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Kinetic and product studies of the reactions of NO₃ with a series of unsaturated organic compounds

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ABSTRACT

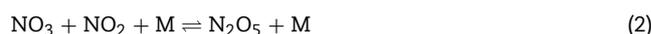
Rate coefficients for the reaction of NO₃ radicals with 6 unsaturated volatile organic compounds (VOCs) in a 7300 L simulation chamber at ambient temperature and pressure have been determined by the relative rate method. The resulting rate coefficients were determined for isoprene, 2-carene, 3-carene, methyl vinyl ketone (MVK), methacrolein (MACR) and crotonaldehyde (CA), as $(6.6 \pm 0.8) \times 10^{-13}$, $(1.8 \pm 0.6) \times 10^{-11}$, $(8.7 \pm 0.5) \times 10^{-12}$, $(1.24 \pm 1.04) \times 10^{-16}$, $(3.3 \pm 0.9) \times 10^{-15}$ and $(5.7 \pm 1.2) \times 10^{-15}$ cm³/(molecule•sec), respectively. The experiments indicate that NO₃ radical reactions with all the studied unsaturated VOCs proceed through addition to the olefinic bond, however, it indicates that the introduction of a carbonyl group into unsaturated VOCs can deactivate the neighboring olefinic bond towards reaction with the NO₃ radical, which is to be expected since the presence of these electron-withdrawing substituents will reduce the electron density in the π orbitals of the alkenes, and will therefore reduce the rate coefficient of these electrophilic addition reactions. In addition, we investigated the product formation from the reactions of 2-carene and 3-carene with the NO₃ radical. Qualitative identification of an epoxide (C₁₀H₁₆OH⁺), caronaldehyde (C₁₀H₁₆O₂H⁺) and nitrooxy-ketone (C₁₀H₁₆O₄NH⁺) was achieved using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) and a reaction mechanism is proposed.

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Introduction

Although the hydroxyl radical (OH) is recognized as the dominant oxidant in the daytime, the NO₃ radical (NO₃) is known to be the main oxidant of volatile organic compounds (VOCs) during the night (Atkinson, 1991; Wayne et al., 1991). NO₃ is produced in the atmosphere via the reaction between O₃ and

NO₂, which can originate from combustion, biomass burning, lightning and bacterial sources (Aldener et al., 2006; Brown et al., 2005; Brown and Stutz, 2012). During the night, NO₃ and NO₂ exist in thermal equilibrium with N₂O₅:



where M is the third body. Oxidation by NO₃ is normally only significant during nighttime due to its rapid photolysis with a lifetime of ~5 sec and the lifetime is significantly

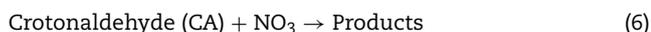
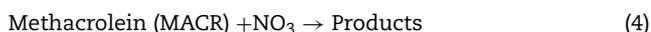
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shorter in the presence of NO (in photochemical steady state with NO₂) during daytime (Finlayson-Pitts and Pitts, 2000), however, it has been shown that NO₃ can be an important daytime oxidant within the canopy in forested environments (Liebmann et al., 2019). Field measurements have reported NO₃ concentrations ranging from lower than the detection limit (10 pptV) to 800 pptV and N₂O₅ concentrations could be as high as 10.9 ppbV dependent on local conditions (Brown and Stutz, 2012).

NO₃ is a major oxidant for a variety of VOCs and sulfur compounds, and is particularly reactive towards unsaturated biogenic VOCs (BVOC), including both isoprene (2-methyl-1,3-butadiene) and the monoterpenes (Wayne et al., 1991). Isoprene is the most abundant non-methane hydrocarbon in the atmosphere with annual global emissions of 500 Tg (Guenther et al., 2006). Reactions of NO₃ with isoprene and monoterpenes could produce both nitrated compounds and secondary organic aerosol (SOA) in variable yields, some model studies have suggested that these reactions may be responsible for a large fraction of regional and global SOA (Griffin et al., 1999; Ng et al., 2008; Perring et al., 2009; Rollins et al., 2009). However, the nitrated compounds can be long-lived in the atmosphere acting as temporary reservoirs of odd nitrogen, which can then be transported downwind to remote regions where their decomposition, and subsequent nitrogen oxide (NO_x) release, will influence the regional ozone production (Aschmann et al., 2011; Atlas, 1988; Buhr et al., 1990; Suarez-Bertoa et al., 2012).

