Rate Constants for the Gas-Phase Reactions of Nitrate Radicals with Geraniol, Citronellol, and Dihydromyrcenol

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ABSTRACT: Terpenes and terpene alcohols are prevalent compounds found in a wide variety of consumer products including soaps, flavorings, perfumes, and air fresheners used in the indoor environment. Knowing the reaction rate of these chemicals with the nitrate radical is an important factor in determining their fate indoors. In this study, the bimolecular rate constants of $k_{NO_3\bullet \, +geraniol}$ $(16.6 \pm 4.2) \times 10^{-12}$, $k_{NO_3\bullet \, +citronellol}$ $(12.1 \pm 3) \times 10^{-12}$, and $k_{NO_3\bullet \, +dihydromyrcenol}$ $(2.3 \pm 0.6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} were measured using the relative rate technique for the reaction of the nitrate radical ($NO_3\bullet$) with 2,6-dimethyl-2,6-octadien-8-ol (geraniol), 3,7-dimethyl-6-octen-1-ol (citronellol), and 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol) at (297 ± 3) K and 1 atmosphere total pressure. Using the geraniol, citronellol, or dihydromyrcenol + $NO_3\bullet$ rate constants reported here, pseudo-first-order rate lifetimes (k') of 1.5, 1.1, and 0.002 h^{-1} were determined, respectively. © 2010 Wiley Periodicals, Inc.* Int J Chem Kinet 1–7, 2010

INTRODUCTION

The indoor environment can be introduced to an assortment of volatile organic compounds (VOCs) through personal consumer products (perfumes, soaps, shampoos, deodorants, etc.) and activities such as cleaning and room deodorizing. The fragrance compounds that make up these products contain several types of organics including terpenes and terpene alcohols, which have been introduced through reformulations to make greener, ecofriendly products. A recent investigation of emissions from a typical pine oil cleaner showed high concentrations (2–200 ppb) on average of terpenes and terpene alcohols even 1 h after cleaning using the prescribed application directions [1]. Furthermore, the concentrations of these compounds remain in the 2–20-ppb range for many hours after the initial cleaning.

Three terpene alcohols that are common additives to a number of consumer products are geraniol (rose scent), citronellol (floral, rose, citrus scent), and dihydromyrcenol (citrus and lavender scent) [2–4]. These

compounds are regularly used in flavorings, perfumes, soaps, air fresheners, and even insect repellants. An investigation of the chemical make-up of 59 European consumer products (including soap bars, surface cleaners, laundry detergents, and dish soap) found citronellol in 28 of the 59 products, geraniol in 24 of 59, and dihydromyrcenol in 12 of 59 [5]. Together, the annual usage for these compounds is in the range of 100–1000 metric tons with geraniol and citronellol also being listed on the Environment Protection Agency (EPA)'s high production volume (HPV) chemicals list [6]. Since terpene alcohols have become abundant indoors, they are subject to several removal processes including air exchange, surface deposition, and chemical reactions. In particular, chemical reactions can occur in the gasphase and/or on surfaces with indoor initiators such as O_3 (ozone), $OH^\bullet$, and NO_3 radicals. These reactions proceed by H abstraction or addition to carbon–carbon double bonds generating a variety of oxygenated organic species [7–9].

The chemistry of the nitrate radical ($NO_3\bullet$) with a number of VOCs has been well studied [10–13]. These reactions can occur quickly compared to a typical air exchange of 0.6 h^{-1} [14]. For example, given the estimated indoor $NO_3\bullet$ concentration (2 × 10^7 molecules cm^{-3}) and previously measured $NO_3\bullet$ rate constants ($k_{NO_3\bullet}$), pseudo-first-order lifetimes ($k'_{NO_3\bullet}$) for limonene (1.1 h^{-1}), linalool (1.0 h^{-1}), terpinolene (8.6 h^{-1}), and α-terpinene (16 h^{-1}) (found in pine oil cleaners) can be calculated [15]. This means, as is the case for α-terpinene, that it will react 27 times faster with the nitrate radical than it can be removed by a typical ventilation rate of 0.6 h^{-1} [14]. As a consequence, these reactions can generate a number of secondary pollutants 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 [16–19].

