Indoor Air 2011; 21: 400–409
wileyonlinelibrary.com/journal/ina
Printed in Singapore. All rights reserved

INDOOR AIR
doi:10.1111/j.1600-0668.2011.00718.x

Hydroxyl radical yields from reactions of terpene mixtures with ozone

Abstract Chamber studies were conducted to quantify hydroxyl radical (OH·) yields and to determine whether water vapor affected OH· formation in the reactions of ozone (O_3) with a single terpene, two-component terpene mixtures, and a commercial pine oil cleaning product (POC). Solid-phase microextraction fibers (SPME) were used for sampling the terpenes and the 2-butanone formation from the hydroxyl reaction with 2-butanol as a measure of OH· yields. Analyses were performed using gas chromatography with flame ionization detection. The individual terpenes' OH· yields from α-terpineol, limonene, and α-pinene were 64 ± 8%, 64 ± 6%, and 76 ± 6%, respectively. OH· yields were also measured from two-component mixtures of these terpenes. In each mixture that contained α-terpineol, the overall OH· yield was lower than the modeled OH· yields of the individual components that comprised the reaction mixture. Reactions of a commercial POC with O_3 were also studied to determine how the individual terpenes react in a complex mixture system, and an OH· formation yield of 51 ± 6% was measured. Relative humidity did not have a significant effect on the OH· formation in the mixtures studied here.

C. D. Forester, J. R. Wells

Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, Morgantown, WV, USA

Key words: Hydroxyl radical yields; Ozone; α-terpineol; Solid-phase microextraction fibers; Commercial cleaning products.

J. R. Wells
Exposure Assessment Branch
Health Effects Laboratory Division
National Institute for Occupational Safety and Health
1095 Willowdale Road, Morgantown
WV 26505, USA
Tel.: 1-304-285-6341
Fax: 1-304-285-6041
e-mail: ozw0@cdc.gov

Received for review 28 September 2010. Accepted for publication 22 March 2011.

Practical Implications
The data presented here demonstrate that mixtures may react differently than the sum of their individual components. By investigating the chemistry of mixtures of chemicals in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products have on indoor environments.

Introduction

Terpenes and terpenoids are one of the largest groups of biogenic volatile organic compounds (VOCs) consisting of over 30,000 chemicals (Breitmaier, 2006; Guenther et al., 1995). They are often hydrocarbons with the chemical formula $(C_5H_8)_n$ but also include alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters (Breitmaier, 2006). Terpenes function as a natural odor attractant in plants for specific insects and because of these pleasant aromas, are frequently incorporated as fragrances in commercial cleaning and air-freshening products used indoors (Singer et al., 2006b). They have excellent solvent properties and are biodegradable, which has led to their inclusion in formulations as suitable replacements for phased-out chemical solvents such as trichloroethane (FPPP, 1998). In 2009, environmental-friendly cleaning products accounted for a $339 million share of the $5 billion cleaning product market (Marketwire, 2010) (RAM, 2009). VOCs emitted by cleaning products and air fresheners during application may react in the gas-phase or on surfaces with initiator species present indoors including ozone (O_3), the hydroxyl radical (OH·), and the nitrate radical (NO_3·). These reactions produce a variety of oxygenated organic species, such as aldehydes, ketones, carboxylic acids and hydroperoxides, which may cause adverse health effects to building occupants (Jarvis et al., 2005). Also, reactions of terpenes with O_3, OH·, and NO_3· are known to form precursors that contribute to the formation of secondary organic aerosols (SOA) (Johnson and Marston, 2008).

Ozone reactions with unsaturated terpenes contribute to additional reactivity indoors because these reactions produce oxygenated organic products and OH·. This additional OH· can further react with VOCs leading to additional increases in the formation of oxygenated species (Aschmann et al., 2002; Chew and Atkinson, 1996; Fick et al., 2002; Paulson et al., 1998;

Destaillats et al., 2006; Fan et al., 2003; Weschler and Shields, 1997, 1996).

Ozone reactions with terpenes proceed through a cycloaddition mechanism to form a cyclic primary ozonide. This highly energetic ozonide rapidly decomposes to a Criegee intermediate (CI) that can unimolecularly rearrange, leading to direct OH· formation or decompose through a series of reactions that may or may not produce OH·. A possible reaction mechanism for direct OH· production from the ozonolysis of α-terpineol is shown in Figure 1 and is based on current literature (Aschmann et al., 2002; Kroll et al., 2001b; Paulson et al., 1998; Johnson and Marston, 2008).

Several studies have measured OH· yields formed from the ozonolysis of individual alkenes (Aschmann et al., 2002; Atkinson and Aschmann, 1993; Chew and Atkinson, 1996; Paulson et al., 1998; Rickard et al., 1999; Siese et al., 2001). Those data provide valuable information for the estimation of OH· concentration in indoor environments. However, predictions or measurements of OH· yields from the mixtures of chemicals are lacking but needed to more accurately understand indoor environment chemistry. In the work presented here, three common monoterpenes, limonene, α-pinene, and α-terpineol (Figure S7 in Supporting Information), were studied because each of these terpenes has a high annual production volume and their use in commercial products is increasing. Hydroxyl radical yields of these terpenes were measured individually and from two-component mixtures. Hydroxyl radical yields were also measured from O_3 reactions with a common pine oil cleaning product (POC) that contained several terpenes including limonene, α-terpineol, *p*-cymene, camphene, and terpinolene (structures may be viewed in the Supporting Information). 2-Butanol was added in excess to scavenge OH· formed, and samples were collected using solid-phase microextraction fibers (SPME) and analyzed using gas chromatography with a flame ionization detector. The formation of 2-butanone was monitored to quantitatively determine the production of OH· (Aschmann et al., 2002). Studies such as this will provide valuable information regarding concurrent or sequential occupant exposures (De Rosa et al., 2004). It will also aid in the predictions of expected indoor environment chemistry of VOC mixtures.