To improve the representation of NO₃ oxidation of VOCs in tropospheric chemistry models, more kinetic studies of these reactions are needed. Especially since there are quite considerable discrepancies in measurements of NO₃ rate coefficients carried out in different laboratories. For example, even the reaction of NO₃ with isoprene, which has been studied extensively, remains quite uncertain, since reported rate constants span a range of a factor of 2 as shown in IUPAC (International Union of Pure and Applied Chemistry) (Ammann et al., 2019; Atkinson et al., 2006). In this work, gas-phase rate coefficient measurements were made for the following reactions:



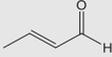
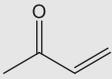
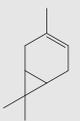
In addition, the experimental rate coefficients obtained for the different VOCs are discussed and compared with regard to their chemical structures. Besides that, some exploratory work is conducted regarding the products formed from the reaction of 2-carene and 3-carene with NO₃, using a high-resolution proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS). To the best of our knowledge, this work provides the first mechanistic study of the reaction of 2-carene with the NO₃ radical.

1. Materials and methods

1.1. 7300 L simulation chamber

Experiments were carried out in the 7300 L indoor simulation chamber at ambient temperature (298 ± 2 K) and pressure (760 ± 5 Torr). This chamber and the associated technique have been described in detail in a previous study (Ren

Table 1 – List of specific masses monitored to detect various studied volatile organic compounds (VOCs) using the proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) along with detection sensitivities.

VOCs	Structure	Mass charge ratio H ⁺ (m/z)	Detection sensitivity (ncps/ppbV)
Methacrolein		71.049	31.73
Crotonaldehyde		71.049	41.71
Methyl vinyl ketone		71.049	34.83
2-Carene		137.133	19.58
3-Carene		137.133	15.93
Isoprene		69.07	7.61

ncps: normalized counts per seconds.

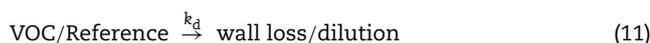
et al., 2019) and is thus described only briefly here. The chamber was made of Teflon foil and surrounded by opaque protection panels. Two Teflon fans were utilized to promote rapid mixing of the reactants. Dry and purified air (relative humidity (RH) < 1%) was used as a bath gas in experiments and also to clean the chamber after each experiment. Known volumes of studied hydrocarbons were injected into a Pyrex impinger and driven into the chamber with a stream of purified air. Concentrations were calculated using the ideal gas law, based on the volume and density of the sample that was injected and the volume of the chamber. In order to compensate for sampling flows and leaks and to avoid any ingress of outside air, 5 L/min of purified air was added continuously during the experiments to maintain a slight overpressure. SF₆ was used to determine the dilution rate in the chamber, which ranged from the 7 × 10⁻⁶ – 8 × 10⁻⁶ sec⁻¹.

A high-resolution PTR-TOF-MS (8000, Ionicon Analytik, Austria) with hydronium ion (H₃O⁺) ion source was employed to monitor the loss of the organic compounds in the chamber. The mass resolution of this instrument is > 5000 m/Δm. The pressure in the PTR-TOF-MS drift tube was maintained at 2.1 mbar and drift voltage of 400 V was used to obtain an electric field (E/N) of 98 Td. The sampling flow from the chamber to the PTR-TOF-MS was approximately 150 mL/min through a 1 m long 1/8 inch OD (outside diameter) Teflon tube, heated to 60°C. The mass spectral data were analyzed by PTR-TOF Data Analyzer software (Müller et al., 2013). The detection sensitivities for the VOCs were derived from the slopes of the calibrations plots of the signal (in normalized counts per second, ncps) versus their corresponding mixing ratios (ppbV) as shown in Table 1. An in situ Fourier transform infrared spectrometry (FTIR, Nicolet 5700, Thermo, USA) coupled to a White-type multipass cell (143 m optical path length) was also equipped to the simulation chamber, mainly for SF₆ detection. NO₃ radicals were generated from the thermal decomposition of N₂O₅.

Concentration ranges of the various chemicals ([Chemicals]) of importance to these experiments are: [alkene] = $0.8 \times 10^{12} - 4.0 \times 10^{12}$ molecule/cm³, [N₂O₅] = $0.1 \times 10^{11} - 1.2 \times 10^{11}$ molecule/cm³, [NO₂] = $2 \times 10^{11} - 5 \times 10^{11}$ molecule/cm³, and [NO₃] = $0.5 \times 10^{10} - 4.9 \times 10^{10}$ molecule/cm³.

