INVESTIGATING INDOOR CHEMISTRY OF TERPINOLENE THROUGH THE USE OF A NEW DERIVATIZATION AGENT

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SUMMARY

The gas-phase ozonolysis of terpinolene was investigated using a new carbonyl derivatization agent: O-*tert*-butylhydroxylamine hydrochloride (TBOX). Reaction products from the terpinolene/O_3 system were collected in a water-filled impinger, TBOX was added, and the mixture was heated to 70°C for two hours followed by extraction with 0.5 mL toluene. Using this lower molecular weight derivatization agent resulted in the observation of a tricarbonyl reaction product: 3,6-dioxoheptanal. Additionally, three other carbonyl compounds were observed: methyl glyoxal, 4-methylcyclohex-3-en-1-one, and 6-oxo-3-(propan-2-ylidene)heptanal. The mechanism(s) for formation of these compounds is most likely due to O_3 addition to terpinolene's carbon-carbon double bonds while the tricarbonyl formation may be due to a reaction from secondary OH• radicals. Understanding the formation of di- and tricarbonyl species as a result of terpene ozonolysis is an important element of indoor occupant exposure assessment.

INTRODUCTION

Terpenes are introduced indoors by outdoor ventilation, emissions from building materials, and the use of various cleaning products (Nazaroff and Weschler, 2004). In indoor environments these terpenes can react with oxidants such as ozone (O_3), the nitrate radical (NO_3•) and the hydroxyl radical (OH•) in the gas phase and/or on indoor surfaces and can transform into oxygenated organic and/or nitrated species. An indoor ozone concentration of 1×10^{12} molecules/cm^3 (50 parts per billion) (ppb) has been typically measured or estimated (Sarwar et al., 2002). Using 50 ppb O_3 and a typical terpene/ozone reaction rate constant (2-20 x 10-16 cm^3 $molec^{-1}$ s^{-1}) , terpene removal rates in the range of 0.9 – 9 h^{-1} are calculated which is faster than 0.6 h^{-1} of typical indoor air exchange (Wilson et al., 1996).

The terpene/O_3 reaction products for terpene normally found indoors encompass a wide variety of oxygenated organic compounds. These reactions proceed by addition to carbon-carbon double bonds which leads to carbon ring opening or fragmentation reactions and the secondary formation of OH• (Atkinson and Arey, 2003). The reaction products formed include: aldehydes, ketones, dicarbonyls, carboxylic acids, and organic nitrates (e.g. hydroxynitrates, dinitrates, etc.) (Atkinson and Arey, 2003; Spittler et al., 2006; Wangberg et al., 1997). It is expected that many of these compounds may have harmful health effects and should be characterized. All of these oxygenated organic compounds have the potential to induce a respiratory response, including work related asthma (WRA) (Magnano et al., 2009). Thus, identifying the terpene/O_3 reaction products for terpenes typically present indoors is critical to characterize occupant exposure (Makela et al., 2011; McHugh et al., 2010; Quirce and Barranco, 2010).

Terpinolene (1-methyl-4-(propan-2ylidene)cyclohexene) is a ubiquitous compound in consumer products used in indoor environments. Due to its volatility and two carbon-carbon double bonds, terpinolene reacts with O_3 approximately nine times faster than limonene. In a gas-phase mixture of terpenes such as limonene and α-terpineol, terpinolene is preferentially oxidized by O_3. This highlights the need to identify the oxidation products of terpinolene as a guide for understanding exposures and potential health effects.

METHODOLOGIES

The experimental method used to investigate the gas-phase ozonolysis of terpinolene is similar to a recent investigation of limonene ozonolysis (Wells and Ham, 2014). Briefly, 50 ppb of O_3 was added to 80 L of air in a Teflon chamber containing approximately 2 ppm of terpinolene. This mixture was allowed to react for 30 minutes then 60 L of this mixture was pulled through a 60 mL Teflon impinge containing 25 mL of deionized water. To this collected sample 100 µL of 250mM aqueous O-*tert*-butylhydroxylamine hydrochloride (TBOX) was added. This sample was then heated in a 70 ^{o}C water bath for 2 h to initiate the derivatization of carbonyl compounds to oximes (Wells and Ham, 2014). After cooling the sample 0.5mL of toluene was added and the sample was shaken to extract the oximes into the toluene layer. Then 100 uL of the toluene layer was removed and placed into an auto-sampler vial and 1 uL was injected into the analysis system.