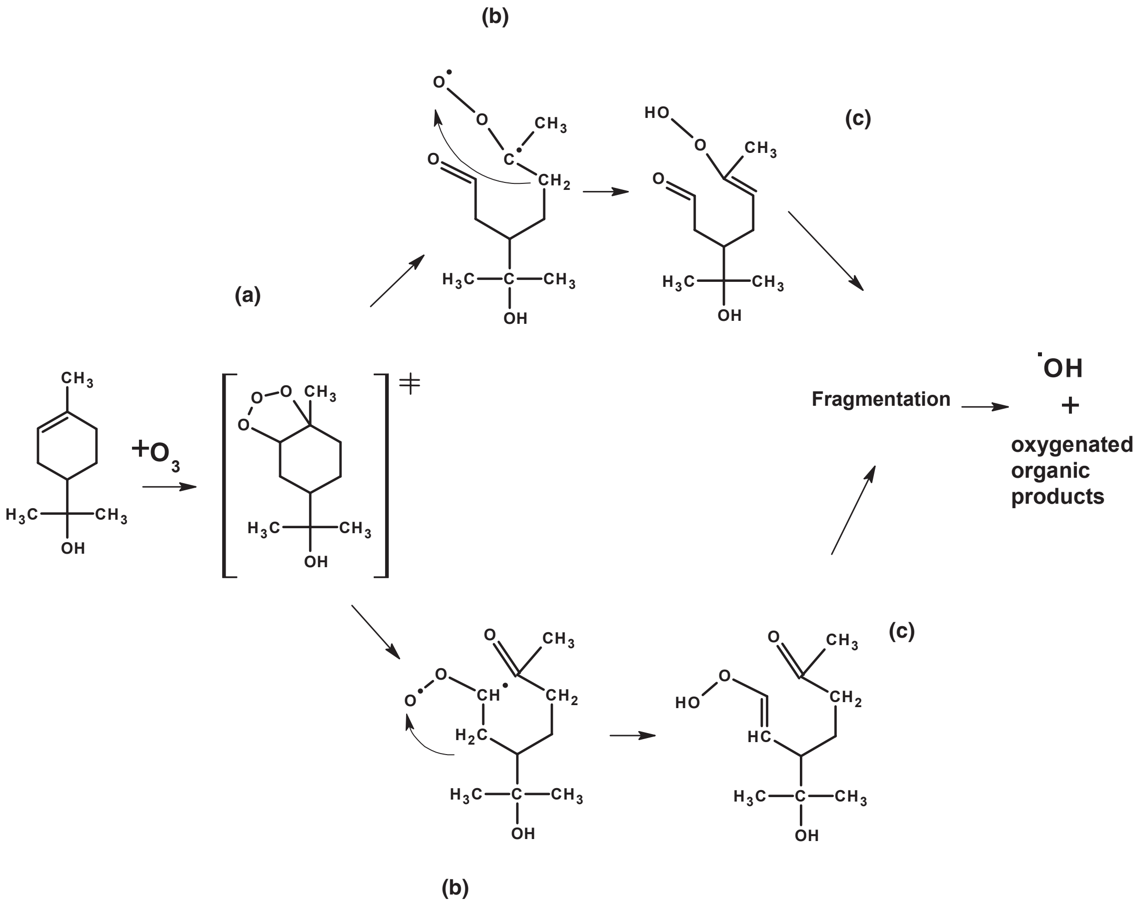

Fig. 1 Simplified ozonolysis of α-terpineol. (a) formation of energetic ozonide. (b) Criegee intermediate. (c) further reactions and fragmentation to oxygenated organic compounds and OH

Experimental methods

Experiments to measure the gas-phase formation of the OH· were conducted with a previously described apparatus (Forester et al., 2007). A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok (Solon, OH, USA) fitting attached to a 45-l Teflon-film chamber. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH, USA) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers for samples analyzed under $< 5\%$ relative humidity (RH) conditions and measured with a 0–100 l/min mass flow controller (MKS, Andover, MA, USA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed that if contaminants were present, they would be below the part per trillion range. For samples analyzed at 50% RH, the dry air from the NIOSH facility flowed through a mass flow controller and into a humidifying chamber where it encountered water and left the chamber nearly saturated. It then passed into a mixing chamber where it was mixed with dry air to a predetermined humidity. The filler system was equipped with a syringe injection port facilitating the introduction of liquid reactants into the chamber. All reactant mixtures and calibration standards were generated by this system.

Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA, USA) in a separate Teflon chamber and transferred using a gas-tight syringe. An additional port was incorporated into the Teflon reaction chamber to facilitate the injection of ozone. The ozone concentration was measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C. The gas-phase mixtures were allowed to react for at least 30 min after each addition of O_3. No steps were taken to prevent secondary reactions between O_3 and reaction products formed but conditions were controlled to minimize side reactions. The O_3 concentration was kept low enough to ensure it was the limiting reagent. The terpene compounds' concentrations were consistent with those typically found in the indoor environment after simulated cleaning product application (Rastogi et al., 2001; Singer et al., 2006b). Typical initial terpene concentrations in the reaction chamber for single compounds and simple mixtures were 0.2 – 1.0 ppm (4.9×10^{12}–2.5×10^{13} molecules/cm^3). Typically, three additions of O_3 with approximate concentrations of 0.03–0.08 ppm (7.4×10^{11}–2.0×10^{12} molecules/cm^3) in each were added to the reaction mixture.

The volume of POC injected into the chamber was scaled from that used by Singer et al., (2006b) in investigations into the emissions of cleaning products and air fresheners when wiping a surface with a full-strength pine oil cleaner in a 50-m^3 dynamic reaction chamber. For the experimental data presented here, the full-strength POC was diluted 1:1 with water and 18 μl of this solution was injected into the 45-l chamber. The total terpene concentration inside the reaction chamber for the commercial pine oil cleaner experiments was approximately 2.0 ppm (4.9×10^{13} molecules/cm^3). Because of this higher concentration of multiple terpenes, the concentration of ozone that was injected into the chamber was also increased. Several ozone injections were added in concentrations ranging from 0.10 to 0.25 ppm (4.9×10^{13}–6.1×10^{13} molecules/cm^3) each for a total ozone addition of 1.0–1.6 ppm over the duration of the experiment.

