 2a-e. Equations used to derive reaction probability, Equation 3.

$$(a) \quad -\frac{d(uC)}{dx} - k_1 C = \frac{dC}{dt}$$

$$(b) \quad \frac{C_L}{C_o} = \exp\left(-\frac{k_1 L}{u}\right)$$

$$(c) \quad k_1 = v_d \frac{A_{bead}}{V_{react}}$$

$$(d) \quad v_d = \left(\frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle}\right)^{-1}$$

$$(e) \quad u = \frac{Q}{A}$$

where

u = mean velocity through the reactor (cm/s)

C = concentration of ozone

x = length of reactor (cm)

L = actual length of reactor (cm)

k₁ = pseudo-first order rate coefficient

v_d = deposition velocity (cm/s)

Q = flow rate through reactor, adjusted for temperature (cc/min)

A = cross-section area of reactor (cm²)

V_{react} = volume of reactor (cm³)
 A_{bead} = bead surface area (m²)
 $\langle v \rangle$ = Boltzman's velocity (cm/s)
 γ = reaction probability

Equation 3. Reaction probability equation.

$$\gamma_{\text{surface}} = 4 \left(\frac{Q}{A} \right) \left(\frac{V_{\text{react}}}{A_{\text{bead}}} \right) \left(\frac{1}{\langle v \rangle L} \right) (-\ln(k_1 L))$$

Where

γ_{surface} = reaction probability on the bare surface

Equation 3 was used to also calculate γ_{total} , the reaction probability on a terpene-laden surface.

Now that the reaction rates on the bare surface and terpene-laden surface are known, Equation 4 is used to solve for the ozone-terpene reaction probability, γ_{terp} .

Equation 4. Ozone-terpene reaction probability equation

$$\gamma_{\text{total}} = f_{\text{terp}} \gamma_{\text{terp}} + (1 - f_{\text{terp}}) \gamma_{\text{surface}}$$

To solve for γ_{terp} , the fraction of terpene coating the surface, f_{terp} , is determined by Equation 5.

Equation 5. Fraction of terpene covering the surface, f_{terp} .

$$f_{\text{terp}} = (\text{molar surface loading})(A_{\text{terp molecule}})N_A$$

where

$A_{\text{terp molecule}}$ = cross-sectional area of a terpene molecule (cm² molecule⁻¹)

N_A = Avagadro's number, 6.023×10^{23} molecules mol⁻¹

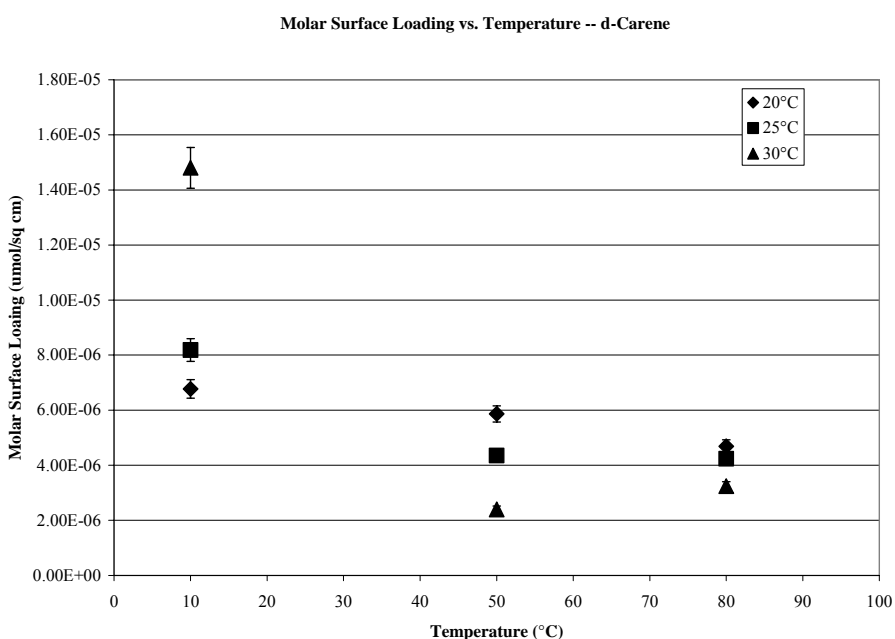
Using Equations 1 through 5, the ozone-terpene reaction probability was calculated for the glass beads at various temperatures and humidities.

