

Potential of select intermediate-volatility organic compounds and consumer products for secondary organic aerosol and ozone formation under relevant urban conditions

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ABSTRACT

Emissions of certain low vapor pressure-volatile organic compounds (LVP-VOCs) are considered exempt to volatile organic compounds (VOC) regulations due to their low evaporation rates. However, these compounds may still play a role in ambient secondary organic aerosol (SOA) and ozone formation. The LVP-VOCs selected for this work are categorized as intermediate-volatility organic compounds (IVOCs) according to their vapor pressures and molecular formulas. In this study, the evaporation rates of 14 select IVOCs are investigated with half of them losing more than 95% of their mass in less than one month. Further, SOA and ozone formation are presented from 11 select IVOCs and 5 IVOC-containing generic consumer products under atmospherically relevant conditions using varying radical sources (NO_x and/or H_2O_2) and a surrogate reactive organic gas (ROG) mixture. Benzyl alcohol (0.41), n-heptadecane (0.38), and diethylene glycol monobutyl ether (0.16) are determined to have SOA yields greater than 0.1 in the presence of NO_x and a surrogate urban hydrocarbon mixture. IVOCs also influence ozone formation from the surrogate urban mixture by impacting radical levels and NO_x availability. The addition of lab created generic consumer products has a weak influence on ozone formation from the surrogate mixture but strongly affects SOA formation. The overall SOA and ozone formation of the generic consumer products could not be explained solely by the results of the pure IVOC experiments.

1. Introduction

Atmospheric fine particulate matter is considered to have significant effects on the earth's energy budget, human health, and visibility (Yee et al., 2013; Naeher et al., 2007; Qin et al., 2013). Secondary organic aerosol (SOA) is estimated to account for a dominant fraction of the fine particle mass in the troposphere (Hallquist et al., 2009; Cappa et al., 2016; Jathar et al., 2017; Ma et al., 2017). However, current models still cannot explain a significant portion of ambient SOA (Presto et al., 2009). In addition, emissions of volatile organic compounds (VOCs) into the air contribute to tropospheric ozone formation, higher concentration of which is a threat to human health and plant ecosystems (Finlayson-Pitts and Pitts, Jr., 1993).

The California Air Resources Board (CARB) defines a low vapor pressure-volatile organic compound (LVP-VOC) as a chemical “compound” containing at least one carbon atom with vapor pressure less than 0.1 mm Hg at 20 °C, or having more than 12 carbon atoms, or having a boiling point greater than 216 °C, or as a chemical mixture being comprised solely of compounds with more than 12 carbon atoms, or as the weight percent of a chemical mixture that boils above 216 °C (CARB, 2015). The CARB estimates LVP-VOC usage in California to be 290 tons/day (Cocker et al., 2014). These low-volatility organic compounds are widely used to produce industrial solvents, coatings, cosmetic, perfume, and pharmaceutical products (Bernard et al., 2013; Vo and Morris, 2014). Vo and Morris (2014) demonstrate that some LVP solvents being categorized as meeting the LVP-VOC nonvolatile

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standards clearly volatilize at ambient conditions, nearly as rapidly as the traditional high volatility solvents they are meant to replace. Shin et al. (2016) develop and evaluate environmental modeling tools and find that when the LVP-VOC in a consumer product is volatilized from the surface to which it has been applied, greater than 90% is available for photochemical reactions either at the source location or in the downwind areas.

Select LVP-VOCs are considered as intermediate-volatility organic compounds (IVOCs) according to their vapor pressures and molecular formulas. These IVOCs have saturation concentrations ranging from 300 to $3 \times 10^6 \mu\text{g m}^{-3}$ (1 – 1000 mg m^{-3}) and are found almost entirely in the vapor phase (Donahue et al., 2012). Much heavier and less volatile IVOCs can potentially form SOA more efficiently than the more abundant but much more volatile traditional VOC SOA precursors (Robinson et al., 2007; Chan et al., 2009). Therefore, conducting research on SOA forming potential from these IVOCs helps to explain the gap between SOA model prediction and ambient measurement. However, not very much experimental work has been published on SOA formation from IVOCs. Most of the work has focused on the SOA forming potential of alkanes (straight chain, branched, and cyclic), naphthalene, alkylnaphthalenes, and exhaust from gasoline and diesel powered vehicles (as summarized below).

Several smog chamber experiments under both high and low NO_x conditions confirm that SOA generated from photo-oxidation of IVOCs may be an important contributor to urban organic aerosol (OA) and should be included in SOA models (Presto et al., 2009; Tkacik et al., 2012). Gentner et al. (2012) find that on-road diesel vehicles are a major source of IVOC emissions in the Los Angeles area. Additionally, substantial formation of SOA is observed from the oxidation of diesel emissions (Weitkamp et al., 2007; Sage et al., 2008; Gentner et al., 2012). Recently, Zhao et al. (2014) estimate that primary IVOCs produce about 30% of newly formed SOA in the afternoon during the California at the Nexus of Air Quality and Climate Change (CalNex) study, about 5 times more than that from single-ring aromatics.