The OH· react with 2-butanol by hydrogen abstraction primarily of the hydrogen on the alcoholic carbon to form 2-butanone (Baxley and Wells, 1998). Previous 2-butanol/OH· rate constant measurements include 8.1×10^{-12} cm^3/molecule per s (Baxley and Wells, 1998) and 8.89×10^{-12} cm^3/molecule per s (Atkinson et al., 1999). Using an average of these rate constants of 8.5×10^{-12} cm^3/molecule per s and a 2-butanol concentration of 180 ppm (4.4×10^{15} molecules/cm^3), the rate of 2-butanol/OH· reactions was calculated to be 37,000/s. This rate is 15 – 50 times greater than rates of limonene/OH· (Atkinson, 2003), α-terpineol/OH· (Wells, 2005), and α-pinene/OH· (Atkinson, 2003), which were calculated using experimental conditions described here. This suggests the 2-butanol's experimental concentration under conditions described here is sufficient to scavenge the OH· formed.

Sampling for the 2-butanone yield experiments was performed using a 75-μm carboxen-polydimethylsiloxane SPME fiber assembly (Supelco, Milwaukee, WI, USA) that was inserted into a 6.4-mm Swagelok fitting attached to the 45-l Teflon-film bag. The SPME fiber was exposed for 5 or 10 min within the bag and then inserted into the injector of an Agilent 6890 gas chromatograph with a flame ionization detector (GC/FID) with HP Chemstation software. Compound separation was achieved by a Restek (Bellefonte, PA, USA) Rtx-1701 (30-m long, 0.53-mm i.d., 1-μm thickness) column. The GC temperature program used was as follows: injection port was set to 250°C and oven temperature began at 34°C for 7 min and was ramped 0.5°C/min to 36°C and then 12°C/min to 240°C. The temperature of the FID was maintained at 250°C.

Calibration curves consisting of 3 – 5 points were generated for 2-butanone and each of the terpenes reacted for both 5- and 10-min exposure times. Commercially available standards were purchased and used for quantification. All samples were quantified by integrating the area under the peak in the GC/FID chromatogram. To ensure that competition for active sites on the SPME fiber between 2-butanol, terpene compounds, and 2-butanone was not an issue, 120 ppm 2-butanol was added to the reaction chamber with the calibration standards. Background experiments using 180 ppm of 2-butanol were also conducted and no interferences were noticed. All plots were linear throughout the calibration range with an R^2 value of >0.95 observed for each calibration curve.

SPME fibers were exposed in the α-terpineol/limonene system to determine appropriate sampling times. The peak areas from either the 5- or 10-min exposure were used for data analysis. The individual compounds and simple mixtures were sampled for 10 min, while an exposure time of 5 min was used for the POC experiments and the 50% RH experiments because of the higher concentrations of reactants in the reaction chamber.

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): α-pinene (98%), limonene (99%), α-terpineol (99%), terpinolene (90%), 2-butanol (99.5%), 2-butanone (99%), and *p*-cymene (99%) and from Fisher Scientific (Fairlawn, NJ): acetonitrile (99.5%). Helium (UHP grade), the GC carrier gas, and hydrogen (UHP) and Zero Air for the FID were supplied by Amerigas (Sabraton, WV, USA) and used as received. Experiments were carried out at 297 ± 3 K.

Kinetic model

One of the objectives of this research was to attempt to predict the overall OH· yield from a mixture of compounds using the OH· yields of the individual compounds and a ratio of their concentrations in the mixture. Because all of the individual OH· yields ranged from 64% to 76% for the compounds studied here, it is anticipated that the OH· yield from the mixture should also be within this range. To further support this, a kinetic model was developed based on the individual terpene yields, concentrations, and O_3 rate constants. This model is similar to one proposed by Pryor and Uppu for investigating competitive reactions of ozone with amino acids (Pryor and Uppu, 1993).

The fraction of ozone expected to react with an individual terpene (F_j) may be determined using Equation 1.

$$F_j = \frac{k_j[\text{terpene}]_j}{\sum_{i=1}^{n} k_i[\text{terpene}]_i}. \tag{1}$$

This equation is based on the initial concentrations of each terpene and their respective ozone rate constants, where k_j is the *j*th terpene's O_3 rate constant that is multiplied by its concentration and divided by the sum of all reactive terpenes' O_3 rate constants multiplied by their respective concentrations. To obtain the individual terpene's contribution to the overall OH· yield, F_j is multiplied by the terpene's measured OH· yield (Y_j) in equation 2.

$$\text{OH yield}_{\text{terpene}\,j} = F_j Y_j. \tag{2}$$

The values for all terpenes are summed in equation 3 to obtain the overall OH· yield for the mixture.

$$\text{OH yield}_{\text{mix}} = \sum\nolimits_{i=1}^{n} F_i Y_i. \tag{3}$$

Results

The formation yield of 2-butanone from the reactions of 2-butanol with OH· has been measured previously (Aschmann et al., 2002; Baxley and Wells, 1998; Chew and Atkinson, 1996). Chew and Atkinson measured a formation yield of 0.69 ± 0.06 (Chew and Atkinson, 1996), Baxley and Wells measured 0.60 ± 0.02 (Baxley and Wells, 1998), and Aschmann et al. reported 0.695 ± 0.073 (Aschmann et al., 2002). For this work, an average of the three studies was used to convert the 2-butanone yield to the hydroxyl radical yield by dividing the 2-butanone yield by 0.66. The loss of the terpene, or combined loss of terpenes in mixtures, was plotted against the formation of 2-butanone, generating a straight line with the slope equal to the 2-butanone yield. The error in each yield value is the 95% confidence level (2 standard deviations) from the random uncertainty in the slope.

Single compounds

The 2-butanone and OH· yields from the individual limonene, α-pinene, and α-terpineol reactions with O_3 at $<5\%$ RH were measured and are listed in Table 1 along with plots of the 2-butanone yields in Figure 2. Hydroxyl radical yields from α-pinene/O_3 reactions have been measured by several research groups using multiple techniques, resulting in an average OH· yield of 81% with a standard deviation between the studies

Table 1 2-Butanone and hydroxyl radical yields from ozone reactions with individual terpenes

Compound <5% relative humidity	2-Butanone % yield	Hydroxyl radical % yield	Literature value % yield
Limonene	42 ± 4	64 ± 6	67 ± 10[a]
α-Pinene	50 ± 4	76 ± 6	81 ± 8[b]
α-Terpineol	42 ± 5	64 ± 8	–

[a] From Aschmann et al., 2002.

