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A chamber study of alkyl nitrate production formed by terpene ozonolysis in the presence of NO and alkanes

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HIGHLIGHTS

- Description of ethyl acetate as an impinger medium for collection of gas-phase organic nitrates.
- Quantified alkyl nitrate formation initiated by terpene ozonolysis for a range of ozone and NO concentrations.
- Ozone and NO concentrations near 100 ppb resulted in the highest organic nitrate yield observed, roughly 5 ppb.

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ABSTRACT

Organic nitrates are relatively long-lived species and have been shown to have a potential impact on atmospheric chemistry on local, regional, and even global scales. However, the significance of these compounds in the indoor environment remains to be seen. This work describes an impinger-based sampling and analysis technique for organic nitrate species, focusing on formation via terpene ozonolysis in the presence of nitric oxide (NO). Experiments were conducted in a Teflon film environmental chamber to measure the formation of alkyl nitrates produced from α-pinene ozonolysis in the presence of NO and alkanes using gas chromatography with an electron capture detector. For the different concentrations of NO and O_3 analyzed, the concentration ratio of $[O_3]/[NO]$ around 1 was found to produce the highest organic nitrate concentration, with $[O_3] = 100$ ppb & $[NO] = 105$ ppb resulting in the most organic nitrate formation, roughly 5 ppb. The experiments on α-pinene ozonolysis in the presence of NO suggest that organic nitrates have the potential to form in indoor air between infiltrated ozone/NO and terpenes from household and consumer products.

1. Introduction

The use of cleaning agents and air fresheners in buildings exposes occupants, especially cleaning personnel, to a wide variety of airborne chemicals (Bello et al., 2009; Gerster et al., 2014; Wolkoff et al., 1998). While many of these chemicals are deemed safe, they can react with other air contaminants to yield potentially harmful secondary products (Nazaroff and Weschler, 2004). For example, terpenes, such as α-pinene, limonene, and terpinolene, can react rapidly with ozone in indoor air producing many secondary pollutants including formaldehyde (Nazaroff and Weschler, 2004). Furthermore, it has previously been shown that ozone-terpene reactions produce the hydroxyl radical, which reacts rapidly with organic compounds, leading to the formation of other potentially toxic air pollutants (Nazaroff and Weschler, 2004; Wolkoff et al., 1998).

In the presence of NO_x ($NO + NO_2$), one class of compounds that can be generated from hydroxyl radical reactions is organic nitrates (Arey et al., 1990). Organic nitrates have been observed in the atmosphere for decades and are thought to make up a significant fraction of the total atmospheric nitrogen oxides (Day et al., 2009; Rollins et al., 2010). Hydrocarbon oxidation in the atmosphere is initiated by free radicals, particularly hydroxyl radicals (•OH), which react by hydrogen abstraction or addition (in the case of unsaturated compounds) (Monks, 2005) to form alkyl radicals (R•) which further react with oxygen to generate peroxyl radicals (RO_2•), (Reaction (1)). Peroxyl radicals can subsequently react with nitric oxide (NO) to form an alkoxyl radical and NO_2 (Reaction (2a)) or alkyl nitrates (Reaction (2b)). (Atkinson and Arey, 2003; Atkinson

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et al., 1983; Yeh and Ziemann, 2014). Furthermore, alkyl nitrates may form through alkoxyl radical reaction with NO_2 (Reaction (3)).

$$R\bullet + O_2 + M \rightarrow RO_2\bullet + M \quad (1)$$

$$RO_2\bullet + NO \rightarrow (ROONO)^* \rightarrow RO\bullet + NO_2 \quad (2a)$$

$$RO_2\bullet + NO \rightarrow (ROONO)^* \rightarrow RONO_2 \text{ (alkyl nitrate)} \quad (2b)$$

$$RO\bullet + NO_2 + M \rightarrow RONO_2 \quad (3)$$

While organic nitrates have been shown to contribute significantly to the sum total nitrogen in the atmosphere, their presence indoors has yet to be determined. Organic nitrates have the opportunity to form indoors through the same mechanisms as those formed in the troposphere. Alkenes known to have significant indoor concentrations (α-pinene, D-limonene, and α-terpinene) react with O_3 at rates faster than typical air exchange rates, producing meaningful yields of OH radicals (Forester and Wells, 2011; Weschler and Shields, 1996). Motivated by knowledge gaps in exposure assessment, significant progress has been made in detection and characterization methods for many of the oxygenated species resulting from O_3/alkene reactions; however, characterization of organic nitrate formation has been marginal.

Given the potential importance of the NO oxidation channel and the current lack of experimental data on organic nitrate formation, this study explored α-pinene ozonolysis in the presence of NO concentrations that have been measured indoors (Weschler and Shields, 1997; Weschler et al., 1994). An impinger-based technique was utilized to collect organic nitrate products formed in chamber reactions, and the products were analyzed using gas chromatography with an electron capture detector (GC-ECD). The levels of ozone and NO in the chamber were varied to identify the conditions most suitable for organic nitrate formation.