1.2. Relative rate kinetic studies

Rate coefficients were determined by following the simultaneous decays of the studied VOCs and reference compounds from their reaction with NO₃ and other loss processes (wall loss, dilution):



where, k_{3-8} and k_{ref} are the rate coefficient for the reactions of NO₃ with the studied VOCs including isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene, 3-carene and reference compounds (cyclohexene, methyl methacrylate, 2-methyl propanal, methyl acrylate, 1,3-cyclohexadiene, α -cedrene), respectively. k_d is the non-reactive loss rate of studied VOCs and reference compounds.

The typical experimental procedure consisted of (1) prior to injection of N₂O₅, the SF₆ and VOCs were introduced into the chamber and kept for one hour to quantify k_d . The dilution rate was followed by monitoring SF₆ throughout the experiment period using the long-path Fourier transform infrared spectrometer equipped to the chamber; (2) sufficient N₂O₅ was continually introduced to the chamber from a stream of purified air, such that a measurable consumption of VOCs occurred on a reasonable timescale (30 min to 1 hr). The decays of both the studied VOCs and reference compounds were continuously monitored using PTR-TOF-MS.

Assuming that the VOCs and reference compounds were lost only by reaction with NO₃ and non-reactive loss, it can be shown that:

$$\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d \times t = \frac{k_{3-8}}{k_{\text{ref}}} \left(\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d \times t \right) \quad (12)$$

where [VOC]₀, [VOC]_t and [ref]₀, [ref]_t are the corresponding concentrations of VOCs and reference compounds at initial time and time t. Hence, plots of $\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d \times t$ against $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d \times t$ should be straight lines of slope $\frac{k_{3-8}}{k_{\text{ref}}}$, with zero intercept.

1.3. Chemicals

The sources of chemicals used and their purities are: isoprene (99%), methacrolein (95%), methyl vinyl ketone (99%), crotonaldehyde ($\geq 99.5\%$), 2-carene (97%), 3-carene ($\geq 90\%$) from Sigma-Aldrich. All the liquid compounds in this study were further purified by repeating freeze, pump, thaw cycles and fractional distillation before use.

N₂O₅ was synthesized in a vacuum line by the reaction of NO₂ with excess O₃ through Reactions (1) and (2) (Zhou et al., 2017). In the first stage of synthesis, NO₂ was produced from the reaction of NO and O₃ in a glass tube. The mixture of NO₂ and O₃ were then flushed into a bulb (1 L) where NO₃ and N₂O₅ are formed. At the end of the synthesis, N₂O₅ crystals were collected in a cold trap (190 K). N₂O₅ crystals were then purified by trap-to-trap distillation under a flow of O₂/O₃, which could be kept for several weeks in a cold trap maintained 190 K.

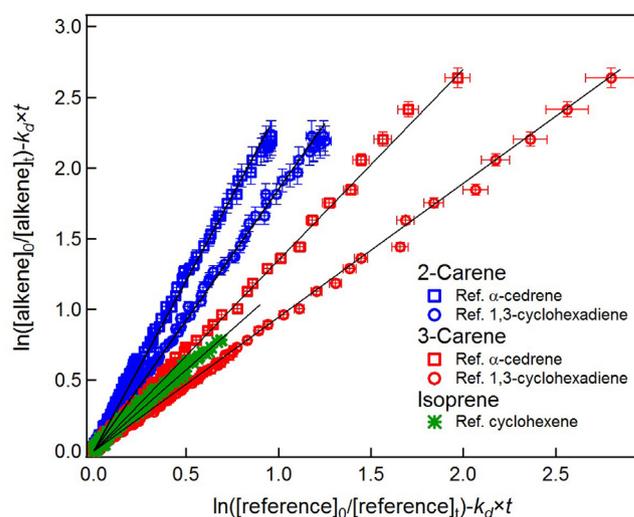


Fig. 1 – Plots of relative kinetic data obtained from the NO₃ reaction with isoprene using cyclohexene as the reference, and NO₃ radical reaction with 2-carene and 3-carene using α -cedrene, 1,3-cyclohexadiene as the reference (Ref.). [alkene]₀: initial concentration of alkene; [alkene]_t: the concentration of alkene at time t; [reference]₀: initial concentration of reference; [reference]_t: the concentration of reference at time t.