[b] Average of values from references, Aschmann et al., 2002; Atkinson et al., 1992; Paulson et al., 1998; Rickard et al., 1999; Siese et al., 2001.

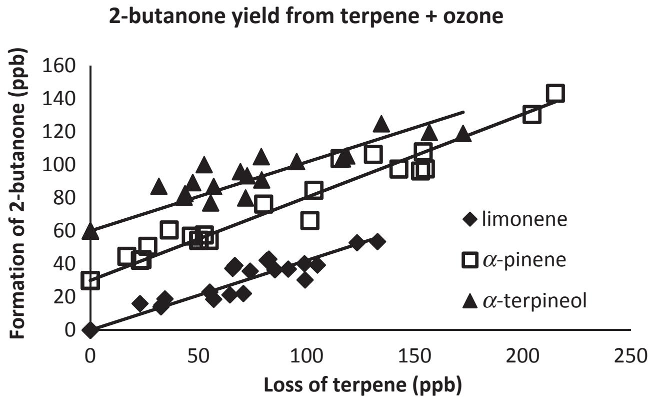

Fig. 2 2-Butanone and OH· yields from individual terpenes: ◆ Limonene: 2-butanone yield = 42 ± 4% yield, OH· yield = 64 ± 6%; ☐ α-Pinene: 2-butanone yield = 50 ± 4% yield, OH· yield = 76 ± 6% (offset vertically by 30 ppb for clarity); and ▲ α-Terpineol: 2-butanone yield = 46 ± 5% yield, OH· yield = 64 ± 8% (offset vertically by 60 ppb for clarity)

of 8% (Atkinson, 2003; Atkinson et al., 1992; Paulson et al., 1998; Rickard et al., 1999; Siese et al., 2001). The result of 76 ± 6% reported here using SPME fibers for sampling is within experimental error of these previous results. The OH· yield from limonene/O_3 reactions reported here is 64 ± 6%, which agrees with the Ashmann et al. experimental result of 67 ± 10% (Aschmann et al., 2002). The OH· yield from α-terpineol/ozone reaction was measured in this work to be 64 ± 8% and has not been reported elsewhere. The agreement of the results reported here for OH· yields of α-pinene and limonene compared with literature values suggests that scavenging of OH· with 2-butanol combined with SPME sampling is an appropriate experimental method for measuring OH· yields.

Mixtures

Each two-component mixture investigation was comprised of at least three separate experiments with different terpene concentration ratios and an average of 4 O_3 injections. The initial concentration ratio in the reaction chamber was approximately equal to the inverse of the ratio of the terpene to O_3 rate constants to equalize the terpenes' reaction rates. In subsequent experiments, the concentration ratio in the reaction chamber was varied and the data from all experiments were combined and plotted to determine the 2-butanone yield (Figures S1–S6 in the Supporting Information). Table 2 contains a summary of all of the mixture yield experiments. These data suggest that the OH· yield is independent of the concentration ratio for the terpenes in the mixtures studied here.

Table 2 2-Butanone and hydroxyl radical yields from ozone reactions with mixtures of terpenes

Mixture	Relative humidity %	2-Butanone % yield	Hydroxyl radical % yield	Modeled prediction	Difference from modeled value
Limonene/α-pinene	<5	49 ± 6	74 ± 10	69	+5
α-Terpineol/limonene	<5	27 ± 2	41 ± 3	64	−23
α-Terpineol/limonene	50	26 ± 2	40 ± 3	64	−24
α-Terpineol/α-pinene	<5	35 ± 3	54 ± 5	69	−15
Commercial pine oil cleaner	<5	34 ± 4	51 ± 6	70	−19
Commercial pine oil cleaner	50	33 ± 2	50 ± 2	70	−20

Limonene/α-pinene

The 2-butanone yield from the limonene/α-pinene/O_3 reaction system with a 10-min SPME exposure time and < 5% RH was measured to be 49 ± 6% corresponding to an OH· yield of 74 ± 10%. This OH· yield agrees within experimental uncertainty with the modeled prediction of a 69% OH· yield from the mixture. Concentration ratios in the limonene/α-pinene experiments ranged from 1:1 to 1:3 with no effect on the OH· yield.

α-Terpineol/limonene

Hydroxyl radicals produced from the reaction of ozone with a mixture of α-terpineol and limonene were measured under a variety of conditions including terpene concentration ratios, sampling time, and RH and are summarized here in Table 1 and in more detail in Table S1 in the Supporting Information. Concentration ratios for α-terpineol/limonene experiments were varied from 1:5 to 7:1. A 2-butanone yield of 27 ± 2% was measured for samples analyzed with < 5% RH and SPME exposure times of both 5 and 10 min. This corresponds to an OH· yield of 41 ± 3%, which is 23 percentage points lower than the modeled OH· yield of 64%.

Experiments to evaluate the effects of water vapor on the OH· yield from the α-terpineol/limonene/O_3 reactions were conducted using 50% RH and a 5-min exposure time. The 2-butanone yield was 26 ± 2% corresponding to a 40 ± 3% OH· yield. Comparison of this with the 41% OH· yield under < 5% RH conditions suggests that water vapor does not affect the production of OH· in this system.

α-Terpineol/α-pinene

A 2-butanone yield of 35 ± 3% from the α-terpineol/α-pinene/O_3 reaction system with a 10-min exposure time and < 5% RH was measured. This corresponds to an OH· yield of 54 ± 5%, which is 15 percentage points lower than modeled OH· yield of 69%. Concentration ratios for the α-terpineol/α-pinene experiments were varied from 1:2 to 1:4 with no apparent effect on the OH· yield.