All samples were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 µm film thickness) column and the following GC oven parameters: 40 ^{o}C for 2 min., then 5 ^{o}C min^{-1} to 200 ^{o}C, then 25 ^{o}C min^{-1} to 280 ^{o}C and held for 5 min. One µL of each sample was injected in the splitless mode, and the GC injector was returned to split mode 5 min after sample injection, with the following injector temperature parameters: 130 ^{o}C for 2 min then 200 ^{o}C min^{-1} to 300 ^{o}C and held for 10 min. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from *m/*z 40-650.

RESULTS AND DISCUSSION

In Figure 1 below the chromatograms of terpinolene only and terpinolene/O_3 are compared. The peaks observed are the derivatized carbonyl compounds formed as a result of the terpinolene/O_3 reaction.

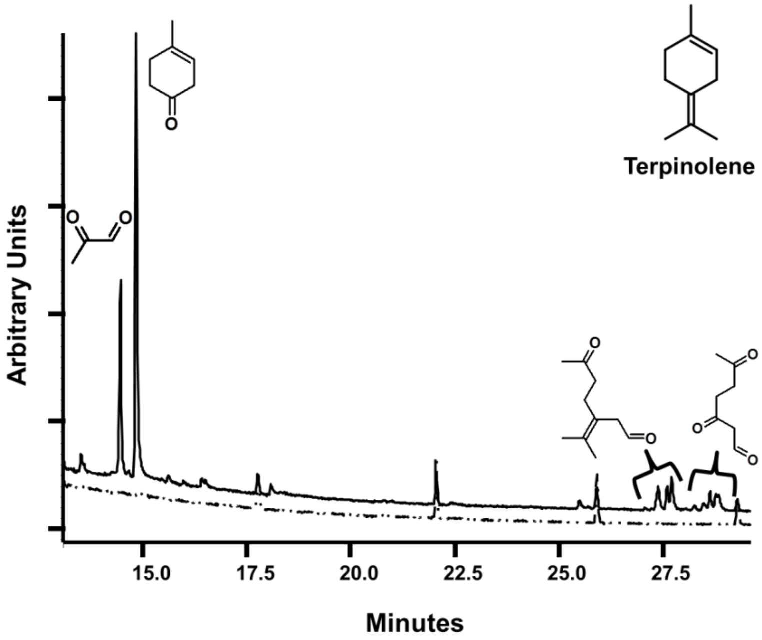

Figure 1. The terpinolene only (dashed line) versus terpinolene/O_3 (solid line) chromatograms are compared. The chromatograms are vertically shifted slightly for clarity. The peaks observed from terpinolene/O_3 system are identified as reaction products and the reaction product structures are shown next to peaks.

The gas-phase oxidation products identified by retention time (in parentheses) are: methyl glyoxal (14.5 min), 4-methylcyclohex-3-en-1-one (14.8 min), 6-oxo-3-(propan-2-ylidene)heptanal (27.4-27.7 min), and 3,6-dioxoheptanal (28.2-28.8 min).

The terpinolene oxidation products observed are similar to previously published results (Harrison and Wells, 2013). The significant difference in the data presented here is the observation of the tricarbonyl species which would not have been possible using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) because the resultant PFBHA oxime (727 amu) would be outside the 650 amu mass range of the mass spectrometer. The formation mechanism of the tricarbonyl, 3,6-dioxoheptanal, is most likely the result of secondary OH• addition to the carbon-carbon double bond of the dicarbonyl 6-oxo-3-(propan-2-ylidene)heptanal. The likely OH• dependence of 3,6-dioxoheptanal is similar to recently published results for tricarbonyl formation in the limonene/O_3 reaction system (Wells and Ham, 2014).

The detection of gas-phase tricarbonyl reaction products could be important results for exposure assessment, terpene mechanism modeling, and particulate formation models.

CONCLUSIONS

The detection of a tricarbonyl reaction product from terpinolene ozonolysis was achieved using a lower molecular weight carbonyl derivatization agent – TBOX. The advantages of this aqueous procedure could be utilized by indoor field sampling efforts. Future work will include the incorporation of TBOX with other derivatization agents in order to identify many other oxygenated species such as alcohols, carboxylic acids and organic nitrates simultaneously in a single sample.

DISCLAIMER

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the Centers for Disease Control and Prevention/the Agency for Toxic Substances and Disease Registry. Mention of any commercial product or trade name does not constitute endorsement by the Centers for Disease Control and Prevention/NIOSH.

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