RESULTS AND DISCUSSIONS

Molar Surface Loading

Figure 4 shows the molar surface loading evaluated for each temperature and relative humidity combination. Recall that each point is a result of 5 to 8 replicate breakthrough experiments. As anticipated, as temperature and humidity increase, the molar surface loading decreases. Typical of VOC-surface interactions, equilibrium partitioning to the surface decreases as temperature increases. The relative humidity effect is probably due to competitive adsorption. As the relative humidity increases, the water competes for surface sites with the terpene, reducing the molar surface loading. One point (30°C and 50% RH) does not appear to follow these trends, and may be an outlier.

Figure 4. Temperature and relative humidity impacts on molar surface loading at equilibrium 1.0 ppm Δ^3 carene.



Overall Reaction Probability

Figures 5 and 6 show the reaction probability for the bare and terpene-laden surfaces. The key result here is that the reaction probability increases by a factor of 20% to 200% for a terpene laden surface. This proves that there is a substantial surface reaction of ozone with Δ^3 carene. For both bare and terpene-laden surfaces, there is a general trend towards lower reaction probabilities with higher humidity. This is consistent with the hypothesis that fewer catalytic surface sites for ozone decomposition are available with

increasing humidity; water perhaps obscures catalytic sites on the bare surface or terpene laden surface. The effect of temperature is more difficult to explain. On the bare surface, the reaction probability (at 10 and 50% RH) decreases with temperature. This is counter-intuitive given that most reaction rates increase with temperature (Arrhenius relationship). Further, for a given RH, fewer water molecules will obscure catalytic sites; reaction rates would be expected to increase. This phenomenon may be explained if the concentration of adsorbed ozone on the surface diminishes with increasing temperature.

On the terpene-laden surface, the effect of temperature is small. Thornberry and Abbott¹⁹ also observed minimal impacts of temperature on their reactions involving gas-phase ozone and various fatty acids over a temperature range from the acids freezing point to room temperature. Since minimal effects were observed over that temperature range, this might explain why we saw little change in our reaction probabilities over a smaller 10°C temperature range.

Figure 5. Temperature and relative humidity impacts on reaction probability for bare surface.

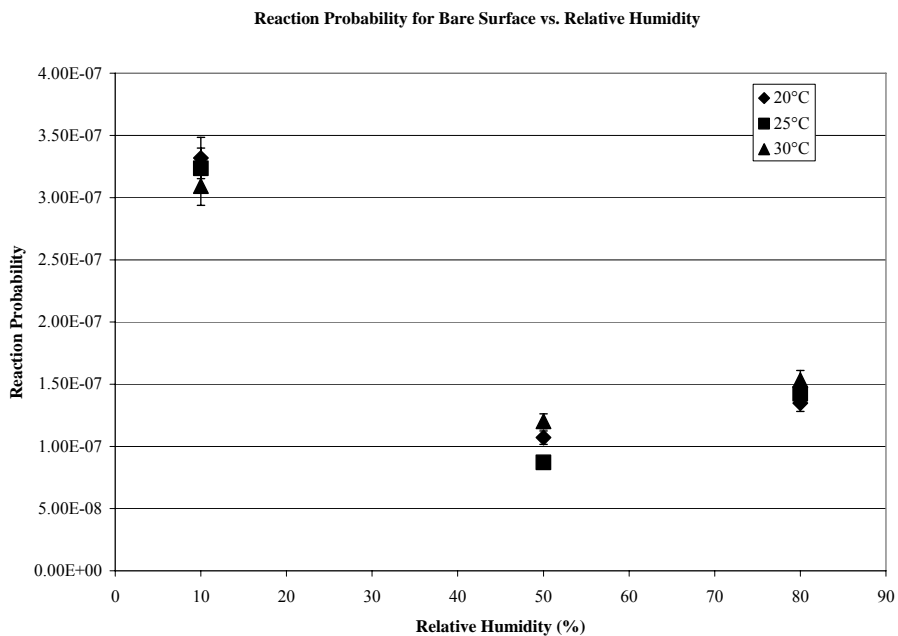
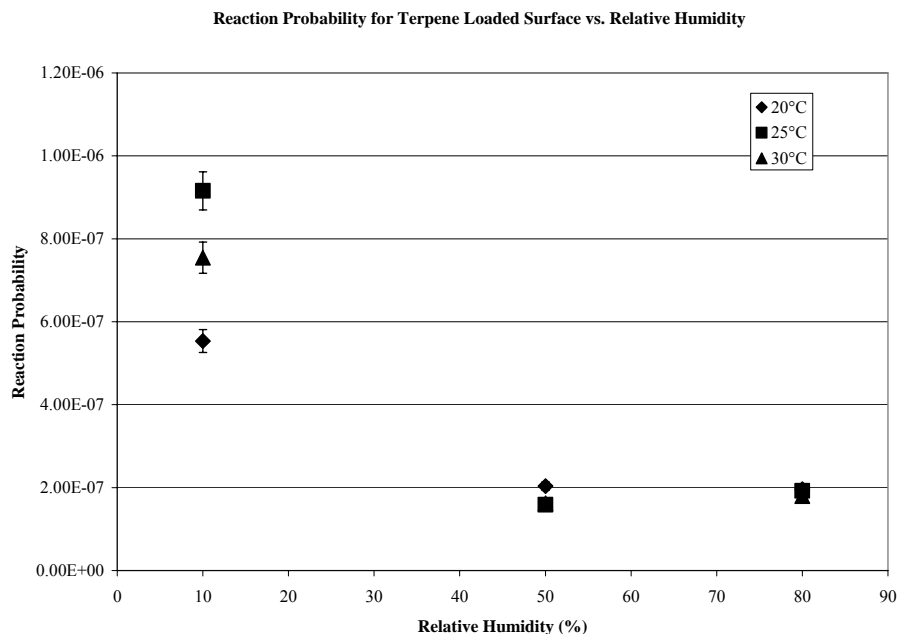