Commercial pine oil cleaner (POC)

Five terpenes were observed and quantified in the POC experiments including limonene, terpinolene, α-terpineol, *p*-cymene, and camphene. The limonene calibration factor was used for the quantitation of *p*-cymene and camphene. α-Terpineol was present in the POC in the highest abundance, constituting approximately 50% of the total terpene concentration, followed by limonene at approximately 20% and terpinolene at approximately 15%. The *p*-cymene and camphene combined were $<20\%$ of the total terpenes in the mixture. Atkinson et al. measured a OH· yield of $\leq$ 18% from camphene/O_3 reactions (Atkinson et al., 1992) and the OH· yield from *p*-cymene/O_3 has not been measured. Because the *p*-cymene/O_3 rate constant is 5×10^{-20} cm^3/molecules per s (Atkinson et al., 1990), it is not expected to compete for ozone with the other terpenes in the POC whose rate constants ranged from 2.1×10^{-16} to 19×10^{-16} cm^3/molecules per s (Atkinson, 2003; Wells, 2005); therefore, it was not included in the OH· yield measurements or modeled calculations.

Table 2 contains modeled values obtained for each of the two-component mixtures investigated using the initial terpene concentrations used in the experiments here. The POC reactions at both $<5\%$ and 50% RH were modeled using initial experimental concentrations, and these values are also contained in Table 2.

All POC SPME exposure times were 5 min. The 2-butanone yield from the POC/ozone reactions for both $<5\%$ and 50% RH conditions is shown in Figure 3. For conditions of $<5\%$ RH, the 2-butanone yield was 34 ± 4% corresponding to an OH· yield of 51 ± 6%. Experiments conducted at 50% RH produced a 2-butanone yield of 33 ± 2% with an OH· yield of 50 ± 2%. These yields are 19 and 20 percentage points below the modeled OH· yield of 70%.

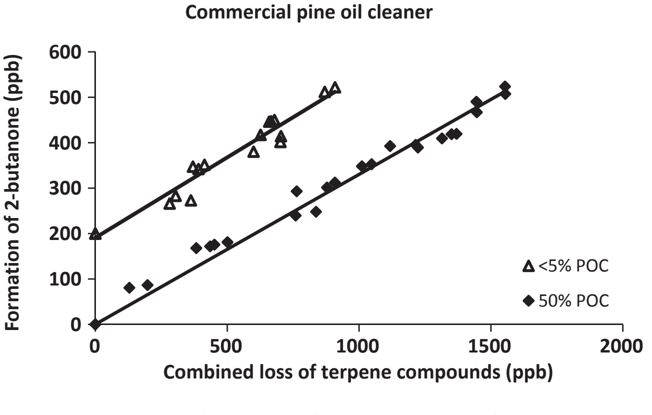

Fig. 3 2-Butanone formation from reactions of a commercial pine oil cleaner with ozone. △ Pine oil cleaning product (POC) < 5% RH, 2-butanone yield = 30 ± 3%, OH· yield = 46 ± 5% (offset vertically 200 ppb for clarity). ◆ POC 50% RH, 2-butanone yield = 28 ± 2%, OH· yield = 43 ± 3%

Discussion

Three two-component mixtures were studied here to measure OH· yields and to determine whether these yields could be predicted based on the OH· yields of individual terpene compounds in the mixture independent of concentration. In all mixtures that contained α-terpineol, the OH· yields were lower than the values predicted by the kinetic model based on the individual terpenes. This pattern was also observed in the POC experiments and is further supported by the experimental data in Table S2 in the Supporting Information. This suggests that some type of unanticipated interaction with α-terpineol occurs either prior to or after O_3 additions.

It is unlikely that reactions involving α-terpineol occurred prior to the addition of O_3. The concentrations observed during background sampling were stable over several hours, and concentrations calculated by integration of terpene peak areas corresponded to the prepared concentrations injected into the reaction chamber.

Terpenes react with ozone to form primary ozonides that quickly dissociate to CIs (Criegee, 1975; Kroll et al., 2001a; Paulson et al., 1999; Johnson and Marston, 2008). Because these CIs are highly energetic, they either undergo unimolecular reactions forming OH· and other radical species that further react to form oxygenated organic products, (Figure 4, Pathway 1), or become stabilized (Pathway 2) via gas-phase collisions forming stabilized Criegee intermediates (SCI) (Johnson and Marston, 2008). These SCI species have a lifetime long enough (<10 μs) to allow bimolecular reactions to occur that do not result in OH· production (Johnson et al., 2001). These bimolecular reactions may occur with water to form acids and/or peroxides (Johnson and Marston, 2008). It is plausible that interactions between the CI and α-terpineol could result in a SCI, thereby accounting for the lower than anticipated OH· yield.

At this time, it is not known whether the occurrence of this phenomenon can be related to the molecular structure and/or size of the compound. The lower than the modeled OH· yields were only observed in systems where α-terpineol was present. To ensure that 2-butanol was not interfering in the OH· formation mechanism, mixtures of α-pinene/limonene/O_3 were investigated. The α-pinene/limonene/O_3 OH· yield reported here is in agreement with its modeled OH· yield. This also indicates that 2-butanol, although present in high concentrations, does not appear to interact with the either the CI or the SCI to negatively affect the OH· yields. Studies are currently underway in this laboratory to further investigate α-terpineol's influence on OH· yields of terpene/O_3 systems.