In the work presented here, the rate constants for geraniol, citronellol, and dihydromyrcenol + NO_3 radical reaction have been measured using the relative rate method. Results have not been previously reported. Determining the kinetics for these abundant fragrance compounds with the NO_3 radical is important in assessing potential exposures of indoor occupants.

EXPERIMENTAL

Apparatus and Materials

Experiments to measure the gas-phase rate constant of the $NO_3\bullet$ with geraniol, citronellol, and dihydromyrcenol were conducted with a previously described apparatus [20,21]. A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Teflon Swagelok (Solon, OH) fitting attached to a 60–85-L Teflon film chamber. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers and measured with a 0–100-L min^{-1} mass flow controller (MKS, Andover, MA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed insignificant contaminant concentrations below the part per trillion range. The filler system was equipped with a syringe injection port, facilitating the introduction of both liquid and gaseous reactants into the chambers with the flowing air stream. All reactant mixtures were generated by this system.
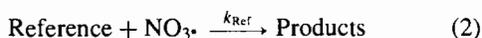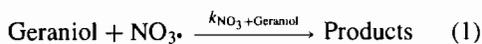
Sampling for all three of the terpene alcohol/$NO_3\bullet$ kinetics experiments was performed using a 65-μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) solid phase microextraction (SPME) fiber (Supelco, Milwaukee, WI,) assembly, which was inserted into a 6.4-mm Swagelok (Solon, OH) fitting attached to a 60–85-L Teflon-film bag. The SPME fiber was exposed for 5 min for geraniol and 30 min for citronellol and dihydromyrcenol within the bag. The SPME 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. The GC temperature program used was the same for both systems: Injection port was set to 250°C, and oven temperature began at 40°C for 6 min and was ramped 20°C min^{-1} to 240°C and held for 2 min. All data were compiled from both systems and were used to determine the $NO_3\bullet$ rate constant for each of the terpene alcohols.

Nitrate radicals were generated by the thermal decomposition of N_2O_5 using a similar method as described by Atkinson et al. [22,23]. N_2O_5 (solid) kept at −75°C was heated and allowed to transfer to an evacuated 2-L collection bottle until pressure was between 0.06 and 0.2 Torr. The collection bottle was then pressurized with ultra-high purity nitrogen up to 1000 Torr and connected to the reaction chamber via a Teflon shutoff valve. The valve to the collection bottle and the chamber shutoff valve was opened, and the system was allowed to equilibrate for 10 s before shutting the valve to the collection bottle. After N_2O_5 was injected into the reaction chamber, the system was allowed to equilibrate for 20 min before sampling.

All compounds were used as received and had the indicated purities, obtained from Sigma-Aldrich (Milwaukee, WI): citronellol (98%), dihydromyrcenol (99%), geraniol (99%), α-pinene (99%), γ-terpinene (98%), nonanal (95%), hexanal (98%), and 2-carene (97%). HPLC-grade methanol and 2-ethylbutanal (98%) were purchased from Fisher Scientfic (Pittsburgh, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV) and was used as received. Experiments were carried out at (297 ± 3) K and 1 atmosphere pressure.

