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# Reaction rates of ozone and terpenes adsorbed to model indoor surfaces

**Abstract** Reaction rates and reaction probabilities have been quantified on model indoor surfaces for the reaction of ozone with two monoterpenes ($\Delta^3$-carene and d-limonene). Molar surface loadings were obtained by performing breakthrough experiments in a plug-flow reactor (PFR) packed with beads of glass, polyvinylchloride or zirconium silicate. Reaction rates and probabilities were determined by equilibrating the PFR with both the terpene and the ozone and measuring the ozone consumption rate. To mimic typical indoor conditions, temperatures of 20, 25, and 30°C were used in both types of experiments along with a relative humidity ranging from 10% to 80%. The molar surface loading decreased with increased relative humidity, especially on glass, suggesting that water competed with the terpenes for adsorption sites. The ozone reactivity experiments indicate that higher surface loadings correspond with higher ozone uptake. The reaction probability for $\Delta^3$-carene with ozone ranged from $2.9 \times 10^{-6}$ to $3.0 \times 10^{-5}$ while reaction probabilities for d-limonene ranged from $2.8 \times 10^{-5}$ to $3.0 \times 10^{-4}$. These surface reaction probabilities are roughly 10–100 times greater than the corresponding gas-phase values. Extrapolation of these results to typical indoor conditions suggests that surface conversion rates may be substantial relative to gas-phase rates, especially for lower volatility terpenoids.

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Key words: Ozone; Terpene; Surface reaction; Reaction probability; Laboratory study.

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**Practical Implications**

At present, it is unclear how important heterogeneous reactions will be in influencing indoor concentrations of terpenes, ozone and their reaction products. We observe that surface reaction probabilities were 10 to 100 times greater than their corresponding gas-phase values. Thus indoor surfaces *do* enhance effective reaction rates and adsorption of terpenes will increase ozone flux to otherwise low-reactivity surfaces. Extrapolation of these results to typical indoor conditions suggests that surface conversion rates may be substantial relative to gas-phase rates, especially for lower volatility terpenoids.

## Introduction

In indoor environments, terpenoid compounds (terpenes) are present at high concentrations relative to outdoor concentrations (Brown et al., 1994; Hodgson et al., 2002). This is because of sources such as wood building materials, air fresheners, personal care products and cleaners (Nazaroff and Weschler, 2004). Many terpenes react rapidly with ozone and generate products that have been shown to cause adverse sensory and respiratory effects (Clausen et al., 2001; Kleno and Wolkoff, 2004; Nielsen et al., 2005; Rohr et al., 2002; Wilkins et al., 2003; Wolkoff et al., 1999, 2000). The products include aerosols (Wainman et al., 2000; Weschler and Shields, 1999), reactive intermediates such as ozonides (Nørgaard et al., 2008; Vibenholt et al., 2009), dicarbonyls (Ham and Wells, 2008; Harrison et al., 2007) and other species of concern such as peroxides (Chen and Hopke, 2009; Venkatachari and Hopke, 2008).

Terpene-ozone research has predominantly focused on the rates and products of the gas-phase reaction. However, a substantial fraction of emitted terpenes may adsorb to indoor surfaces (Singer et al., 2007) and there react with ozone. The effective surface rates (or reaction probabilities) may be much greater than anticipated based on gas-phase kinetics alone. For example, Stokes et al. (2008, 2009) showed that the reaction probability of a surface-attached alkene can be up to 5 orders of magnitude greater than for the same reaction in the gas-phase. The surface reaction may also generate products unlike those produced by

the gas-phase reaction (Ham and Wells, 2008). While studying gas-phase reactions, Pommer (2003) and Fick (2003) observed that reaction rates between terpenes and ozone was much higher than predicted, possibly as a result of reactions on the surfaces used in those experiments. While testing for secondary pollutants created when common household products were exposed to ozone, Destaillats et al. (2006) observed that the chamber removal rate of ozone remained high even after gas-phase terpenes concentrations had dropped to low concentrations by ventilation. This suggested terpenes remained on the surface, enhancing ozone reactivity with that surface. Similarly, Fick et al. (2005) concluded that the inner surfaces of a heat exchanger were responsible for increased terpene conversion rates.

At present, it is unclear how important these heterogeneous reactions will be in determining indoor concentrations of both terpenes and ozone. The objective of this study was to measure the increased ozone uptake rate on surfaces and estimate the surface-specific reaction probability of ozone with two common monoterpenes ($\Delta^3$-carene and d-limonene, hereafter written 'carene' and 'limonene') adsorbed to materials that mimic indoor surfaces, under a range of temperature and humidity conditions. This fundamental information will be used to better understand how this class of reactions influences indoor air quality. For example, we seek to answer questions regarding (i) whether there is any surface-specific effect, i.e. does the ozone-terpene reaction occur faster than anticipated in the gas-phase; and (ii) whether indoor surfaces significantly enhance overall conversion rates of these compounds compared to gas-phase reactions alone.

## Materials and methods

### Overview

To measure the rate of ozone-terpene surface reactions, a laboratory plug-flow reactor (PFR) was packed with beads that act as 'model' indoor surfaces. Using spheres made of materials commonly found in buildings, we can more precisely quantify reaction rates relevant to these kinds of surfaces than is possible with a real surface such as a piece of carpet or vinyl flooring. The packed section of the PFR has a very high surface area to volume ratio and a short residence time and allows us to observe conversion that is due almost entirely to surface reactions, not gas-phase chemistry.