The O_3 rate constants for the major terpenes comprising the POC, terpinolene, α-terpineol, and

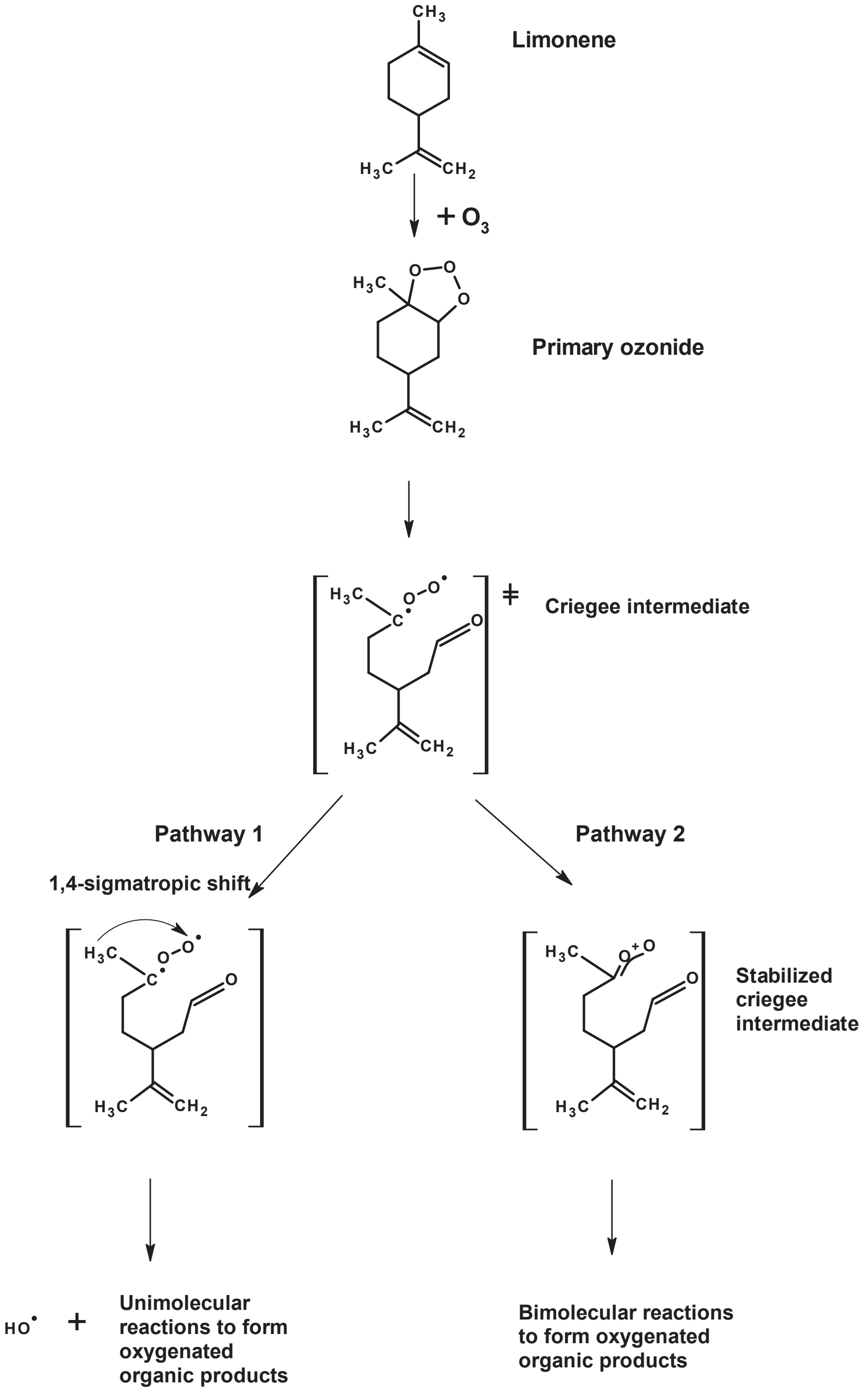

Fig. 4 Ozonolysis of limonene

limonene are 19×10^{-16} cm^3/molecules per s (Atkinson, 2003); 3×10^{-16} cm^3/molecules per s (Wells, 2005); and 2.1×10^{-16} cm^3/molecules per s (Atkinson, 2003), respectively. These compounds' removal rates after addition of O_3 were consistent with their individual terpene/O_3 rate constants (Figure 5).

A detailed tracking of the individual POC components was conducted to improve the understanding of the indoor chemistry of mixtures. The consumption of the individual POC terpene compounds, α-terpineol, terpinolene, and limonene, was monitored throughout the experiments and plotted against total ozone additions (Figure 5a). Initial terpene concentrations were α-terpineol – 1122 ppb, terpinolene – 342 ppb, and limonene – 439 ppb for an initial concentration ratio of approximately 1:3:2. Reaction rates for an initial

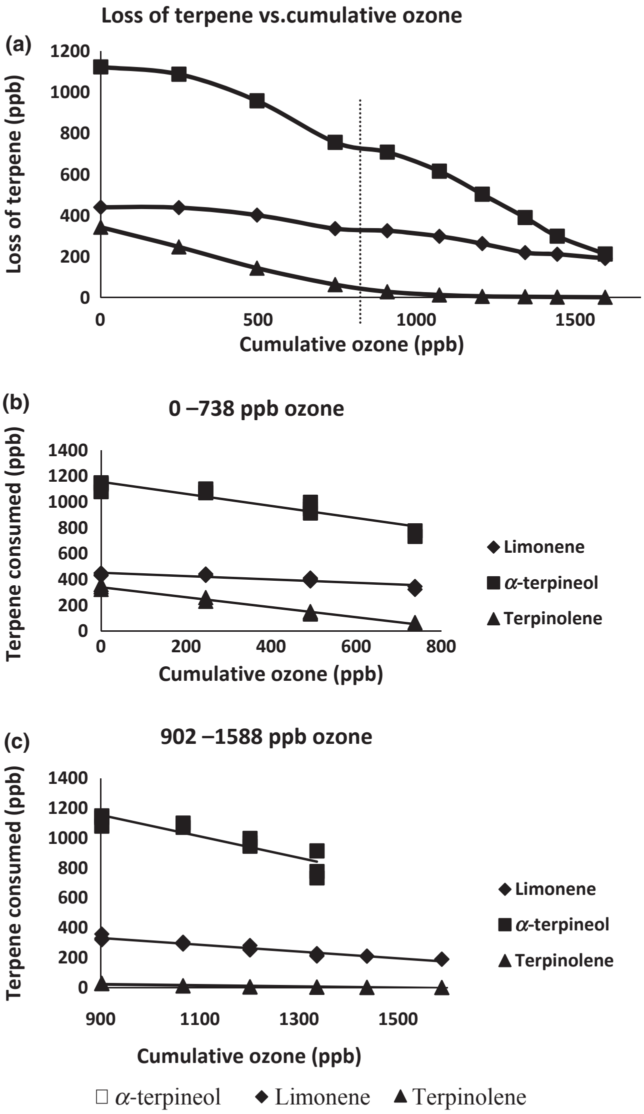

Fig. 5 Terpene consumption from pine oil cleaner (50% RH) reactions with ozone. (a) Point-to-point plot of individual terpene losses (ppb) vs. cumulative ozone (ppb). (b) Individual terpene losses with 0–738 ppb ozone, terpinolene 80% consumed. (c) Individual terpene losses with 902–1599 ppb ozone, terpinolene 100% consumed, α-terpineol 80% consumed

