



# Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources



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## HIGHLIGHTS

- Impacts of O<sub>3</sub>, OH, and NO<sub>3</sub> on indoor residential VOC conversion were modeled.
- Time averaged equations were used in Monte Carlo modeling for four settings.
- New and established sources of radical oxidants were considered in the modeling.
- Total VOC conversion was dominated by ozonolysis and OH reactions, and not NO<sub>3</sub>.
- Source of OH by HONO photolysis was strong, but NO<sub>3</sub> by NO<sub>2</sub> + SCI reactions was not.

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## ABSTRACT

Indoor chemistry may be initiated by reactions of ozone (O<sub>3</sub>), the hydroxyl radical (OH), or the nitrate radical (NO<sub>3</sub>) with volatile organic compounds (VOC). The principal indoor source of O<sub>3</sub> is air exchange, while OH and NO<sub>3</sub> formation are considered as primarily from O<sub>3</sub> reactions with alkenes and nitrogen dioxide (NO<sub>2</sub>), respectively. Herein, we used time-averaged models for residences to predict O<sub>3</sub>, OH, and NO<sub>3</sub> concentrations and their impacts on conversion of typical residential VOC profiles, within a Monte Carlo framework that varied inputs probabilistically. We accounted for established oxidant sources, as well as explored the importance of two newly realized indoor sources: (i) the photolysis of nitrous acid (HONO) indoors to generate OH and (ii) the reaction of stabilized Criegee intermediates (SCI) with NO<sub>2</sub> to generate NO<sub>3</sub>. We found total VOC conversion to be dominated by reactions both with O<sub>3</sub>, which almost solely reacted with *D*-limonene, and also with OH, which reacted with *D*-limonene, other terpenes, alcohols, aldehydes, and aromatics. VOC oxidation rates increased with air exchange, outdoor O<sub>3</sub>, NO<sub>2</sub> and *D*-limonene sources, and indoor photolysis rates; and they decreased with O<sub>3</sub> deposition and nitric oxide (NO) sources. Photolysis was a strong OH formation mechanism for high NO, NO<sub>2</sub>, and HONO settings, but SCI/NO<sub>2</sub> reactions weakly generated NO<sub>3</sub> except for only a few cases.

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## 1. Introduction

Indoor volatile organic compounds (VOCs) are oxidized by ozone (O<sub>3</sub>), the hydroxyl radical (OH), or the nitrate radical (NO<sub>3</sub>). Indoor chemistry research has mostly focused on O<sub>3</sub>/terpene reactions, both because O<sub>3</sub> is easy to generate, manipulate, and measure compared to OH and NO<sub>3</sub> and because terpenes are emitted indoors by building materials and consumer products and are often present at significant indoor concentrations (Baumann

et al., 1999; Logue et al., 2011; Singer et al., 2006; Toftum et al., 2008). Also, since O<sub>3</sub>/terpene reaction rate constants are about 10<sup>-4</sup>–10<sup>-2</sup> ppb<sup>-1</sup> h<sup>-1</sup>, when viewed within the context of typical indoor O<sub>3</sub> concentrations of ~1–50 ppb, reactions with terpenes compete with loss due to air exchange and influence indoor pollutant loadings (Atkinson and Arey, 2003; Weschler, 2000).

While OH/ and NO<sub>3</sub>/terpene reaction rate constants are generally four to five orders of magnitude faster, typical indoor OH concentrations (~10<sup>-7</sup>–10<sup>-5</sup> ppb) and NO<sub>3</sub> concentrations (~10<sup>-6</sup>–10<sup>-3</sup> ppb) suggest terpenes may react meaningfully with NO<sub>3</sub> as well as O<sub>3</sub> but that reactions of terpenes with OH are too slow to influence terpene conversion for most settings (Nazaroff

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and Weschler, 2004; Nojgaard, 2010). However, impacts of all three of these oxidants should be considered because OH and NO<sub>3</sub> can react with many VOCs, in contrast with alkene-only O<sub>3</sub> reactions (Atkinson and Arey, 2003). Therefore, the purpose of this work is to challenge the (perhaps implicit) assumption of a limited indoor reaction scheme based mostly on O<sub>3</sub> and NO<sub>3</sub> reactions with terpenes (and alkenes) and explore total VOC conversion by O<sub>3</sub>, OH, and NO<sub>3</sub> in typical indoor environments.