Two experimental results were obtained: (i) the equilibrium surface concentration, by adsorption of carene and limonene; and (ii) the rate of ozone uptake on the surface. Adsorption experiments resulted in a molar surface concentration and a fractional coverage. The ozone uptake experiments were used to determine the rate (parameterized by the deposition velocity) at which ozone is consumed on a model surface with and without adsorbed terpenes. The results of adsorption and ozone uptake experiments are combined to estimate a surface-specific ozone-terpene reaction probability. Parameters were obtained for range of temperature and humidity levels that are typical of indoor environments.

### Materials

For the adsorption experiments, the beads [glass, polyvinyl chloride (PVC) and zirconium silicate ($ZrSiO_4$)], approximately one to two millimeters in diameter, were used to represent typical household surfaces. Glass beads purchased from MO-SCI Specialty Products L.L.C. represented window glass. PVC beads purchased from Engineering Laboratories Inc. represented vinyl flooring, typically found in kitchens and bathrooms. Zirconium silicate purchased from Ceroglass, Inc. (Columbia, TN, USA) represented porous mineral surfaces, such as granite countertops. Prior to the experiment, the beads were sonicated in distilled water and dried in a 35–100°C oven for several hours. After drying, the beads were placed in a Teflon reactor (described later).

Carene and limonene were obtained from Sigma-Aldrich, at 97% and 99% purity, respectively. Ozone was generated by passing air over an ultraviolet lamp ozone generator (Model 600; Jelight Inc., Irvine, CA, USA).

The terpene was introduced into the system as a gas mixture. This was prepared by injecting 87 $\mu$l of the terpene into a 1.8-l gas cylinder and then backfilling with ultrapure nitrogen until the total pressure in the tank pressure reached 100 psi (690 kPa). Three 9-ml samples of the gas were collected 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 of a known concentration. A control gas for the adsorption experiment was created by injecting 20 ml of methane gas into a 1.8-l gas cylinder and then backfilling with ultrapure nitrogen until the tank pressure reached 100 psi.

### Methods

The Teflon plug-flow reactor system shown in Figure 1 was used for adsorption and reaction experiments. The reactor is 1.8 cm in diameter and 50 cm in length. The reactor is completely filled with the beads, and the bed porosity was ~40% (based on nonporous spheres, measured gravimetrically). Target concentrations of terpene, ozone, and moisture were obtained by controlling the mixture of gas streams (dry, humidified, with terpene, and with ozone).

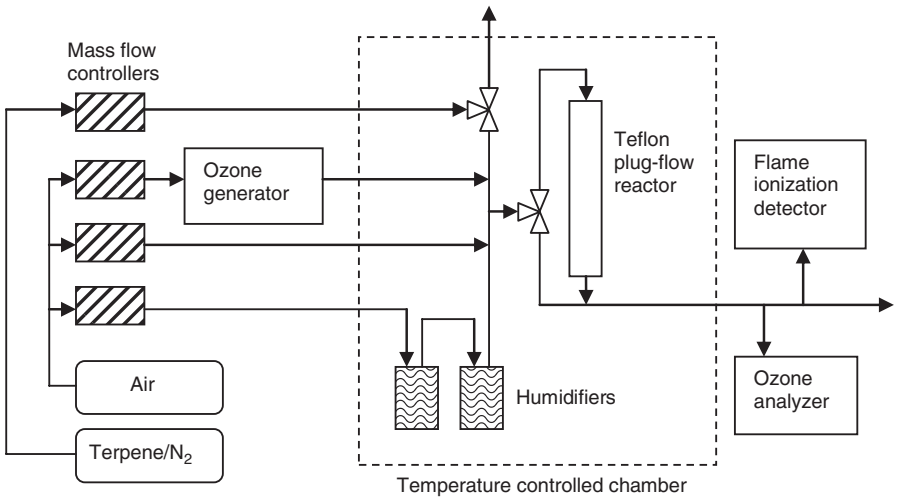


**Fig. 1** Experimental apparatus for measuring adsorption isotherms and, separately, ozone uptake rates on a model surface when a terpene is introduced into the system

Teflon solenoid valves allowed streams to be directed to and away from the mixed stream, and also controlled whether the stream was directed to the reactor or to a bypass stream.

A temperature-controlled chamber housed the reactor and solenoid valves. The temperature of the chamber was set at either 20, 25, or 30°C for carene experiments and 25°C for limonene experiments. Two gas sparging bottles used to adjust the humidity of the reactor gas stream from 10 to 80% were also located inside the temperature-controlled chamber.

*Adsorption.* For adsorption experiments, either diluted methane (inert trace gas) or terpene streams (1.0 l/min) were directed to the reactor in a step-change fashion, and the outlet gas was sampled by a continuous flow flame ionization detector. Mass adsorbed was determined by comparing breakthrough curves for the monoterpene against that obtained for methane in separate experiments. The inlet concentration was adjusted to 1.0 ppm. Either species was introduced to the system with a solenoid valve that was switched on or off in 15-min intervals to create adsorption and desorption curves at the reactor outlet. The sequence was repeated over a minimum of 4 h to generate a large number of replicate curves. This experiment was repeated with each chemical ($\Delta^3$-carene and d-limonene), at three different humidity levels (10, 50 and 80%), and introduced individually to each type of surface in separate experiments.