2. Experimental methods

2.1. Materials

Isopropyl nitrate (≥98.0%), isobutyl nitrate (96%), 2-ethylhexyl nitrate (97%), (+)-α-pinene (≥99%), cyclohexane (HPLC grade, ≥99.9%), toluene (HPLC grade, ≥99.9%), hexane (≥99%), bromocyclohexane (98%), silver nitrate (≥99.0%), and acetonitrile (biotech grade, ≥99.93%) were purchased from Sigma-Aldrich (St. Louis, MO). Methanol (HPLC grade ≥99%), ethyl acetate (99.9%), and methylene chloride (99.9%) were purchased from Fisher Scientific. Deionized water (DI H_2O) was distilled, deionized to a resistivity of 18 MΩ cm, and filtered using a Milli-Q® filter system (Billerica, MA). Helium and N_2 (UHP grades) were supplied by Butler Gas (McKees Rocks, PA) and used as received.

Experiments were performed at 297 ± 3 K and 1 atm in a collapsible 80 L reaction chamber that has been described previously (Ham et al., 2015, 2016; Jackson et al., 2017). Briefly, the collapsible reaction chamber was constructed from 5-mil fluorinated ethylene propylene copolymer (FEP) Teflon film (Welch Fluorocarbon Inc., Dover, NH) and sealed using a W-600T double foot sealer (Sealer Sales, Northridge, CA). Compressed air was provided from the National Institute for Occupational Safety and Health (NIOSH) facility and was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) to remove moisture. Compressed air flowed through a mass flow controller (MKS, Andover, MA) and into a humidifying chamber where it was mixed with dry air to the predetermined relative humidity (RH) of 50%. The 80 L reaction chamber was equipped with a heated syringe injection port constructed of a 6.4-mm Swagelok (Solon, OH) tee fitting with a 10 mm septum (Restek, Bellefonte, PA) which allowed for the introduction of liquid reactants into the chamber with the flowing air stream. Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon chamber. Aliquots of this O_3/air mixture were added to the 80 L Teflon reaction chamber using a gas-tight syringe. O_3 concentrations were measured using a Thermo Electron (Waltham, MA) ultraviolet photometric ozone analyzer Model 49i. Aliquots of NO were added to the reaction chamber from a 100 ppm tank (Butler Gas, McKees Rocks, PA) using a gas-tight syringe, and concentrations were measured using a Thermo Electron NOx analyzer Model 42i.

2.2. Impinger solvent comparison

Standard solutions of isopropyl nitrate, isobutyl nitrate, and 2-ethylhexyl nitrate were made in methanol. Aliquots of the standards were injected into collapsible chambers containing 80 L of air at 50% RH to give 100 ppb of each compound. Then, 40 L was pulled using a pump (URG 3000-02Q, Chapel Hill, NC) at 4 L/min, from the chamber through 10 mL of varying solvents (ethyl acetate, toluene, hexane, methanol, or water) in a 60 mL Teflon impinger (Savillex, Eden Prairie, MN). After collection, a 100 μL aliquot was taken from the impinger medium and placed in a 2 mL autosampler vial with a 100 μL glass insert (Restek, Bellefonte, PA). All samples were analyzed using an Agilent (Santa Clara, CA) 6890N GC with an Agilent μECD detector (Model: NER004P). Compound separation was achieved by an Agilent DB-5MS (0.25 mm I.D., 20 m long, 0.25 μm film thickness) column and the following GC oven parameters: 40 °C for 2 min, then 5 °C/min to 200 °C, then 25 °C/min to 280 °C and held for 5 min. One μL of each sample was injected in the splitless mode with the injector temperature at 130 °C. The μECD detector temperature was 300 °C and the N_2 makeup gas flow was 60 mL/min. Additional experiments were performed by varying the volume of solvent contained in the impinger as well as chilling the impinger before and during collection to prevent solvent evaporation.

2.3. Standard nitrate linear regression

The commercially available compounds isopropyl nitrate, isobutyl nitrate, and 2-ethylhexyl nitrate were used to determine the recovery efficiencies of the previously described system. The standards were injected into the 80 L chamber through the heated syringe injection port to give known final concentrations of 0.1, 0.5, and 1 ppb. Then, 40 L (1/2 total chamber volume) of the 50% RH chamber air was pulled through 10 mL of ethyl acetate and analyzed using GC-ECD as described above. In order to determine the efficiency of collection, each experiment was repeated where the nitrates were not injected into the chamber, but instead were injected directly into the ethyl acetate impinger after the 40 L had been drawn through. To demonstrate a 100% recovery efficiency, half of the volumes of the standard organic nitrate solution previously injected into the chamber were added to the impinger and analyzed by GC-ECD as described above. A linear regression was performed on the experimental data obtained from the measurement of the peak area of the compounds of known concentrations in the chamber.

2.4. Organic nitrate formation from terpene ozonolysis

In an 80 L volume of air at 50% RH, O_3 (20–100 ppb; $0.5–2.5 \times 10^{12}$ molecules cm^{-3}) was added to 1.7 ppm (+)-α-pinene (4.3×10^{13} molecules cm^{-3}), nitric oxide (18–141 ppb; $0.5–3.5 \times 10^{12}$ molecules cm^{-3}), and 283 ppm of cyclohexane, 232 ppm of hexane, or 265 ppm of pentane (7.0×10^{15}, 5.7×10^{15},