Procedures

The experimental procedures for determining the geraniol, citronellol, and dihydromyrcenol + NO_3· reaction kinetics were similar to those described previously [20,21].

$$\text{Geraniol} + NO_3\cdot \xrightarrow{k_{NO_3 + Geraniol}} \text{Products} \quad (1)$$

$$\text{Reference} + NO_3\cdot \xrightarrow{k_{Ref}} \text{Products} \quad (2)$$

Using geraniol as an example for any one of the three terpene alcohol/NO_3· experiments, the rate equations for reactions (1) and (2) are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\text{Geraniol}]_0}{[\text{Geraniol}]_t}\right) = \frac{k_{NO_3 + Geraniol}}{k_{Ref}}\ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right) \quad (3)$$

If reaction with NO_3· is the only removal mechanism for geraniol and reference, a plot of $\ln([\text{geraniol}]_0/[\text{geraniol}]_t)$ versus $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{NO_3\cdot + geraniol}$ (Fig. 1). The NO_3· rate constant

Figure 2 3,7-Dimethyl-6-octen-1-ol (citronellol) relative rate plot with α-pinene (▲) and γ-terpinene (□) as reference compounds. The NO_3· + citronellol rate constant, $k_{NO_3\cdot + citronellol}$, was measured to be $(12.1 \pm 3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

experiments for geraniol employed the use of two reference compounds: 2-carene and γ-terpinene. The use of two different reference compounds with different NO_3· rate constants strengthens the accuracy of the geraniol/NO_3· rate constant measurement and demonstrates that other reactions are not removing geraniol. (The results using the above equations for citronellol and dihydromyrcenol are shown in Figs. 2 and 3.)

For the geraniol/NO_3· kinetic experiments, the typical concentrations of the pertinent species in the 60–85-L Teflon chamber were 0.20–0.46 ppm (0.5–1.1 × 10^{13} molecules cm^{-3}) geraniol, 0.11–0.26 ppm (0.3–0.6 × 10^{13} molecules cm^{-3}) 2-carene or γ-terpinene, and 0.1–0.2 Torr of N_2O_5 in air. In all NO_3· experiments, the gas-phase mixtures were allowed to reach equilibrium before initial species concentration ($[X]_0$) samples were collected.

For the citronellol/NO_3· kinetic experiments, the typical concentrations of the pertinent species in the

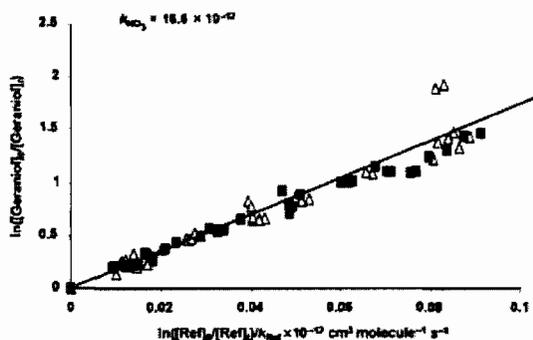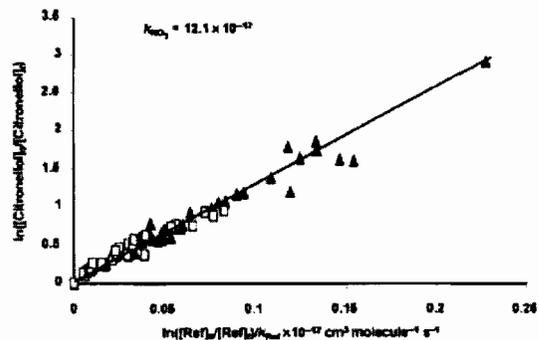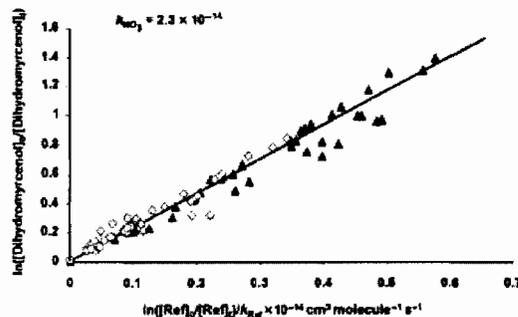**Figure 1** 2,6-Dimethyl-2,6-octadien-8-ol (geraniol) relative rate plot with 2-carene (△) and γ-terpinene (■) as reference compounds. The NO_3· + geraniol rate constant, $k_{NO_3\cdot + geraniol}$, was measured to be (16.6 ± 4.2) cm^3 molecule^{-1} s^{-1}.