The adsorption results were 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 quantified by calculating the difference between the integrated molar rate exiting the reactor in the absence of adsorption (methane) and the integrated molar rate exiting the reactor with adsorption (terpene).

$$\text{Molar surface concentration} = \frac{QC_o}{A_{\text{beads}} \cdot MW} \left[ \int_0^t C'_{\text{meth}}(t)dt - \int_0^t C'_{\text{terp}}(t)dt \right] \quad (1)$$

where $Q$ is the gas flow rate ($m^3$/s), adjusted for temperature, $C_o$ is the inlet concentration of the terpene (g/$m^3$), $A_{\text{beads}}$ is the bead surface area ($m^2$), $MW$ is the molecular weight of the terpene (g/mol). To account for differences in FID responses between methane and the terpenes, the responses (in mV) were normalized by the steady-state maximum response. The adsorption curves from 6 to 10 experiments (for both methane and terpene) were normalized and then combined to generate an average normalized curve. This procedure reduced experimental/instrumental noise and allowed us to quantify weak adsorption with more precision. In equation (1), $C'_{\text{meth}}(t)$ is the normalized methane concentration at time $t$, and $C'_{\text{terp}}(t)$ is the normalized terpene concentration at time $t$. Both are unitless.

*Ozone uptake.* For ozone uptake experiments, 2.0 l/min of compressed air was introduced into the system and divided to achieve the desired relative humidity levels. A 0.015 l/min stream of diluted ozone, generated using ultraviolet light, was mixed with the main stream to produce a reactor inlet mixing ratio of approximately 220 ppb. The ozone concentration reduction through the reactor was used to determine the substrate reactivity and reaction probability in the absence of terpenes (bare) and with terpenes.

With the ozone concentration stabilized, the terpene solenoid valve was turned on and the ozone concentration allowed to restabilize for 20 min. It was then switched off for 20 min. This sequence was repeated at least 16 times. The difference between the inlet ozone and outlet ozone concentrations were used to determine the substrate reactivity in the presence of terpenes, the total reaction probability of the surface and the terpene-ozone reaction probability.

*Reactive uptake and reaction probabilities.* The reaction between ozone and the terpene is assumed to occur only on the surface and conversion is pseudo-first order. The concentration of terpenes is significantly larger than the concentration of ozone (method of excess). The residence time of the reactor is $< 2$ s, and the calculated gas-phase conversion of ozone under these conditions is less than 2%. Therefore, a standard pseudo-first-order reaction was used to derive the deposition velocity, $v_d$, and reaction probability for the surface (Cano-Ruiz et al., 1993; Morrison and Nazaroff, 2000).

$$\frac{C_L}{C_o} = \exp\left(-\frac{v_d A_{beads} L A p}{V_{reactor} Q}\right) \quad (2)$$

$$v_d = \left(\frac{1}{v_t} + \frac{4}{\gamma_{surface}\langle v\rangle}\right)^{-1} \quad (3)$$

where, $C_o$ is the inlet ozone concentration (ppb), $C_L$ is the outlet ozone concentration (ppb), $L$ is the length of reactor (m), $v_d$ is the local deposition velocity (m/s), $v_t$ is the transport-limited deposition velocity, $Q$ is the flow rate through reactor, adjusted for temperature ($m^3$/s), $A$ is the cross-section area of reactor ($m^2$), $p$ is the bed porosity of the beads, $V_{reactor}$ is the volume of reactor ($m^3$), $< v >$ is the Boltzman's velocity (m/s), $\gamma_{surface}$ is the reaction probability of substrate with ($\gamma_{surface,t}$) or without ($\gamma_{surface,o}$) adsorbed terpenes (dimensionless).

For the conditions here, the transport-limited deposition velocity can be estimated from the equivalent heat-transfer correlation for a packed bed (Perry and Green, 2008). This value is approximately 400 m/h and is much larger than the measured $v_d$ from our experiments. Therefore, the boundary layer is not the limiting resistance to ozone flux to the surface and equations (2) and (3) can be combined and simplified as,

$$\gamma_{surface} = \left(\frac{4 Q V_{react}}{A_{bead} A L p < v >}\right) \ln\left(\frac{C_o}{C_L}\right). \quad (4)$$

To determine the terpene-ozone reaction probability, we assume that $\gamma_{surface,t}$ is a linear combination of fractional contribution of sites with and without adsorbed terpenes. Sites with adsorbed terpenes are assumed to be identical and the reaction rate is characterized by the ozone-terpene reaction probability, $\gamma_{terp}$.

$$\gamma_{surface,t} = f_{terp}\gamma_{terp} + (1 - f_{terp})\gamma_{surface,o}. \quad (5)$$

To solve for $\gamma_{terp}$, the fraction of terpene coating the surface, $f_{terp}$, is derived from the molar surface loading (see Equation 1),

$$f_{terp} = (\text{molar surface loading})(A_{terp\,molecule})N_A \quad (6)$$

where $A_{terp\ molecule}$ is the cross-sectional area of a terpene molecule ($m^2$/molecule) and $N_A$ is Avogadro's number. This traditional definition of reaction probability, $\gamma_{terp}$, relies on the assumption that ozone reacts with the adsorbed terpene as the result of a collision from the gas-phase (Eley-Rideal mechanism). Note that $\gamma_{terp}$ is relatively insensitive to the choice of surface area (geometric, BET, etc.) under these experimental conditions. As $f$, and $\gamma_{surface,o}$, approach zero, $\gamma_{terp}$ becomes independent of $A_{bead}$.