addition of 250 ppb O_3 were α-terpineol – 0.002/s, terpinolene – 0.012/s, and limonene – 0.001/s (Atkinson, 2003; Wells, 2005). Figure 5a is a point-to-point plot of terpene consumption vs. ozone additions. This plot is divided into Figure 5b,c with trend lines to provide a more detailed account of the behavior of the individual terpenes.

Figure 5b shows the consumption of terpenes through the cumulative additions of 738 ppb O_3. After the addition of 738 ppb of O_3, 80% of the terpinolene, 30% of α-terpineol, and 21% of limonene were consumed. Figure 5c shows terpene consumption from the cumulative additions of O_3 from 902 – 1588 ppb which marked the end of the experiment. At the termination of the experiment, more than 99% of the terpinolene, 80% of the α-terpineol, and 57% of the limonene were consumed. During this phase of the experiment, α-terpineol losses were almost double when compared with those of limonene and coincide with the calculated reaction rates. At the end of the experiment, the reaction chamber contained a mixture of approximately 1:0:1 α-terpineol/terpinolene/limonene.

Relative humidity was varied in the α-terpineol/limonene/O_3 and POC/O_3 experiments to determine whether water vapor had an effect on the OH· yields. The results from both the two-component system and the POC experiments suggest that water vapor did not affect the OH· production. The OH· yields for the samples analyzed < 5% RH and 50% RH when plotted separately, agreed within experimental error. However, even though water vapor did not affect OH· production, it may have an effect on other products formed in ozonolysis reactions. It has recently been shown that hydrogen bonding of water molecules in the gas-phase can alter the reaction kinetics and energetic barriers, thereby possibly allowing energetically unfavorable reactions to proceed (Vohringer-Martinez et al., 2010).

The total concentration of OH· formed from the 50% RH POC/ozone experiment was 782 ppb (1.9×10^{13} molecules/cm^3) in a scaled reaction system with a POC volume representative of an actual cleaning event. While these experiments were conducted in a closed system with no air exchange, surface deposition, or other loss processes to remove OH·, the data could suggest that the OH· formed from the ozonolysis reactions of cleaning product emissions could increase the indoor background OH· concentration which could result in additional VOC/OH· reactions as was seen by Singer et al. (Singer et al., 2006a). These additional reactions could further increase the formation of oxygenated organic compounds and impact building occupant exposure.

In the work presented here, SPME fibers were used to determine gas-phase OH· formation using 2-butanol to scavenge OH·. The measurements of OH· yields from limonene and α-pinene reactions with ozone agreed with previously published results. Because of possible reactivity between α-terpineol and SCIs, the experimental OH· yield was lower than the modeled OH· yield in all mixtures that contained α-terpineol. Further investigations are needed to determine whether all terpene alcohols exhibit this antagonistic effect on OH· production. However, even with decreased OH· yields, concentrations of OH· formed in gas-phase reactions of O_3 with cleaning product emissions may produce sufficient OH· to raise the indoor concentrations, thus allowing for additional gas-phase reactions with other indoor pollutants.

Disclaimer

Additional yield plots of products, terpene structures, and experimental data and theoretical yields based on concentration may be viewed in the Supporting Information.

Supporting Information

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

Fig. S1 2-Butanone yield 28 ± 2%, OH· yield = 43 ± 3% from α-terpineol/limonene/ozone reactions.
Fig. S2 2-Butanone yield 30 ± 2%, OH· yield = 45 ± 3% from α-terpineol/limonene/ozone reactions.
Fig. S3 2-Butanone yield 28 ± 3%, OH· yield = 42 ± 5% from α-terpineol/limonene/ozone reactions.
Fig. S4 2-Butanone yield 27 ± 2%, OH· yield = 41 ± 4% from α-terpineol/limonene/ozone reactions.
Fig. S5 2-Butanone yield 35 ± 3%, OH· yield = 54 ± 5% from α-terpineol/α-pinene/ozone reactions.
Fig. S6 2-Butanone yield 49 ± 6%, OH· yield = 74 ± 10% from α-pinene/limonene/ozone reactions.
Fig. S7 Structures of terpenes.
Table S1 2-Butanone and hydroxyl radical percent yields from α-terpineol/limonene mixture reactions with ozone under a variety of conditions.
Table S2 Selected experimental data.

References

Aschmann, S.M., Arey, J. and Atkinson, R. (2002) OH radical formation from the gas-phase reactions of O_3 with a series of terpenes, *Atmos. Environ.*, **36**, 4347–4355.

Atkinson, R. (2003) Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, *Atmos. Chem. Phys. Discuss.*, **3**, 4183–4358.

Atkinson, R. and Aschmann, S.M. (1993) OH radical production from the gas-phase reactions of O_3 with a series of alkenes under atmospheric conditions, *Environ. Sci. Technol.*, **27**, 1357–1363.

Atkinson, R., Hasegawa, D. and Aschmann, S.M. (1990) Rate constants for the gas-phase reactions of O_3 with a series of monoterpenes and related compounds at 296-k +/-2-k, *Int. J. Chem. Kinet.*, **22**, 871–887.

Atkinson, R., Aschmann, S.M., Arey, J. and Shorees, B. (1992) Formation of OH radicals in the gas-phase reactions of O_3 with a series of terpenes, *J. Geophys. Res. Atmos.*, **97**, 6065–6073.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J., Troe, J. and Evaluation, I.S.G.K.D. (1999) Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: supplement vii, *J. Phys. Chem. Ref. Data*, **28**, 191–393.