Figure 3 2,6-Dimethyl-7-octen-2-ol (dihydromyrcenol) relative rate plot with nonanal (▲), hexanal (◇), and 2-ethylbutanal (○) as reference compounds. The NO_3· + dihydromyrcenol rate constant $k_{NO_3 + dihydromyrcenol}$, was measured to be $(2.3 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

60–85-L Teflon chamber were 0.16–0.27 ppm (0.4–0.7 × 10^{13} molecules cm^{-3}) citronellol, 0.16–0.31 ppm (0.4–0.8 × 10^{13} molecules cm^{-3}) α-pinene, or γ-terpinene, and 0.1–0.14 Torr of N_2O_5 in air.

For the dihydromyrcenol/$NO_3\cdot$ kinetic experiments, the typical concentrations of the pertinent species in the 60–85-L Teflon chamber were 0.1–0.15 ppm (0.27–0.37 × 10^{13} molecules cm^{-3}) dihydromyrcenol, 0.1–2 ppm (0.27–4.92 × 10^{13} molecules cm^{-3}) nonanal, hexanal or 2-ethylbutanal, and 0.1–0.2 Torr of N_2O_5 in air. The total ion chromatogram (TIC) from the Agilent 5975 mass selective detector was used to determine geraniol, citronellol and dihydromyrcenol, and reference concentrations.

To determine possible chromatographic interferences from reference/$NO_3\cdot$ and reaction products, geraniol, citronellol and dihydromyrcenol, and the reference compounds were mixed and were allowed to react with $NO_3\cdot$ radical in separate experiments and were analyzed as described previously [24]. No chromatographic interferences were observed. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 4.1% ($n = 20$) was achieved with the described sampling methods utilizing the Agilent 6890/5975 GC/MS systems.

RESULTS

Terpene Alcohols/$NO_3\cdot$ Reaction Rate Constants

The $NO_3\cdot$ rate constant for geraniol was obtained using the relative rate method described above. The plot of a modified version of Eq. (3) is shown in Fig. 1. The ln ($[Ref]_0/[Ref]_t$) term is divided by the respective reference rate constant (2-carene (19 ± 5) × 10^{-12} cm^3 molecule^{-1} s^{-1} and γ-terpinene (29 ± 7.3) × 10^{-12} cm^3 molecule^{-1} s^{-1}) [25] and multiplied by 10^{-12} cm^3 molecule^{-1} s^{-1}, resulting in a unitless number. This yields a slope that is equal to the $NO_3\cdot$/geraniol rate constant, $k_{NO_3\cdot +geraniol}$, divided by 10^{-12} cm^3 molecule^{-1} s^{-1}. This modification allows for a direct comparison of the two reference compound/geraniol data sets. The slope of the line shown in Fig. 1 yields an $NO_3\cdot$ bimolecular rate constant, $k_{NO_3\cdot +geraniol}$, of (16.6 ± 0.4) × 10^{-12} cm^3 molecule^{-1} s^{-1}. The use of 2-carene and γ-terpinene as references resulted in $NO_3\cdot$ + geraniol bimolecular rate constants of (17.6 ± 0.7) and (15.5 ± 0.3) × 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. The data points at the origin are experimental points before $NO_3\cdot$ addition, $t = 0$, and the data showed no detectable loss of geraniol or reference. The error

in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants (±25% for 2-carene and γ-terpinene) used to derive the geraniol/$NO_3\cdot$ rate constant yields a final value for $k_{NO_3\cdot +geraniol}$, of (16.6 ± 4.2) × 10^{-12} cm^3 molecule^{-1} s^{-1} [25]. The geraniol/$NO_3\cdot$ rate constant, $k_{NO_3\cdot +geraniol}$, has not been previously reported. The ratios $k_{NO_3\cdot +geraniol}/k_{NO_3\cdot +2-carene}$ and $k_{NO_3\cdot +geraniol}/k_{NO_3\cdot +\gamma-terpinene}$ incorporating the uncertainties are 0.88 ± 0.22 and 0.58 ± 0.15, respectively.