Figure 6. Temperature and relative humidity impacts on reaction probability for terpene-laden surface.



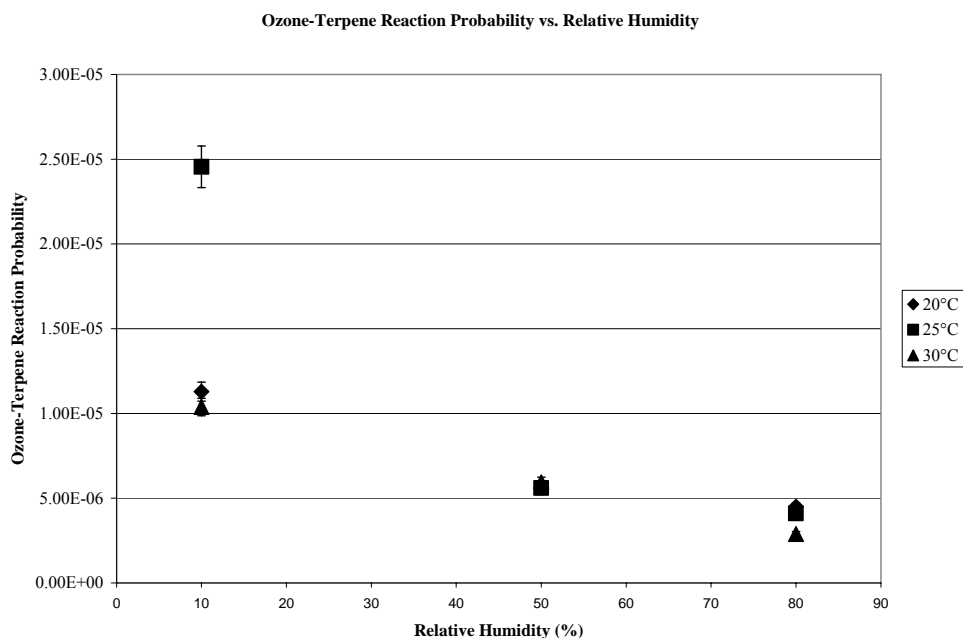
Ozone-Terpene Reaction Probability

The ozone-terpene reaction probability, γ_{terp} , is shown in Figure 7 and ranges from 0.3 to 2.5×10^{-5} . Thus for every million ozone molecule encounters with a terpene molecule on the surface, between three and twenty encounters will lead to a reaction between the ozone and terpene. To put this in context, ozone reaction probabilities on indoor surfaces range from $<10^{-7}$ for glass, about 10^{-5} for aged carpet and $>10^{-4}$ for new carpet and brick. Substantial coverage of this terpene on glass could substantially increase the overall reactivity of that surface. Conversely, adsorption to new carpet would probably not substantially increase ozone uptake, but could modestly increase uptake on older carpet.

This reaction probability, γ_{gas} , can be compared with the gas-phase reaction probability to discern if the reaction rate is enhanced by surface interactions. The gas-phase reaction probability for this reaction can be estimated by multiplying the second-order ozone-carene reaction rate ($3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) by the gas density at that temperature ($2.5 \times 10^{19} \text{ molecules cm}^{-3}$) and dividing by the bimolecular collision rate ($3 \times 10^9 \text{ s}^{-1}$): $\gamma_{\text{gas}} = 3 \times 10^{-7}$. Thus, Δ^3 -carene is 10 to 80 times more likely to react with ozone if it is adsorbed to this surface.

