



A new agent for derivatizing carbonyl species used to investigate limonene ozonolysis



J.R. Wells*, Jason E. Ham

Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Road, Morgantown, WV 26505, USA

HIGHLIGHTS

- Lower molecular weight agent for carbonyl derivatization.
- Aqueous collection and derivatization of gas-phase dicarbonyls and limonene ozonolysis products.
- Multi-functional carbonyls detected from limonene ozonolysis

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ABSTRACT

A new method for derivatizing carbonyl compounds is presented. The conversion of a series of dicarbonyls to oximes in aqueous solution and from gas-phase sampling was achieved using *O*-*tert*-butylhydroxylamine hydrochloride (TBOX). Some advantages of using this derivatization agent include: aqueous reactions, lower molecular weight oximes, and shortened oxime-formation reaction time. Additionally, the TBOX derivatization technique was used to investigate the carbonyl reaction products from limonene ozonolysis. With ozone (O_3) as the limiting reagent, four carbonyl compounds were detected: 7-hydroxy-6-oxo-3-(prop-1-en-2-yl)heptanal; 3-Isopropenyl-6-oxoheptanal (IPOH), 3-acetyl-6-oxoheptanal (3A6O) and one carbonyl of unknown structure. Using cyclohexane as a hydroxyl (OH^\bullet) radical scavenger, the relative yields (peak area) of the unknown carbonyl, IPOH, and 3A6O were reduced indicating the influence secondary OH radicals have on limonene ozonolysis products. The relative yield of the hydroxy-dicarbonyl based on the chromatogram was unchanged suggesting it is only made by the limonene + O_3 reaction. The detection of 3A6O using TBOX highlights the advantages of a smaller molecular weight derivatization agent for the detection of multi-carbonyl compounds. The use of TBOX derivatization if combined with other derivatization agents may address a recurring need to simply and accurately detect multi-functional oxygenated species in air.

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1. Introduction

Occupants are exposed to a number of chemicals (either by inhalation or through skin absorption) in the indoor environment by: emissions from building materials (e.g. vinyl and linoleum floorings, carpets, treated woods, office furniture, etc.), applications of paints, lacquers, cleaning agents, air fresheners, and formation of reaction products of indoor chemistry. These chemicals are mainly composed of volatile organic compounds (VOCs) and semi-VOCs that may act as a single irritant or combine in mixtures resulting in a synergistic effect. The key to

unraveling the complexity of indoor chemical exposures is to first identify those compounds which are suspected irritants and determine their expected concentrations indoors. The challenges in accurately characterizing the indoor environment are in the sheer number of compounds found indoors and the fact that most are not directly detectable by typical analytical methods due to either their instability during the analytical procedure or short lifespan.

In general, the specific health effects of many of the VOCs and semi-VOCs that have been identified indoors have been studied (Anderson et al., 2012, 2010, 2007; Banerjee and Annesi-Maesano, 2012; Billionnet et al., 2011; de Blas et al., 2012; Gallego et al., 2012; Mizukoshi et al., 2010; Nyrud et al., 2012; Peng et al., 2013; Wang et al., 2011; Yu and Kim, 2012; Zhou et al., 2011). However, the presence of these compounds does not fully explain the irritation

* Corresponding author.

E-mail addresses: rwells@cdc.gov, ozw0@cdc.gov (J.R. Wells).

levels that have been observed/reported in epidemiological literature (Annesi-Maesano et al., 2012; Dalton and Jaen, 2010; Fong et al., 2010; Hulin et al., 2012; Lan et al., 2011; Lin et al., 2012; Logue et al., 2012; Milner et al., 2011; Mohai et al., 2011; SCHER, 2007). It is anticipated that these elevated irritation levels may be explained by exposure to oxidation products such as: aldehydes, ketones, dicarbonyls, carboxylic acids, and organic nitrates that elude conventional analytical methods. This is why current research efforts into improved derivatization chemistry and better analytical instrumentation/methods have received considerable attention.

The detection of carbonyl compounds, which can be significant fractions of both gas-phase and particulate matter (PM), has been a focus in characterization of both indoor and outdoor environments (Kundu et al., 2012; Leungsakul et al., 2005a, 2005b; Pan et al., 2009; Pathak et al., 2012). Furthermore, toxicological studies of dicarbonyls have implicated these compounds in both respiratory inflammation and sensitization. Anderson et al. investigated the allergic responses of dicarbonyls (such as glyoxal, methyl glyoxal, glutaraldehyde, 4-oxopentanal, and diacetyl) in a series of *in vitro* exposure studies (Anderson et al., 2010). These studies showed that exposures to a variety of these dicarbonyls lead to increased expression of inflammatory cytokines such as IL-6, IL-8, and TNF- α . These results indicated that dicarbonyls stimulate the release of proinflammatory mediators from lung epithelial cells and suggest that these oxygenated products may be contributing to adverse health effects. A recent publication by (Wolkoff et al., 2013) suggested that indoor terpene oxidation conditions leading to 4-oxopentanal and/or 3-isopropenyl-6-oxoheptanal (IPOH) formation parameters should be more accurately characterized based on the carbonyls' derived human reference values for sensory irritation. There has been increasing interest in structure reactivity models for respiratory sensitization/irritation and some models identified associations between number of functional groups (carbonyl, alcohol, carboxylic acid, etc.) in a molecule, exposure to that molecule, and occupational asthma (Dworak et al., 2013; Enoch et al., 2012; Jarvis et al., 2005; Mekenyan et al., 2014; Pralong et al., 2013; Tarlo and Lemiere, 2014). Clearly these concepts between terpene oxidation and health effects are still developing, and data is still needed to meaningfully assess air quality.