The $NO_3\cdot$ rate constant for citronellol was also obtained using the relative rate method, and a plot of a modified version of Eq. (3) is shown in Fig. 2. The ln ($[Ref]_0/[Ref]_t$) term is divided by the respective reference rate constant (α-pinene (6.16 ± 1.54) × 10^{-12} cm^3 molecule^{-1} s^{-1} and γ-terpinene (29 ± 7.3) × 10^{-12} cm^3 molecule^{-1} s^{-1}) [25] and was multiplied by 10^{-12} cm^3 molecule^{-1} s^{-1}. The slope of the line shown in Fig. 2 yields an $NO_3\cdot$ bimolecular rate constant, $k_{NO_3\cdot +citronellol}$, of (12.1 ± 0.2) × 10^{-12} cm^3 molecule^{-1} s^{-1}. The use of α-pinene and γ-terpinene as references resulted in $NO_3\cdot$ + citronellol bimolecular rate constants of (12.2 ± 0.3) and (11.6 ± 0.5) × 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. The error in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants (±25% for α-pinene and γ-terpinene) used to derive the citronellol/$NO_3\cdot$ rate constant yields a final value for $k_{NO_3\cdot +citronellol}$, of (12.1 ± 3) × 10^{-12} cm^3 molecule^{-1} s^{-1} [25]. The citronellol/$NO_3\cdot$ rate constant, $k_{NO_3\cdot +citronellol}$, has not been previously reported. The ratios $k_{NO_3\cdot +citronellol}/k_{NO_3\cdot +\alpha-pinene}$ and $k_{NO_3\cdot +citronellol}/k_{NO_3\cdot +\gamma-terpinene}$ incorporating the uncertainties are 1.96 ± 0.49 and 0.42 ± 0.11, respectively.

As with geraniol and citronellol, the $NO_3\cdot$ rate constant for dihydromyrcenol was also obtained using the relative rate technique. The plot of a modified version of Eq. (3) of the results is shown in Fig. 3. The ln ($[Ref]_0/[Ref]_t$) term is divided by the respective reference rate constant (nonanal (2.0 ± 0.5) × 10^{-14}, hexanal (1.6 ± 0.4) × 10^{-14}, and 2-ethylbutanal (4.5 ± 1.1) × 10^{-14} cm^3 molecule^{-1}s^{-1}) and multiplied by 10^{-14} cm^3 molecule^{-1} s^{-1} [25]. The slope of the line shown in Fig. 3 yields an $NO_3\cdot$ bimolecular rate constant, $k_{NO_3\cdot +dihydromyrcenol}$, of (2.3 ± 0.1) × 10^{-14} cm^3 molecule^{-1} s^{-1}. The use of nonanal, hexanal, and 2-ethylbutanal as references resulted in $NO_3\cdot$ + dihydromyrcenol bimolecular rate constants of (2.3 ± 0.1) and (2.4 ± 0.1) and (2.6 ± 0.2) × 10^{-14} cm^3 molecule^{-1} s^{-1}, respectively. The error in the rate constant stated above

is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants ($\pm 25\%$ for nonanal, hexanal, and 2-ethylbutanal) used to derive the dihydromyrcenol/NO_3. rate constant yields a final value for $k_{NO_3. +dihydromyrcenol}$, of $(2.3 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [25]. The dihydromyrcenol/NO_3. rate constant, $k_{NO_3. +dihydromyrcenol}$, has not been previously reported. The ratios $k_{NO_3. +dihydromyrcenol}/k_{NO_3. +nonanal}$, $k_{NO_3. +dihydromyrcenol}/k_{NO_3. +hexanal}$, and $k_{NO_3. +dihydromyrcenol}/k_{NO_3. +2-ethylbutanal}$ incorporating the uncertainties are 1.15 ± 0.29, 1.44 ± 0.36, and 0.51 ± 0.13, respectively.
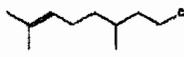
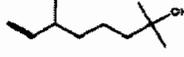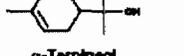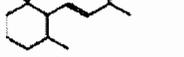## DISCUSSION