Figure 7. Reaction cross section values.

Comment [JJ2]: Explain error bars – standard deviations? For points with no error bars, are the standard deviations too small to show?



It is premature to make comparisons between indoor conversion rates in the gas phase and on indoor surfaces because too little is known about coverage and reaction probabilities on the many varied surface types indoors. However, taking these reaction probability values and those obtained during future experiments with plastic beads, reaction probabilities can be estimated for other types of indoor surfaces. These predictions can then be put to the test by performing experiments in a fully furnished room-sized chamber.

CONCLUSIONS

We have shown that an ozone-terpene reaction does occur on indoor surfaces and there may be a catalytic effect with less sites available for reaction as humidity and temperature increase. However, the effect of temperature and humidity on this reaction appears to be minimal but this will be confirmed with future experiments. The existing data is not sufficient to draw any conclusions regarding indoor conversion rates. Additional experiments with the Δ^3 -carene are in progress on zirconium silicate (representing mineral surfaces) and plastic, other types of surfaces commonly found indoors. In addition, other terpenes such as limonene (commonly found in citrus-scented products) and α -terpineol (a terpene alcohol) will be done to demonstrate whether some chemicals are more reactive on the surface than others.

The results suggest that when terpene-containing products such as air fresheners and cleaners are used indoors where ozone is present, reactions occur not only in the gas-

phase but also on surfaces. In addition, the adsorption of the terpenes on the surface likely contribute to reactions with ozone that occur after the initial exposure. In the future, a comparison of surface reactions rates versus gas-phase reaction rates may indicate that surface reactions are actually more important than gas-phase reactions in generating or removing gas-phase contaminants.

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REFERENCES

1. Nazaroff, W.; Weschler, C. *Atmospheric Environment*, **2004**, 38, 2841-2865.
2. Hodgson, A.; Beal, D.; McIlvaine, J. *Indoor Air*, **2002**, 12, 235-242.
3. Sarwar, G.; Olson, D.; Corsi, R.; Weschler, C. *Journal of Air & Waste Management Association*, **2004**, 54, 367-377.
4. Atkinson, R.; Aray, J. *Atmospheric Environment*, **2003**, 37, S197-S219.
5. *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J.I.; Howe-Grant, M., Eds; John Wiley and Sons, Inc.: New York, NY, **1997**; Vol 23, p833-882.
6. Wolkoff, P.; Clausen, P.; Wilkins, C.; Nielsen, G. *Indoor Air*, **2000**, 10, 82-91.
7. Wolkoff, P.; Clausen, P.; Wilkins, C.; Hougaard, K.; Nielsen, G. *Atmospheric Environment*, **1999**, 33, 693-698.
8. Clausen, P; Wilkins, C.; Wolkoff, P.; Nielsen, G. *Environment International*, **2001**, 26, 511-522.
9. Weschler, C.; Shields, H. *Indoor Air*, **2000**, 10, 92-100.
10. Commeto-Muñiz, J.E.; Cain, W.S.; Abraham, M.H. *Experimental Brain Research*, **1998**, 118, 180-188.
11. *Integrative Synthesis in Air Quality Criteria for Particulate Matter*; United States Environmental Protection Agency: Washington D.C. **2004**.
12. Destailats, H.; Singer, B.; Coleman, B.; Lunden, M.; Hodgson, A.; Weschler, C.; Nazaroff, W. *10th Annual Conference on Indoor Air and Climate (Indoor Air 2005)*; Beijing, China, **2005**.

13. Singer, B.; Coleman, B.; Destailats, H.; Hodgson, A.; Lunden, M.; Weschler, C.; Nazaroff, W. *Atmospheric Environment*, **2006**, 40, 6696-6710.
14. Pommer, L. Ph.D. Thesis, Umeå University, 2003.
15. Fick, J. Ph.D. Thesis, Umeå University, 2003.
16. Fick, J.; Pommer, L.; Åstrand, A.; Östin, R.; Nilsson, C.; Andersson, B. *Atmospheric Environment*. **2005**, 39, 6315-6325.
17. Destailats, H.; Lunden, M.; Singer, B.; Coleman, B.; Hodgson, A.; Weschler, C.; Nazaroff, W. *Environmental Science and Technology*, **2006**, 40, 4421-4428.
18. Weber Jr., W.J. *Environmental Systems and Processes – Principles, Modeling, and Design*; John Wiley & Sons Inc.: New York, NY, **2001**; pp 279.
19. Thornberry, T.; Abbatt, J. *Physical Chemistry Chemical Physics*, **2004**, 6, 84-93.