## Results and discussions

### Molar surface concentration and fractional coverage

Shown in Figure 2 are the normalized FID signal results for $\Delta^3$-carene and methane for the reactor filled with glass beads. Each plot is an average of 6–10 replicate 1.0 ppm step-change injections obtained at 25°C and three relative humidity values. The area between the plots is proportional to the molar surface concentration by equation (1).

Molar surface concentrations varied by terpene, temperature, and surface. Results for each condition are provided in Table S1. Carene exhibited surface concentrations 1.2–4 times higher, for the same conditions and surface, than limonene, even though the predicted vapor pressure for carene is about 20% larger. Increasing relative humidity reduces adsorbed mass on glass and $ZrSiO_4$, but not on PVC. The RH effect is probably attributed to competitive adsorption

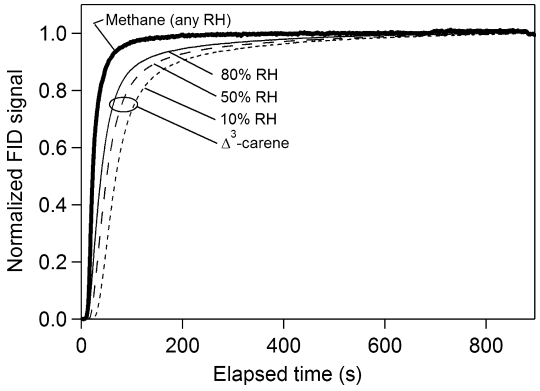


**Fig. 2** An example of the derivation of the molar surface loading from an experiment performed at 25°C and 10% relative humidity. The area between the methane (non-adsorbing) curve and $\Delta^3$-carene curve is proportional to the molar surface loading of the terpene

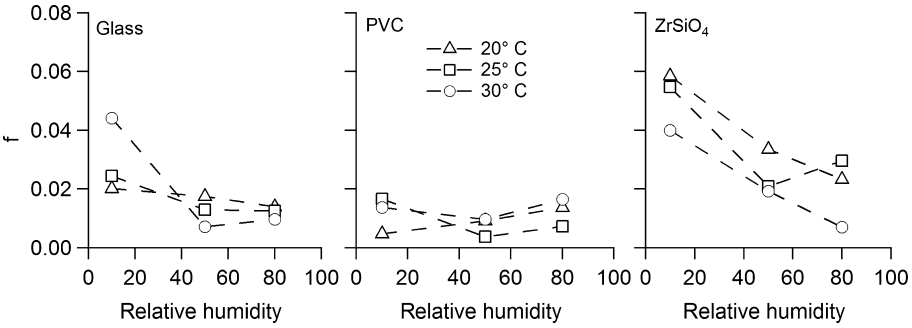


**Fig. 3** Relative humidity and fractional coverage for surfaces at equilibrium with 1.0 ppm $\Delta^3$-carene

especially on the more polar glass and $ZrSiO_4$ surfaces. The surface concentration is highest on $ZrSiO_4$ beads and lowest on PVC beads. For carene and limonene, the surface concentration ranges from 0.1 to $2.0 \times 10^{-4}$ mmol/m$^2$ and from 0.07 to $0.9 \times 10^{-4}$ mmol/m$^2$, respectively.

Fractional coverage is shown in Figure 3 for carene on all surfaces and for each condition. Fractional coverage, here based on geometric projected area of a sphere, ranges from 0.004 to 0.06 for carene and represents an upper bound. Accounting for roughness and porosity (not quantified), the fractional coverage will be lower. Therefore, the coverage is relatively low and multilayer adsorption is not likely to be significant. Fractional coverage ranged from 0.002 to 0.03 for limonene on all surfaces. Relative measurement uncertainty for molar surface concentration and fractional coverage ranged from 5 to 30%.

### Reaction Probability

Surface reaction probabilities and the resulting terpene-specific reaction probability are shown in Figure 4 for carene on glass at 25°C. Uncertainty ranges shown are based on propagation of measurement uncertainty through equations 4–6. Introducing carene at 1 ppm to the reactor increases the background reaction probability by $2.2 \times 10^{-7}$ on average for glass, $3.5 \times 10^{-7}$ for PVC and $3.9 \times 10^{-7}$ for $ZrSiO_4$ (averaged over all conditions). For all conditions and surfaces, carene increased the reaction probability of the surface by 70% on average. This consistent increase demonstrates that there is a substantial surface reaction of ozone with $\Delta^3$-carene. Somewhat larger increases in surface reaction probability were observed for the 1 ppm d-limonene experiments: $6.2 \times 10^{-7}$ for glass, $2.9 \times 10^{-6}$ for PVC and $7.6 \times 10^{-7}$ for $ZrSiO_4$. Averaged over all conditions and surfaces, limonene increases the surface reaction probability by 225%. For both bare and terpene-laden glass and $ZrSiO_4$ surfaces, there was a general trend toward lower reaction probabilities with higher humidity. This is consistent with the hypothesis that there are fewer sites available for catalytic ozone decomposition as humidity increases; water perhaps obscures these sites on the bare surface or terpene-laden surface. However, for the PVC, the surface reaction probability was not significantly influenced by temperature or humidity.