The nitrate radical (NO_3.) can react by H-atom abstraction or NO_3. addition to the carbon–carbon double bond(s) of geraniol, citronellol, or dihydromyrcenol [10,26,27]. The measured values, $k_{NO_3. +geraniol}$, $k_{NO_3. +citronellol}$, and $k_{NO_3. +dihydromyrcenol}$

reported here are $(16.6 \pm 4.2) \times 10^{-12}$, (12.1 ± 3), $\times 10^{-12}$, $(2.3 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively. The geraniol/NO_3. and citronellol/NO_3. rate constants are in good agreement (i.e., within the 25% error using the reference compounds) with calculated values of 18.8 and 9.4×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, using estimation methods previously described by Atkinson [28]. However, the measured dihydromyrcenol/NO_3. rate constant is approximately 250 times slower than the calculated value of 9.4×10^{-12} cm^3 molecule^{-1} s^{-1} using the same estimation methods.

The measured $k_{NO_3. +geraniol}$ of 16.6×10^{-12} cm^3 molecule^{-1} s^{-1} can be compared with the previously measured $k_{OH. +geraniol}$ (231×10^{-12}) and $k_{O_3. +geraniol}$ of (9.3×10^{-16}) cm^3 molecule^{-1} s^{-1}; see Table I). The measured $k_{NO_3. +citronellol}$ of 12.1×10^{-12} cm^3 molecule^{-1} s^{-1} can also be compared with the previously measured $k_{OH. +citronellol}$ of 170×10^{-12} and $k_{O_3 +citronellol}$ of 2.4×10^{-16} cm^3 molecule^{-1} s^{-1}; see Table I). The OH$^\bullet$ rate constants for both geraniol and citronellol are approximately ten times greater

Table I Nitrate Radical Rate Constants and Pseudo-First Order Rate Constants for Some Common Indoor Fragrance Compounds

Fragrance Compound	k_{OH} ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1})	k_{O_3} ($\times 10^{-16}$ cm^3 molecule^{-1} s^{-1})	$k_{NO_3.}$ ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1})	k'_{OH} (h^{-1})	k'_{O_3} (h^{-1})	$k'_{NO_3.}$ (h^{-1})
Geraniol	231[a]	9.3[a]	16.6	0.1	1.6	1.5
Citronellol	170[b]	2.4[b]	12.1	0.08	0.4	1.1
Dihydromyrcenol	38[c]	0.02[c]	0.02	0.02	0.004	0.002
α-Terpineol	190[d]	3.0[d]	16[f]	0.08	0.5	1.4
β-Ionone	118[e]	0.19[e]	9.4[g]	0.05	0.03	0.8
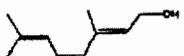
For psuedo-first-order calculations (k'), the following estimated indoor concentrations were used: [OH$^\bullet$] = 1×10^5, [O$_3$] = 5×10^{11}, and [NO$_3$.] = 2×10^7 molecules cm^{-3} [33].
[a] Forester et al. [34].
[b] Ham et al. [35].
[c] Forester et al. [30].
[d] Wells [9].
[e] Forester et al. [29].
[f] Jones and Ham [21].
[g] Harrison and Ham [20].

than the measured nitrate radical rate constants for these terpene alcohols. This observed ratio ($k_{OH•}/k_{NO_3}$) seems to correlate with other measured terpenes such as α-terpineol (11.9), β-ionone (12.6), limonene (13.4), sabinene (11.7), α-pinene (8.5), and 3-carene (9.7) [9,15,20,21,29]. This rough approximation may be used as crude estimation of nitrate radical rate constants for structurally similar species; however, this approximation should be used cautiously as observed in the case of dihydromyrcenol.