For carbonyl compounds there have been numerous publications regarding detection and quantification using either dinitrophenyl hydrazine, methoxyamine, or *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyamine (PFBHA) (Cirera-Domenech et al., 2013; Dai et al., 2012; Forester and Wells, 2009; Gomez Alvarez et al., 2012; Halket and Zaikin, 2005; Hudson et al., 2011; Kowalewski and Gierczak, 2011; Lopez-Aparicio and Hak, 2013; Rossignol et al., 2012). Current methodologies have included derivatization techniques to transform these compounds for gas chromatography/mass spectrometry (GC/MS) detection. Derivatization is required for these compounds as they thermally degrade during injection or during the GC oven ramp. Two common derivatization agents used for carbonyl compounds are dinitrophenyl hydrazine (DNPH) and PFBHA (Borras and Antonio Tortajada-Genaro, 2012; Bunkoed et al., 2012; Cirera-Domenech et al., 2013; Dai et al., 2012; Pacolay et al., 2008; Yu et al., 1998). Both of these methods have been successfully used to improve understanding of volatile organic compound oxidation mechanisms. There are some limitations using these methods such as 24-h derivatization reaction times, formation of oximes with 700+ molecular weights, and multiple sample processing steps. A derivatization agent that could reduce or eliminate these limitations would benefit both oxidation research as well as indoor/outdoor field sampling campaigns.

A new method has been developed for simultaneous detection of multiple carbonyl compounds in aqueous samples driven, in part, by the identified need to use lower molecular weight derivatization agents in the characterization of reaction products from terpene oxidation. Aqueous sample collection simplified trapping of gaseous species and added a point of practicality for potential incorporation into field sampling campaigns. This method was developed using a mixture of commercially available dicarbonyls and then utilized to investigate gas-phase limonene ozonolysis. The selection of *O*-*tert*-butylhydroxylamine hydrochloride (TBOX) was based on the successful oxime formation chemistry of PFBHA (Yu et al., 1998, 1995). This method provided the sensitivity, ease of use, and wide-ranging applicability needed for detection of carbonyl compounds at expected indoor air concentrations. Additionally, there has been a recent in-depth model (Carslaw, 2013) which explored both the ozone and OH \cdot radical initiated mechanisms of limonene oxidation chemistry. The modeling results highlighted the need to collect and identify multifunctional oxidized species resulting from terpene oxidation (Carslaw, 2013). The limonene ozonolysis data presented here was compared to this model.

2. Experimental methods

2.1. Chemicals and solvents

All compounds were used as received and had the following purities: from Sigma–Aldrich/Fluka (St. Louis, MO): *O*-*tert*-Butylhydroxylamine hydrochloride, (TBOX, 99%), limonene (99+%), toluene (HPLC grade, 99+%), cyclohexane (HPLC grade, 99+%), glyoxal (40 wt% in water), methyl glyoxal (40 wt% in water), 2,4-pentanedione (99+%), and glutaraldehyde (50 wt% in water); from TCI America (Portland, OR) 2,3-heptanedione (98%); from Fisher Scientific (Pittsburgh, PA): methanol (HPLC grade, 99.9%). Water (DI H₂O) was distilled, deionized to a resistivity of 18 M Ω cm, and filtered using a Milli-Q[®] filter system (Billerica, MA). Helium (UHP grade), the carrier gas, was supplied by Butler Gas (McKees Rocks, PA) and used as received.

Ozone (O₃) was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon chamber. Aliquots of this O₃/air mixture were added to the Teflon reaction chamber using a gas-tight syringe. O₃ concentrations were measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C.

2.2. Methods and materials

Experiments were carried out at (297 \pm 3) K and 1 atm pressure. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous CaSO₄ (Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This treated dry air from the NIOSH facility flowed through a mass flow controller and into a humidifying chamber and was subsequently mixed with dry air to the pre-determined relative humidity of 50%. The filler system was equipped with a heated syringe injection port facilitating the introduction of liquid reactants into the chamber. All reactant mixtures were generated by this system.

A 2.46 \times 10⁻⁴ M solution of dicarbonyls (glyoxal, methyl glyoxal, 2,3-heptanedione, 2,4-pentanedione, and glutaraldehyde; Table S1 of Supporting Information) in methanol was used for preparation of liquid and gas-phase samples. This mixture was utilized as a stock solution for testing derivatization chemistry (both liquid and gas-phase collection) as well as oxime chromatography and mass spectrometry.

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