Nitrate radical kinetics and products with common fragrance compounds

Joel C. Harrison[*], Jason E. Ham and J. R. Wells

National Institute for Occupational Safety and Health, Morgantown, WV 26505

[*]*Corresponding email: jch5@cdc.gov*

Keywords: *terpenes, terpene alcohols, solvents, nitrate radical, kinetics*

1 Introduction

The chemistry of the nitrate radical (NO_3•) with a number of volatile organic compounds (VOCs) has been well studied (Atkinson 1994). In the indoor environment these reactions can effectively compete with typical air exchange rates of 0.6 h^{-1} (Wilson et al. 1996). Therefore understanding the fate of these chemicals due to reaction with NO_3• is important in determining occupant exposures. These reactions can generate a number of oxygenated products indoors such as: alcohols, aldehydes, ketones, dicarbonyls, carboxylic acids, and organic nitrates all of which have the potential to cause a number of adverse health effects including asthma, allergy and respiratory irritation (Charles et al. 2009; Magnano et al. 2009).

The relative rate technique was used to determine the NO_3• reaction kinetics of some chemicals found in common indoor cleaners, α-terpineol, geraniol, citronellol, β-ionone, dihydromyrcenol , 2-butoxyethanol and benzyl alcohol using gas chromatography mass spectrometry (GC/MS).

Products from the reaction of these chemicals and NO_3• were determined using the chemical derivatization agents *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with GC/MS.

2 Materials/Methods

All compounds were used as purchased from Sigma - Aldrich (Milwaukee, WI) and had the following purities: α-terpineol (90%), geraniol (99%), citronellol (98%), dihydromyrcenol (99%), β-ionone (95%), 2-butoxyethanol (99.5%), benzyl alcohol (99.8%), *O*-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine (PFBHA) (98+%) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (99%).

Experiments were performed in a 65 - 90 L Teflon® film chamber at 297 ± 3 K. Typical initial compound (α-terpineol, geraniol, citronellol, β-ionone, dihydromyrcenol, 2-butoxyethanol and benzyl alcohol) concentrations in the reaction chamber were 0.3 – 0.9 ppm (0.7 – 2 x 10^{13} molecule cm^{-3}).

Nitrate radicals were generated by the thermal decomposition of N_2O_5 using a similar method as described by Atkinson *et al.* (1988). N_2O_5 (solid) kept at -75°C was heated and transferred to an evacuated 2 L collection bottle. Typical initial NO_3• concentrations based on pressure in the reaction chamber were estimated to be 0.12 - 6 ppm (0.3 - 15 × 10^{13} molecules cm^{-3})

Sampling for all of the VOCs/NO_3• kinetics experiments were achieved using a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) solid phase micro-extraction (SPME) fiber (Supelco, Milwaukee, WI,) inserted in the reaction chamber. The SPME fiber was then inserted through a Merlin Microseal (Half Moon Bay, CA) and into the heated injector of one of two Agilent (Wilmington, DE) 6890 gas chromatographs each with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software.

3 Results

The bimolecular rate constants for α-terpineol (17 ± 4 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), geraniol (16.8 ± 4 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), citronellol (12.1 ± 3 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), β-ionone (9.5 ± 2 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), dihydromyrcenol (2.3 ± 0.6 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1}), benzyl alcohol (4 ± 1 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}) and 2-butoxyethanol (2 ± 0.5 x 10^{-15} cm^3 $molecule^{-1}$ s^{-}

^{1}) have been measured using the relative rate technique with GC/MS.

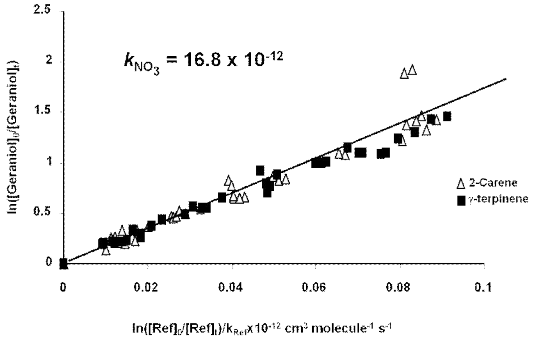

Figure 1. 2,6-dimethyl-2,6-octadien-8-ol (geraniol) relative rate plot with 2-carene (Δ) and γ-terpinene (■) as reference compounds. The geraniol/ NO_3• rate constant, $k_{NO_3\cdot+\text{geraniol}}$, was measured to be (16.8 ± 4 x 10^{-12}) cm^{3}molecule^{-1}s^{-1}.

A number of oxidation products were detected for some of these terpene/NO_3• reactions: acetone, benzaldehyde, glyoxal, methylglyoxal and other more unusual organic nitrates, such as, 5-(1-hydroxy-1-methylethyl)-2-oxocyclohexyl nitrate and 3-oxobutane-1,2-diyl nitrate.

4 Discussion/Conclusions

Given the estimated indoor NO_3• concentration (2 x10^7 molecules/cm^3) (Sarwar et al. 2002) and the measured NO_3• rate constants (k_{NO_3}•), the pseudo-first order lifetimes (k'_{NO_3}•) for a particular compound can be calculated (Nazaroff and Weschler 2004). In the case for α-terpineol, k'_{NO_3}• (1.2 h^{-1}) means that it will react twice as fast with the NO_3• than it can be removed by building ventilation (0.6 hr^{-1}). (Wilson et al. 1996).

Table 1. Calculated pseudo-first order lifetimes

Compound	(k'_{NO_3}•) h^{-1}
α-terpineol	1.2
geraniol	1.2
citronellol	0.9
β-ionone	0.7
dihydromyrcenol	0.002
benzyl alcohol	0.0003
2-butoxyethanol	0.0001

Based on kinetic information consumer product formulations could be designed to reduce the fraction of oxidized VOCs in the indoor environment. Determining the kinetics and products for these compounds with the NO_3 radical is important in assessing potential exposures of indoor occupants.

5 References

Atkinson R, Aschmann SM, Pitts JN. 1988. Rate constants for the gas-phase reactions of the NO3 radical with a series of organic compounds at 296 +/- 2K. J Phys Chem 92: 3454-3457.

Atkinson R. 1994. Gas-phase tropospheric chemistry of organic compounds. J Phys Chem Ref Data, Monograph 2: 215.

Charles LE, Loomis D, Demissie Z. 2009. Occupational hazards experienced by cleaning workers and janitors: A review of the epidemiologic literature. Work 34(1): 105-116.

Magnano M, Silvani S, Vincenzi C, Nino M, Tosti A. 2009. Contact allergens and irritants in household washing and cleaning products. Contact Dermatitis 61(6): 337-341.

Nazaroff WW, Weschler CJ. 2004. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. Atmos Environ 38(18): 2841-2865.

Sarwar G, Corsi R, Allen D, Weschler CJ. Production and levels of selected indoor radicals: a modeling assessment. In: Proceedings of the Indoor Air 2002, 2002. Monterey, CA. 80-85.

Wilson AL, Colome SD, Tian Y, Becker EW, Baker PE, Behrens DW, et al. 1996. California residential air exchange rates and residence volumes. J Expos Anal Environ Epidem 6: 311-326.