Excellent reviews and investigative research on indoor oxidants are available (e.g. Carslaw, 2007; Drakou et al., 2000; Nazaroff and Weschler, 2004; Sarwar et al., 2002; Weschler, 2000, 2011; Weschler and Shields, 1996, 1997). We recount a brief distillation of this literature regarding the influence of O<sub>3</sub>, OH, and NO<sub>3</sub> on VOC conversion and indoor chemistry due to gas-phase reactions. After that, we discuss some new, possibly influential advances in our understanding of sources of oxidants indoors, for both OH and NO<sub>3</sub>. Finally, we use a modeling analysis within a Monte Carlo framework to estimate the magnitudes and determinants of gas-phase conversion rates of VOCs due to O<sub>3</sub>, OH, and NO<sub>3</sub> in typical residences, and explore the impacts of both the established and newer sources of these oxidants.

### 1.1. Established background on O<sub>3</sub>, OH, and NO<sub>3</sub> sources and reactions

The initiator and main driver of indoor chemistry is O<sub>3</sub>, which is largely the result of outdoor-to-indoor transport, and indoor O<sub>3</sub> concentrations are often 20–70% of ambient values (Weschler, 2000). Ozone reacts in the gas-phase with alkenes, or it reacts heterogeneously with building materials or surface-sorbed alkenes, such as squalene or monoterpenes (Atkinson and Arey, 2003; Springs et al., 2011; Wang and Morrison, 2006; Wang and Waring, 2014; Waring and Siegel, 2013; Wells et al., 2008; Weschler, 2000; Wisthaler and Weschler, 2010). However, we focus explicitly on gas-phase oxidation of VOCs. Reaction rates of O<sub>3</sub> and indoor-emitted terpenoids have been widely studied, for instance with  $\alpha$ -limonene,  $\alpha$ - and  $\beta$ -pinene, terpinolene,  $\gamma$ -terpinene,  $\alpha$ -terpineol, linalool, and dihydromyrcenol, among others (e.g. Arey et al., 1990; Atkinson, 1990; Atkinson et al., 1990, 1992b; Forester et al., 2006; Grosjean and Grosjean, 1999; Wells, 2005).

The O<sub>3</sub> reacts with the alkene at the carbon double bond following the so-called Criegee mechanism, forming a primary ozonide that cleaves to yield a carbonyl and an excited Criegee intermediate (CI\*), also known as a carbonyl oxide (Atkinson and Arey, 2003; Criegee, 1975). That CI\* is either quenched to form a stabilized Criegee intermediate (SCI) that may react with water or an oxygenated organic (the 'SCI channel'); or it can rearrange to form an excited hydroperoxide and then decompose to form an alkyl radical (R\*) and OH (the 'hydroperoxide channel') (Atkinson and Aschmann, 1993; Atkinson et al., 1992a; Kroll and Seinfeld, 2008). These O<sub>3</sub>/alkene reactions are considered the main driver of indoor OH concentrations; due to their short lifetimes, outdoor-to-indoor transport of OH radicals is not a strong indoor source (Carslaw, 2007; Sarwar et al., 2002; Weschler and Shields, 1996).

OH/VOC reactions lead to the formation of alkyl radicals, alkoxy radicals (RO\*), peroxy radicals (RO<sub>2</sub>\*) and other species which transform by decomposition, isomerization, or hydrolysis, leading to the formation of oxygenated compounds, such as alcohols, carbonyls, carboxylic acids, and hydroxycarbonyls (Atkinson and Arey, 2003; Finlayson-Pitts and Pitts, 2000; Forester et al., 2007; Kroll and Seinfeld, 2008; Orlando and Tyndall, 2012; Orlando et al., 2003; Wells, 2005). Oxygenated organics formed by O<sub>3</sub> or OH reactions can be acute or chronic irritants, and they can sorb to surfaces, oxidize further, contribute to aerosol formation, or be removed by

air exchange (Aalto-Korte et al., 2005; Anderson et al., 2007, 2012; Bein and Leikauf, 2011; Jakubowski and Czerczak, 2010; Jarvis et al., 2005; Kroll and Seinfeld, 2008; Weschler, 2011). The quantification of OH indoors is challenging, but OH has been predicted or measured at  $\sim 10^{-7}$ – $10^{-5}$  ppb (Carslaw, 2007; Sarwar et al., 2002; Weschler and Shields, 1996, 1997). OH-driven chemistry could play a minor role in terpenoid conversion indoors (Nazaroff and Weschler, 2004), however a recent investigation by Carslaw (2013) suggests that OH and O<sub>3</sub> contribute more or less equally to  $\alpha$ -limonene oxidation.