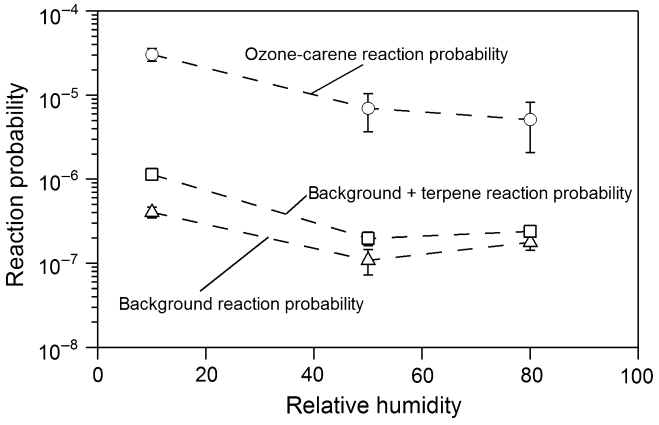


**Fig. 4** Surface reaction probabilities and the resulting $\Delta^3$-carene-specific reaction probability on glass at 25°C

The terpene-specific reaction probabilities that result from solving equation (4) are also shown on Figure 4. To significantly increase the surface reaction probability (100–200%) with a low fractional coverage, the terpene-specific reaction probability is substantially larger than that for the average surface site.

The ozone-carene reaction probabilities for all surfaces and conditions are shown in Figure 5. The reaction probability ranges from $0.36 \times 10^{-5}$ to $7.3 \times 10^{-5}$ and tends to decrease with increasing humidity. There is no consistent trend with temperature, and the span of values is smaller for the 10°C temperature range than for the 70% humidity range. Thornberry and Abbatt (2003) observed minimal impacts of temperature on the reaction probability for the reaction of gas-phase ozone with fatty acids over a temperature range from the acids' freezing point to room temperature. In this system, water on the surface may act to make the terpene more or less available for reaction (e.g. by displacement, solvation

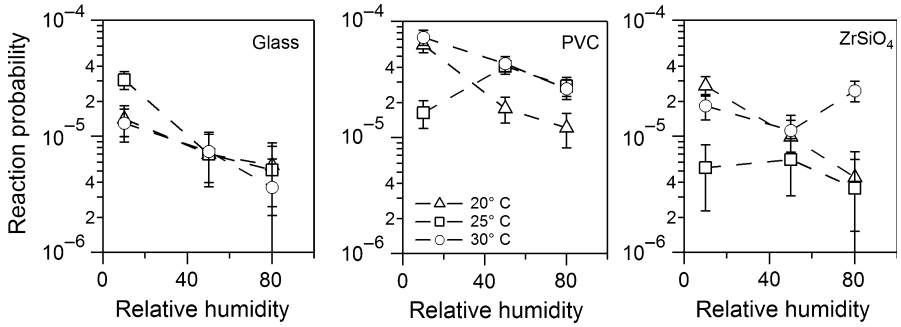


**Fig. 5** Relative humidity impacts on the $\Delta^3$-carene reaction probability ($\gamma$)

or modifying surface polarity). This would cause the calculated (effective) reaction probability to vary, even if its 'true' reaction probability has not changed. The reaction probability for carene on PVC is significantly higher than for glass or $ZrSiO_4$. It is possible that adsorbed carene is more available for the reaction with ozone on PVC than on the other surfaces, or that its orientation on a less polar surface makes it more reactive. Further, the reaction probability may not entirely reflect reactions taking place with the terpenes alone, but also with low-volatility products that remain on the surface. Low-volatility products of ozonation of limonene may retain one of its ozone-reactive double bonds (Walser et al., 2008). Gas-phase ozonation reactions with terpenes are also known to generate high-molecular weight oligomers; aldol condensation reactions can result in unsaturated carbon-carbon bonds (Tolocka et al., 2004). Sufficiently rapid formation of aldol condensation products requires the presence of a strong acid (Kroll and Seinfeld, 2008). The materials studied in this research, and indoor surfaces in general, may not be sufficiently acidic to promote rapid formation of oligomers uniformly across the surface. However, sulfuric acid aerosols that deposit on indoor surfaces could promote local formation of reactive oligomers. Formation of low-volatility ozonides and peroxides (Docherty et al., 2005) may also promote further reactions with adsorbed terpene and thus increase the terpene conversion rate over and above that initiated by ozonation alone. Overall, the effective reaction probability reported here is specific to the surface and environmental conditions.

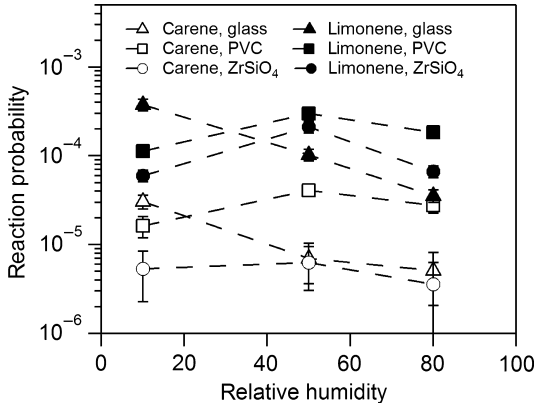


**Fig. 6** Reaction probability ($\gamma$) for $\Delta^3$-carene and d-limonene on all surfaces at 25°C

Shown in Figure 6 are the results at 25°C for carene and limonene on all surfaces. The reaction probability for limonene on the surface is, on average, 13 times higher than for carene. This may be reflective of limonene's higher gas-phase reactivity (10 times higher than carene) and the fact that it has two double bonds. This reaction probability can be compared with the gas-phase reaction probability, $\gamma_{gas}$, 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 ($3 \times 10^{-17}$ cm$^3$/molecule/s) by the gas density at that temperature ($2.5 \times 10^{19}$ molecules/cm$^3$) and dividing by the bimolecular collision rate ($3 \times 10^9$/s): $\gamma_{gas} = 3 \times 10^{-7}$. Thus, adsorbed carene is 10–240 times more likely to react with ozone assuming the Eley-Rideal mechanism is appropriate for this system. Similarly, limonene is 10–120 times more likely to react with ozone than in the gas-phase ($\gamma_{gas} \sim 2.5 \times 10^{-6}$). However, (Dubowski et al., 2004) has shown that Langmuir-Hinshelwood mechanism may be a more likely mechanism for ozone reactions with surface-bound species and these reaction probability results then represent 'effective' values that cannot be compared directly with gas-phase kinetic parameters. Uncertainties are large enough to preclude drawing conclusions about patterns or trends relative to temperature or humidity.