High SOA yields are also observed from reactions of C_{12} – C_{17} n-alkanes, C_{10} – C_{15} cyclic alkanes, and C_{16} branched alkanes with OH radicals in the presence of high NO_x in an environmental smog chamber (Lim and Ziemann, 2005, 2009; Presto et al., 2010; Loza et al., 2014). The yields from photo-oxidation of C_{12} cyclic alkanes are also high under low NO_x condition (Loza et al., 2014). However, Tkacik et al. (2012) do not report high yields for high- NO_x photo-oxidation of C_{12} straight chain, branched, and cyclic alkanes at lower CO_A (organic aerosol concentration) that are more representative of typical atmospheric aerosol concentrations. Under low NO_x conditions, the yields are high for photo-oxidation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene (Chan et al., 2009; Chen, et al., 2016).

This work experimentally examines SOA and ozone formation from the photo-oxidation of select IVOCs and generic consumer products containing one of the select IVOCs under urban low NO_x (18.7–36.4 ppb) concentrations in the presence of a surrogate mixture used to control the chamber reactivity and mimic urban atmospheric activity. Controlling chamber reactivity with a surrogate reactive organic gas (ROG) mixture has been previously explored to study ozone formation by measuring incremental reactivities of representative volatile organic compounds (VOCs) (Carter et al., 1995, 2005). The atmospheric availability of select IVOCs, SOA mass yields, ozone formation, and bulk SOA chemical composition and physical properties from select IVOCs and mixtures containing some of them are explored. This paper provides fundamentals for constraining modeling research to better estimate SOA and ozone formation from IVOCs.

2. Materials and methods

2.1. IVOC volatilization rates

Evaporation rates of individual IVOCs were studied gravimetrically

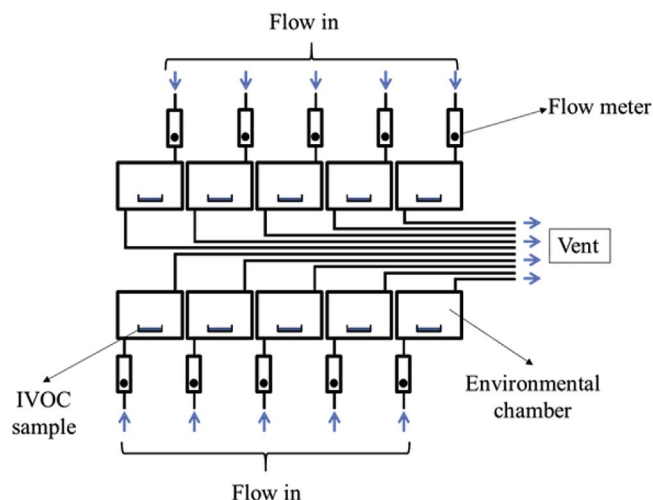


Fig. 1. Schematic for IVOC volatilization measurement.

within miniature (~ 30 L) evaporation chambers operating as continuous stirred tank reactors (CSTRs, Fig. 1). The residence time of the chambers was set to 3.5 exchanges of air per hour. The air entering these chambers was purified (Aadco 737) and had no detectable particles (< 0.2 particles cm^{-3}), non-methane hydrocarbons (< 1 ppb), and NO_x (< 10 ppt). The dew point of the air was less than -60°C . The temperature of individual environmental chambers was maintained at 25°C .

The evaporative mass flux was measured by a mass balance approach with the pure compounds being placed on aluminum boats (capacity 20 ml, top I.D. 43 mm, Sigma-Aldrich) and weighed. Samples were weighed daily for the first ten days and then weekly thereafter for compounds with slow evaporative rates for a period of six months. A bank of 10 of these systems was utilized in parallel to simultaneously measure the evaporation rate of the ten IVOC samples.

2.2. Surrogate ROG mixture

A surrogate ROG mixture was developed by Carter et al. (1995), to represent the major classes of hydrocarbons and aldehydes measured in ambient urban atmospheres, with one compound used to represent each model species used in condensed lumped-molecule mechanism. Total surrogate concentrations used were 1.1 ppmC. The concentration of each species in the surrogate ROG mixture can be found in Table 1.

2.3. Photo-oxidation experiments in UCR CE-CERT environmental smog chamber

SOA and ozone formation from photo-oxidation of IVOCs were studied in the UCR CE-CERT dual indoor smog chambers (2 mil FEP Teflon film), which are described in detail elsewhere (Cocker, D. R., et al., 2001). The chambers were located in a temperature and

Table 1
Composition of surrogate ROG mixture.

| ppb/ppmC | Compound ^a |
|----------|------------------------|
| 20.6 | <i>m</i> -Xylene |
| 89.8 | <i>n</i> -Butane |
| 20.7 | <i>n</i> -Octane |
| 13.6 | <i>trans</i> -2-Butene |
| 23.1 | Toluene |
| 16.3 | Ethylene |
| 13.6 | Propylene |

^a All the chemicals are purchased from Sigma-Aldrich (≥ 95.0 – 99.0%).

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