NO<sub>3</sub> is also formed by O<sub>3</sub> reactions, but in this case from O<sub>3</sub> reacting with NO<sub>2</sub> to yield NO<sub>3</sub> and O<sub>2</sub> (Atkinson et al., 1992b; Nazaroff and Cass, 1986; Weschler et al., 1994). After formation, the NO<sub>3</sub> and remaining NO<sub>2</sub> are in equilibrium with dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), which can also react with water to form nitric acid (HNO<sub>3</sub>) indoors (Weschler et al., 1994). NO<sub>3</sub>/VOC reactions yield alkyl, alkoxy, and peroxy radicals, and stable carbonyls and oxygenated compounds that may contain organic nitrate groups (Ham, 2013; Harrison and Ham, 2010; Harrison and Wells, 2012; Jones and Ham, 2008). Organic nitrates are 'under investigated', but research on health effects and indoor NO<sub>x</sub> cycles have emphasized the need for more research (Carslaw, 2007; Carslaw et al., 2012). Like OH, NO<sub>3</sub> is difficult to measure; however, modeling and inference experiments have estimated concentrations with an upper bound of  $\sim 10^{-3}$  ppb (Nojgaard, 2010; Weschler et al., 2006). An average NO<sub>3</sub>/terpenoid reaction rate constant of  $\sim 10^3$  ppb<sup>-1</sup> h<sup>-1</sup> suggests that NO<sub>3</sub>/terpenoid chemistry could impact indoor air (Flemmer and Ham, 2012; Ham, 2013; Harrison and Ham, 2010; Jones and Ham, 2008; Nazaroff and Weschler, 2004).

### 1.2. Recent advances on OH and NO<sub>3</sub> sources

Recent measurements by Alvarez et al. (2013) have identified photolysis of HONO, which is formed from combustion or NO<sub>2</sub> hydrolysis on indoor surfaces (Finlayson-Pitts et al., 2003; Girman et al., 1982; Spicer et al., 1993; Traynor et al., 1982), as a source of indoor OH. Previously, it was assumed that actinic light fluxes indoors attenuating through windows were not strong enough to photolyze HONO. However, to test for this source, OH, O<sub>3</sub>, NO<sub>2</sub>, NO and HONO concentrations, relative humidity, and the actinic light flux were monitored over time in a classroom setting (Alvarez et al., 2013). HONO photolyzes at wavelengths of  $\leq 405$  nm, and light in the range of 340–405 nm was measured. The authors demonstrated that larger calculated HONO photolysis rates corresponded to observed increases in OH. The Alvarez et al. (2013) experiments suggest the possibility of enhanced OH/VOC chemistry in settings with high concentrations of HONO and/or NO<sub>2</sub> and large indoor actinic fluxes, as also recently discussed by Gligorovski and Weschler (2013).

As discussed above, O<sub>3</sub>/alkene reactions form stabilized Criegee intermediates (SCI). While the SCI has been an accepted species for nearly 40 years (Criegee, 1975), its indoor reactive chemistry is now being purposefully investigated. Lifetimes of tens of minutes are estimated for SCIs formed from ozonolysis of alkenes, which implies the possibility of CI\*-driven chemistry being influential indoors beyond the 'hydroperoxide channel' OH formation pathway (Mauldin et al., 2012). The SCI has been shown to oxidize sulfur dioxide (SO<sub>2</sub>) to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), an important species for outdoor particulate matter formation, and also to oxidize NO<sub>2</sub> to NO<sub>3</sub>, which would represent a new source of this radical indoors (Mauldin et al., 2012; Ouyang et al., 2013; Taatjes et al., 2013; Welz et al., 2012). Consideration of these new sources of OH and NO<sub>3</sub> implies that NO<sub>2</sub> may play an even more important and central role in the oxidation of VOCs indoors than previously recognized.

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