In indoor environments, ozone uptake on surfaces will not be significantly impacted by adsorbed limonene or carene. To put these reaction probabilities 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 either terpene on glass could substantially increase the overall reactivity of that

surface. Conversely, adsorption to new carpet is unlikely to substantially increase ozone uptake (Coleman et al., 2008). Substantial coverage would require very high indoor concentrations of terpenes. Limonene and pinene are commonly detected in buildings, but typically at mixing ratios less than 10 ppb (Hodgson and Levin, 2003). These experiments were conducted at 1.0 ppm, to generate a measureable increase in surface reactivity. At this concentration, the highest surface reaction probability achieved was $4 \times 10^{-6}$, which is a bit lower than the area averaged value for building surfaces (Nazaroff et al., 1993). Therefore, except for unusually large indoor concentrations, ozone uptake on indoor surfaces would not be substantially increased because of adsorbed limonene or carene.

Lower volatility terpenes may however significantly influence conversion rates, ozone removal rates and indoor concentrations of both. For example, the gas-phase ozone-terpene reaction rate for terpineol is similar to that of limonene, but its vapor pressure is about 100 times lower. Substantial fractional coverage of terpineol may occur at low ppb concentrations. Shu and Morrison (2009) reported that adsorbed terpineol significantly increases ozone uptake on glass and PVC surfaces where 20–50 ppb terpineol is present in the gas-phase. Shown in Figure 7 are modeled deposition velocities and ozone removal rates as a function of the fractional coverage, $f$. In an analysis similar to that by Coleman and Nazaroff (2008), these are determined by applying equations 3 and 5 for the specific indoor environment where the surface area to volume ratio is 2 per meter (Hodgson et al., 2004). For a building that consists primarily of PVC flooring, glass, paint and other low-reactivity surfaces, the background reaction probability, $\gamma_b$, would presumably be low (in the absence of human skin oils and other coatings). Taking $\gamma_b = 10^{-7}$, an adsorbed terpene with $\gamma_{terp} = 10^{-4}$ (similar to limonene) will substantially increase deposition velocities and the surface-specific ozone removal rate (right-hand axis). For a typical building, the background reaction probability has been estimated to be $\gamma_b = 10^{-5}$ (Nazaroff et al., 1993). For this condition, the same adsorbed terpene ($\gamma_{terp} = 10^{-4}$) increases ozone removal moderately, but not substantially.

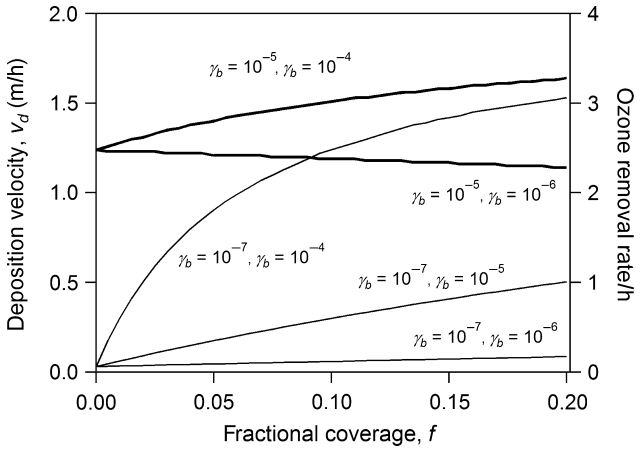


**Fig. 7** Deposition velocities and ozone removal rates as a function of the fractional coverage, $f$, for a building with a surface area to volume ratio = 2 per meter

Even if the ozone removal rate is not enhanced significantly, the conversion rate of terpenes on the surface, relative to that in the gas-phase, may increase measurably. To compare surface conversion rates with gas-phase rates, we first assume that the flux of ozone is attributed to reactions with a linear combination of surface reaction sites. Thus, the terpene conversion rate at the surface is

$$\text{surface conversion rate} = \frac{\gamma_{terp}\langle v\rangle}{4} f C_{O3} A \qquad (7)$$

where $f$ is the fraction coverage of the terpene as defined previously, and $A$ is the projected surface area of the building. The conversion rate in the gas-phase is

$$\text{gas phase conversion rate} = k_2 C_{terp} C_{O3} V \qquad (8)$$

where $k_2$ is the second-order rate gas-phase rate constant and $V$ is the volume of the building. For carene, we apply the average $\gamma_{terp}$ ($2 \times 10^{-5}$), average $f$ at 1 ppm (0.02), a lower-end surface area to volume ratio for a residence [$A/V$ = 0.03/cm; (Hodgson et al., 2004; Singer et al., 2004)], the gas-phase rate constant ($3 \times 10^{-17}$ cm$^3$/molecule/s) and letting $C_{terp}$ equal 1 ppm ($2.5 \times 10^{13}$ molecules/cm$^3$) to correspond with $f$. Thus, we estimate that 13% of carene conversion will take place on indoor surfaces, and the remaining conversion in the gas-phase. For limonene, with a higher gas-phase rate constant ($2.5 \times 10^{-16}$ cm$^3$/molecule/s), lower fractional coverage (0.01), and higher surface reaction probability ($1.6 \times 10^{-4}$), about 5% of the conversion takes place on indoor surfaces. For low volatility terpenes, the conversion rate will likely be dominated by surface reactions.