2. Results and discussion

2.1. Rate constants of NO₃ reaction with studied VOCs

The rate coefficients for isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene reaction with NO₃ radical were obtained in the 7300 L ICARE simulation chamber using references including cyclohexene, 2-methyl propanal, methyl methacrylate, methyl acrylate, 1,3-cyclohexadiene and α -cedrene. The concentration of VOCs ranged from 0.8×10^{12} to 4.1×10^{12} molecule/cm³ as shown in Table 2. The recommended rate constants for the reaction of reference compounds with NO₃ at 298 K are: $k_{2\text{-methyl propanal}} = (1.17 \pm 0.23) \times 10^{-14}$ cm³/(molecule•sec) (Calvert et al., 2011), $k_{\text{methyl methacrylate}} = (2.98 \pm 0.35) \times 10^{-15}$ cm³/(molecule•sec) (Zhou et al., 2017), $k_{1,3\text{-cyclohexadiene}} = (1.15 \pm 0.35) \times 10^{-11}$ cm³/(molecule•sec) (Calvert et al., 2000), $k_{\alpha\text{-cedrene}} = (8.20 \pm 0.73) \times 10^{-12}$ cm³/(molecule•sec) (Calvert et al., 2000), $k_{\text{methyl acrylate}} = (1.10 \pm 0.55) \times 10^{-16}$ cm³/(molecule•sec) (Calvert et al., 2011) and $k_{\text{cyclohexene}} = (5.90 \pm 1.77) \times 10^{-13}$ cm³/(molecule•sec) (Calvert et al., 2000).

Figs. 1 and 2 show straight lines of $\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d \times t$ as a function of $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d \times t$ with zero intercept. It can be observed that all individual experiments are in good agreement. The rate coefficient ratio of $\frac{k}{k_{\text{ref}}}$ (where k is the rate coefficient) was expected from the linear fitting of Figs. 1 and 2, which was fitted using the protocol of Brauers and Finlayson-Pitts (1997) by taking into account errors on both abscissa and ordinate scales. These errors were estimated from the calibration curve before the experiments. The relative rate ratios, $\frac{k}{k_{\text{ref}}}$, obtained for the studied VOCs are shown in Table 2. The quoted uncertainties on the $\frac{k}{k_{\text{ref}}}$ are 2 times the standard deviation in the least-squares fit of $\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d \times t$ vs $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d \times t$, and then multiplied 2.9 as the Student t-distribution contribution

Table 2 – Experimental conditions and rate constants for the reaction of isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene with NO₃ radical by relative method.

VOC	[VOC] ($\times 10^{12}$ molecule/cm ³)	Reference ^a	No. of runs	$\frac{k_{3-8}}{k_{ref}} \pm \text{error}^b$	$k \pm 2\sigma$ (cm ³ /(molecule•sec)) ^c
Methacrolein	1.7–4.1	2-Methyl propanal	2	0.23±0.07	$(2.7 \pm 0.6) \times 10^{-15}$
		Methyl methacrylate	2	0.90±0.27	$(2.7 \pm 0.5) \times 10^{-15}$
				Average^d	$(2.7 \pm 0.8) \times 10^{-15}$
Crotonaldehyde	2.0–4.0	2-Methyl propanal	2	0.42±0.06	$(4.9 \pm 0.7) \times 10^{-15}$
		Methyl methacrylate	2	1.87±0.29	$(5.6 \pm 0.6) \times 10^{-15}$
				Average^d	$(5.3 \pm 1.0) \times 10^{-15}$
Methyl vinyl ketone	1.0–4.0	Methyl acrylate	2	1.11±0.15	$(1.3 \pm 0.6) \times 10^{-16}$
2-Carene	0.8–1.7	1,3-Cyclohexadiene	2	0.36±0.04	$(2.2 \pm 0.6) \times 10^{-11}$
		α -Cedrene	2	1.66±0.23	$(2.5 \pm 0.3) \times 10^{-11}$
				Average^d	$(2.5 \pm 0.6) \times 10^{-11}$
3-Carene	0.8–2.8	1,3-Cyclohexadiene	2	0.39±0.03	$(1.1 \pm 0.4) \times 10^{-11}$
		α -Cedrene	2	1.71±0.20	$(1.4 \pm 0.2) \times 10^{-11}$
				Average^d	$(1.3 \pm 0.4) \times 10^{-11}$
Isoprene	0.8–3.3	Cyclohexene	2	1.19±0.18	$(6.8 \pm 1.0) \times 10^{-13}$

^a k_{ref} is shown in the text.