The measured $k_{NO_3•+dihydromyrcenol}$ of 2.3×10^{-14} cm^3 molecule^{-1} s^{-1} can be compared with the previously measured $k_{OH•+dihydromyrcenol}$ of 38×10^{-12} and $k_{O_3+dihydromyrcenol}$ of 2.0×10^{-18} cm^3 molecule^{-1} s^{-1}. The slow $k_{NO_3•+dihydromyrcenol}$ reported here follows a similar trend with the previously measured $k_{O_3+dihydromyrcenol}$. These much slower measured rate constants compared to calculated values suggest that the larger NO$_3$• and O$_3$ molecules are inhibited by possible folding of the dihydromyrcenol carbon chain. This folding could influence the electron density of the carbon–carbon double bond and also heighten steric hindrance. From previously published gas-phase and surface experiments of dihydromyrcenol/O$_3$, it was hypothesized that the long aliphatic chain in dihydromyrcenol molecule and the OH group at the opposite end may interact by molecular folding in the gas phase which impedes the ozone reacting to the carbon–carbon double bond [30,31]. The measured value $k_{OH•+dihydromyrcenol}$ of 38×10^{-12} cm^3 molecule^{-1} s^{-1} is in good agreement to the calculated value 37×10^{-12} obtained by using the EPA's AOPWIN rate constant software, indicating that the size of the OH• molecule makes it more favorable for reaction compared to O$_3$ or NO$_3$• [32].

Indoor Nitrate Radical Chemistry

Indoor environment concentrations of the nitrate radical (2×10^7 molecules cm^{-3}), hydroxyl radical (1×10^5 molecules cm^{-3}), and ozone (5×10^{11} molecules cm^{-3}) have been previously estimated by Sarwar et al. [33]. Using the geraniol + NO$_3$• and citronellol + NO$_3$• rate constants reported here, pseudo-first-order rate constants (k') of 1.5 and 1.1 h^{-1} were determined, respectively (see Table I). A comparison of these values to a typical indoor air exchange rate of 0.6 h^{-1} suggests that NO$_3$ radical chemistry is an important removal mechanism for both geraniol and citronellol [14]. When compared to the pseudo-first-order rate constants (k'_{OH} and k'_{O_3}; see Table I) for both geraniol ($k'_{OH•+geraniol} = 0.1$ h^{-1} and $k'_{O_3+geraniol} = 1.6$ h^{-1}) and citronellol ($k'_{OH•+citronellol} = 0.08$ h^{-1} and $k'_{O_3+citronellol} = 0.4$ h^{-1}), it is evident that nitrate radical

chemistry could play a critical role in the transformation of geraniol and citronellol in the indoor environment.

Using the dihydromyrcenol + NO$_3$• rate constant reported here, a pseudo-first-order rate constant (k') of 0.002 h^{-1} was determined. A comparison of this value to a typical indoor air exchange rate of 0.6 h^{-1} suggests that indoor air exchange is the most likely removal mechanism for dihydromyrcenol [14]. When compared to the pseudo-first-order rate constants of the OH• ($k_{OH•+dihydromyrcenol} = 38 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k' = 0.02$ h^{-1}) and ozone ($k_{O_3+dihydromyrcenol} = 2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, $k' = 0.004$ h^{-1}), room air exchange is still expected to be the most likely loss mechanism for dihydromyrcenol in the indoor environment. Dihydromyrcenol is consistently slow reacting with O$_3$ and/or NO$_3$•, and this could be used as an advantage in formulating cleaning products or room deodorizers as this could decrease the potential formation of oxidation products and indoor exposures.

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