The aforementioned analysis is based on the physically simplistic assumption that terpenes adsorb uniformly on a clean surface and are equally available for reaction. Real indoor surfaces are porous and coated in a complex mixture of low-volatility compounds (Liu et al., 2003). Terpenes that penetrate into pores, or dissolve into an oily surface film, are less likely to encounter ozone than those that are present at the true interface between gas and condensed material. By using real surfaces in these experiments, the increase in ozone flux that we observe in our experiments is reasonably representative. However, the necessary mild cleaning procedure makes the surfaces somewhat less representative by removing some of the oily film.

## Conclusions

Our results confirm (quantitatively) that when terpene-containing products such as air fresheners and cleaners are used indoors, ozone reactions will occur in the gas-phase and on surfaces. Even if the cleaners have only been applied to a small area (such as a countertop), all indoor surfaces will support the terpene-ozone chemistry because of initial emission, transport and subsequent adsorption to all available surfaces. In addition, slow desorption of terpenes from indoor surfaces extend the period of reactivity, potentially long after air exchange has significantly reduced air concentrations (as in Destaillats et al., 2006).

Although surface reactions of the volatile monoterpenes tested here are unlikely to significantly influence indoor air concentrations of the reactants, surface ozonolysis of less volatile terpenoids could significantly influence air concentrations of products. The fractional coverage of compounds such as alcohol terpenes will be much higher for a much lower air concentration, shifting the conversion from gas to surface. Most scented consumer product, cleaners, perfumes, etc. are composed of mixtures of terpenes of varying volatility. Thus, significant coverage of multiple terpenes on indoor surfaces will likely increase ozone removal rates noticeably, above and beyond that predicted by gas-phase chemistry alone. Further, as products generated on the surface (Ham and Wells, 2008) can differ from those generated by gas-phase chemistry, surface chemistry could significantly increase air concentrations of compounds unique to the heterogeneous chemistry of terpenes.

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## Supporting Information

Additional Supporting Information may be found in the online version of this article:

**Table S1** Surface loading (mmol/m$^2$) of carene and limonene at equilibrium with 1.0 ppm in the gas-phase.

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## References

Brown, S.K., Sim, M.R., Abramson, M.J. and Gray, C.N. (1994) Concentrations of volatile organic compounds in indoor air-a review, *Indoor Air*, **4**, 123–134.

Cano-Ruiz, J.A., Kong, D., Balas, R.B. and Nazaroff, W.W. (1993) Removal of reactive gases at indoor surfaces: combining mass transport and surface kinetics, *Atmos. Environ.*, **27a**, 2039–2050.

Chen, X. and Hopke, P.K. (2009) Secondary organic aerosol from α-pinene ozonolysis in dynamic chamber system, *Indoor Air*, **19**, 335–345.

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, *Environ. Int.*, **26**, 511–522.

Coleman, B.K. and Nazaroff, W.W. (2008) *Byproducts from ozone reactions with residual surface chemicals*, Indoor Air 2008, Copenhagen, Denmark.

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

Destaillats, H., Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J. and Nazaroff, W.W. (2006) Indoor secondary pollutants from household product emissions in the presence of ozone. A bench-scale chamber study, *Environ. Sci. Technol.*, **40**, 4421–4428.

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 $O_3$, *Environ. Sci. Technol.*, **39**, 4049–4059.

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, *J. Phys. Chem. A.*, **108**, 10473–10485.

Fick, J. 2003. Chemical reactions in ventilation systems: ozonolysis of monoterpenes. PhD thesis, Department of Chemistry, Umeå University, Umeå, Sweden.

Fick, J., Pommer, L., Åstrand, A., Östin, R., Nilsson, C. and Andersson, B. (2005) Ozonolysis of monoterpenes in mechanical ventilation systems, *Atmos. Environ.*, **39**, 6315–6325.

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

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, *Atmos. Environ.*, **41**, 4482–4491.

Hodgson, A.T. and Levin, H. 2003. *Volatile Organic Compounds in Indoor Air: A Review of Concentrations Measured in North America since 1990*, Berkeley, California, Lawrence Berkeley National Laboratory LBNL-56786.

Hodgson, A.T., Beal, D. and McIlvaine, J.E.R. (2002) Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house, *Indoor Air*, **12**, 235–242.

Hodgson, A.T., Ming, K. and Singer, B.C. 2004. *Quantifying Object and Material Surface Areas in Residences*, Berkeley, CA, Lawrence Berkeley National Laboratory LBNL-56786.

Kleno, J. and Wolkoff, P. (2004) Changes in eye blink frequency as a measure of trigeminal stimulation by exposure to limo-

nene oxidation products, isoprene oxidation products and nitrate radicals, *Int. Arch. Occup. Environ. Health*, **77**, 235–243.

Kroll, J.H. and Seinfeld, J.H. (2008) Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, **42**, 3593–3624.

Liu, Q.T., Chen, R., McCarry, B.E., Diamond, M.L. and Bahavar, B. (2003) Characterization of polar organic compounds in the organic film on indoor and outdoor glass windows, *Environ. Sci. Technol.*, **37**, 2340–2349.