Baxley, J.S. and Wells, J.R. (1998) The hydroxyl radical reaction rate constant and atmospheric transformation products of 2-butanol and 2-pentanol, *Int. J. Chem. Kinet.*, **30**, 745–752.

Breitmaier, E. (2006) *Terpenes: Flavors, Fragrances, Pharmaca, Pheromones*, Weinheim, Germany, Wiley-VCH.

Chew, A.A. and Atkinson, R. (1996) OH radical formation yields from the gas-phase reactions of O_3 with alkenes and monoterpenes, *J. Geophys. Res. Atmos.*, **101**, 28649–28653.

Criegee, R. (1975) Mechanism of ozonolysis, *Agnew. Chem. Int. Ed*, **14**, 745.

De Rosa, C.T., El-Masri, H.A., Pohl, H., Cibulas, W. and Mumtaz, M.M. (2004) Implications of chemical mixtures in public health practice, *J. Toxicol. Environ. Health, Part B: Crit. Rev.*, **7**, 339–350.

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.

Fan, Z.H., Lioy, P., Weschler, C., Fiedler, N., Kipen, H. and Zhang, J.F. (2003) Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions, *Environ. Sci. Technol.*, **37**, 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, *Atmos. Environ.*, **36**, 3299–3308.

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, *Atmos. Environ.*, **41**, 1188–1199.

FPPP (1998) Florida pollution prevention program pollution prevention fact sheet industrial cleaning #6 terpene cleaners Fppp 1998, http://www.p2pays.org/ref/17/16066.pdf April 26, 2011.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P. (1995) A global-model of natural volatile organic-compound emissions, *J. Geophys. Res. Atmos.*, **100**, 8873–8892.

Jarvis, J., Seed, M.J., Elton, R.A., Sawyer, L. and Agius, R.M. (2005) Relationship between chemical structure and the occupational asthma hazard of low molecular weight organic compounds, *Occup. Environ. Med.*, **62**, 243–250.

Johnson, D. and Marston, G. (2008) The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere, *Chem. Soc. Rev.*, **37**, 699–716.

Johnson, D., Lewin, A.G. and Marston, G. (2001) The effect of Criegee-intermediate scavengers on the OH yield from the reaction of ozone with 2-methylbut-2-ene, *J. Phys. Chem. A*, **105**, 2933–2935.

Kroll, J.H., Clarke, J.S., Donahue, N.M., Anderson, J.G. and Demerjian, K.L. (2001a) Mechanism of hox formation in the gas-phase ozone-alkene reaction. 1. Direct, pressure-dependent measurements of prompt OH yields, *J. Phys. Chem. A*, **105**, 1554–1560.

Kroll, J.H., Sahay, S.R., Anderson, J.G., Demerjian, K.L. and Donahue, N.M. (2001b) Mechanism of hox formation in the gas-phase ozone-alkene reaction. 2. Prompt versus thermal dissociation of carbonyl oxides to form OH, *J. Phys. Chem. A*, **105**, 4446–4457.

Marketwire (2010) U.S. Market for green household cleaning products enters forefront of consumer consciousness with shift toward more eco-friendly and sustainable lifestyles, http://www.marketwire.com/press-release/US-Market-Green-Household-Cleaning-Products-Enters-Forefront-Consumer-Consciousness-1265177.htm April 26, 2011.

Paulson, S.E., Chung, M., Sen, A.D. and Orzechowska, G. (1998) Measurement of OH radical formation from the reaction of ozone with several biogenic alkenes, *J. Geophys. Res. Atmos.*, **103**, 25533–25539.

Paulson, S.E., Chung, M.Y. and Hasson, A.S. (1999) OH radical formation from the gas-phase reaction of ozone with terminal alkenes and the relationship between structure and mechanism, *J. Phys. Chem. A*, **103**, 8125–8138.

Pryor, W.A. and Uppu, R.M. (1993) A kinetic-model for the competitive reactions of ozone with amino-acid-residues in proteins in reverse micelles, *J. Biol. Chem.*, **268**, 3120–3126.

RAM (2009) Research and markets; Environmentally friendly cleaning products in the united states Ram 2009 http://www.researchandmarkets.com/reportinfo.asp?report_id = 693872 April 26, 2011.

Rastogi, S.C., Heydorn, S., Johansen, J.D. and Basketter, D.A. (2001) Fragrance chemicals in domestic and occupational products, *Contact Dermatitis*, **45**, 221–225.

Rickard, A.R., Johnson, D., Mcgill, C.D. and Marston, G. (1999) OH yields in the gas-phase reactions of ozone with alkenes, *J. Phys. Chem. A*, **103**, 7656–7664.

Siese, M., Becker, K.H., Brockmann, K.J., Geiger, H., Hofzumahaus, A., Holland, F., Mihelcic, D. and Wirtz, K. (2001) Direct measurement of OH radicals from ozonolysis of selected alkenes: a euphore simulation chamber study, *Environ. Sci. Technol.*, **35**, 4660–4667.

Singer, B.C., Coleman, B.K., Destaillats, H., Hodgson, A.T., Lunden, M.M., Weschler, C.J. and Nazaroff, W.W. (2006a) Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone, *Atmos. Environ.*, **40**, 6696–6710.

Singer, B.C., Destaillats, H., Hodgson, A.T. and Nazaroff, W.W. (2006b) Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids, *Indoor Air*, **16**, 179–191.

Vohringer-Martinez, E., Tellbach, E., Liessmann, M. and Abel, B. (2010) Role of water complexes in the reaction of propionaldehyde with OH radicals, *J. Phys. Chem. A*, **114**, 9720–9724.

Wells, J.R. (2005) Gas-phase chemistry of alpha-terpineol with ozone and OH radical: rate constants and products, *Environ. Sci. Technol.*, **39**, 6937–6943.

Weschler, C.J. and Shields, H.C. (1996) Production of the hydroxyl radical in indoor air, *Environ. Sci. Technol.*, **30**, 3250–3258.

Weschler, C.J. and Shields, H.C. (1997) Measurements of the hydroxyl radical in a manipulated but realistic indoor environment, *Environ. Sci. Technol.*, **31**, 3719–3722.