Morrison, G.C. and Nazaroff, W.W. (2000) The rate of ozone uptake on carpets: experimental studies, *Environ. Sci. Technol.*, **34**, 4963–4968.

Nazaroff, W.W. and Weschler, C.J. (2004) Cleaning products and air fresheners; exposure to primary and secondary air pollutants, *Atmos. Environ.*, **38**, 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. Modeling of Indoor Air Quality and Exposure. N. L. Nagda. Philadelphia, PA, American Society for Testing and Materials. *ASTM STP* **1205**, 81–104.

Nielsen, G.D., Larsen, S.T., Hougaard, K.S., Hammer, M., Wolkoff, P., Clausen, P.A., Wilkins, C.K. and Alarie, Y. (2005) Mechanisms of acute inhalation effects of (+) and (−)-α-pinene in BALB/c mice, *Basic. Clin. Pharmacol. Toxicol.*, **96**, 420–428.

Nørgaard, A.W., Nøjgaard, J.K., Clausen, P.A. and Wolkoff, P. (2008) Secondary ozonides of substituted cyclohexenes: a new class of pollutants characterized by collision-induced dissociation mass spectrometry using negative chemical ionization, *Chemosphere*, **70**, 2032–2038.

Perry, R. and Green, D., 2008. *Perry*'s Chemical Engineer's Handbook, New York, McGraw-Hill.

Pommer, L. 2003. *Oxidation of Terpenes in Indoor Environments: A Study of Influencing Factors*, Umeå, Sweden, Department of Chemistry, Umeå University. PhD.

Rohr, A.C., Wilkins, C.K., Clausen, P.A., Hammer, M., Nielsen, G.D., Wolkoff, P. and Spengler, J.D. (2002) Upper airway and pulmonary effects of oxidation products of (+)-α-pinene, d-limonene, and isoprene in BALB/c mice, *Inhalation Toxicology*, **14**, 663–684.

Shu, S. and Morrison, G.C., 2009. *Surface Reaction Rate of Ozone and Alpha-Terpineol on Polyvinylchloride and Glass*. Healthy Buildings 2009, Syracuse, NY.

Singer, B.C., Revzan, K.L., Hotchi, T., Hodgson, A.T. and Brown, N. (2004) Sorption of organic gases in a furnished room, *Atmos. Environ.*, **38**, 2483–2494.

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, *Atmos. Environ.*, **41**, 3251–3265.

Stokes, G.Y., Buchbinder, A.M., Gibbs-Davis, J.M., Scheidt, K.A. and Geiger, F.M. (2008) Heterogeneous ozone oxidation reactions of 1-pentene, cyclopentene, cyclohexene, and a menthenol derivative studied by sum frequency generation, *J. Phys. Chem. A.*, **112**, 11688–11698.

Stokes, G.Y., Chen, E.H., Walter, S.R. and Geiger, F.M. (2009) Two reactivity modes in the heterogeneous cyclohexene ozonolysis under tropospherically relevant ozone-rich and ozone-limited conditions, *J. Phys. Chem. A.*, **113**, 8985–8993.

Thornberry, T. and Abbatt, J.P.D. (2003) Heterogeneous reaction of ozone with liquid unsaturated fatty acids: detailed kinetics and gas-phase product studies, *Phys. Chem. Chem. Phys.*, **6**, 84–93.

Tolocka, M.P., Jang, M., Ginter, J.M., Cox, F.J., Kamens, R.M. and Johnston, M.V. (2004) Formation of oligomers in secondary organic aerosol, *Environ. Sci. Technol.*, **38**, 1428–1434.

Venkatachari, P. and Hopke, P.K. (2008) Characterization of products formed in the reaction of ozone with α-pinene: case for organic peroxides, *J. Environ. Monitor.*, **10**, 966–974.

Vibenholt, A., Nørgaard, A.W., Clausen, P.A. and Wolkoff, P. (2009) Formation and stability of secondary ozonides from monoterpenes studied by mass spectrometry, *Chemosphere*, **76**, 572–577.

Wainman, T., Zhang, J., Weschler, C.J. and Lioy, P.J. (2000) Ozone and limonene in indoor air: a source of submicron particle exposure, *Environ. Health Perspect.*, **108**, 1139–1145.

Walser, M.L., Desyaterik, Y., Laskin, J., Laskin, A. and Nizkorodov, S.A. (2008) High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene, *Phys. Chem. Chem. Phys.*, **10**, 1009–1022.

Weschler, C.J. and Shields, H.C. (1999) Indoor ozone/terpene reactions as a source of indoor particles, *Atmos. Environ.*, **33**, 2301–2312.

Wilkins, C.K., Wolkoff, P., Clausen, P.A., Hammer, M. and Nielsen, G.D. (2003) Upper airway irritation of terpene/ozone oxidation products (TOPS). Dependence on reaction time, relative humidity and initial ozone concentration, *Toxicol. Lett.*, **143**, 109–114.

Wolkoff, P., Clausen, P.A., Wilkins, C.K., Hougaard, K.S. and Nielsen, G.D. (1999) Formation of strong airway irritants in a model mixture of (+)-α-pinene/ozone, *Atmos. Environ.*, **33**, 693–698.

Wolkoff, P., Clausen, P.A., Wilkins, C.K. and Nielsen, G. (2000) Formation of strong airway irritants in terpene/ozone mixtures, *Indoor Air*, **10**, 82–91.