^b The error for $\frac{k_{3-8}}{k_{ref}}$ are 2 times of standard deviation in the least-squares fit of $\ln \frac{[VOC]_0}{[VOC]_t} - k_d \times t$ vs. $\ln \frac{[Reference]_0}{[Reference]_t} - k_d \times t$, and then multiply 2.9 as the Student t-distribution contribution due to the limited number of measurements.

^c The uncertainties for k (the rate coefficient) were combined the precision of our measured values with the quoted uncertainties in the rate constant of references by using the propagation of uncertainty in Eq. (2).

^d Weighted average as shown in Eqs. (3) and (4).

k_{3-8} and k_{ref} : the rate coefficient for the reactions of NO₃ with the studied VOCs and reference compounds, respectively; $\frac{k_{3-8}}{k_{ref}}$: the rate coefficients ratio of studied VOCs with reference compounds; $[VOC]_0$: initial concentration; $[VOC]_t$: VOCs concentration at time t ; k_d : the non-reactive loss rate; t : reaction time; σ : uncertainties.

due to the limited number of measurements. The rate constants obtained for the studied VOCs, k_{3-8} , according to different reference compounds are also shown in Table 2. The uncertainties for k combined the precision of our measured values with the quoted uncertainties in the rate constant of references by using the following propagation of uncertainty (Zhou et al., 2017):

$$\sigma = \frac{k}{k_{ref}} k_{ref} \sqrt{\left[\frac{\sigma_{k_{ref}}}{k_{ref}} \right]^2 + \left[\frac{\sigma_{\frac{k}{k_{ref}}}}{\frac{k}{k_{ref}}} \right]^2} \quad (13)$$

where σ is the uncertainty.

As shown in Table 2, good agreement between the rate coefficients using different reference compounds for methacrolein, crotonaldehyde, 2-carene and 3-carene suggests that individual experiments and the reference rate coefficients used demonstrate a high level of consistency. The determined rate constants of studied VOCs were obtained from the weighted average of the k from each individual reference (Ren et al., 2019), shown as $k_{average}$ in Table 2:

$$k_{average} = (w_1 k_1 + w_2 k_2 + \dots + w_i k_i) / (w_1 + w_2 + \dots + w_i) \quad (14)$$

where $w_i = 1/\sigma_i$, σ_i is the error, and k_i is the rate coefficient obtained with each individual reference.

The error (σ_{av}) was given by:

$$\sigma_{av} = 2 \times (1/\sigma_1 + 1/\sigma_2 + \dots + 1/\sigma_i)^{-0.5} \quad (15)$$

2.2. Comparison with the literature

Table 3 summarizes the rate constants measured by this work with data from the literature for the reactions of the NO₃ radical with isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene. As shown in Table 3, the ki-

netics of the isoprene reaction with NO₃ radical has been studied extensively using both absolute and relative methods. We recalculate the values for the studies of Atkinson et al. (1984), Barnes et al. (1990) and Stabel et al. (2005) using more recent recommended reference values (trans-2-butene and 2-buten-1-ol) from IUPAC (Atkinson et al., 2006; Zhao et al., 2011). Although the rate coefficient obtained in this work is in good agreement with most of previous studies, a larger difference is observed compared with the work of Benter and Schindler (1988), Barnes et al. (1990) and Ellermann et al. (1992). With the exception of Barnes et al. (1990), both Benter and Schindler (1988) and Ellermann et al. (1992) applied absolute method using DF-MS (discharge flow system and mass spectrometer and PR-A (pulse radiolysis combined with kinetic spectroscopy in the visible). As shown in Table 3, higher values were also observed for crotonaldehyde for two absolute determinations (Cabañas et al., 2001; Salgado et al., 2008) compared with the relative measurements (Atkinson et al., 1987; Ullerstam et al., 2001; this work). As mentioned by Zhao et al. (2011), Canosa-Mas et al. (1988) and Wille et al. (1991), additional removal of VOCs may occur due to its side reactions initiated by F atoms/OH radicals or additional loss of NO₃ may result from its reaction with NO₂, alkyl and peroxy radicals in these experiments. As a result, we recommend a weighted rate constant of isoprene + NO₃ of $(6.6 \pm 0.8) \times 10^{-13}$ cm³/(molecule•sec) based on all the studies except Benter and Schindler (1988), Barnes et al. (1990) and Ellermann et al. (1992), which is in good agreement with IUPAC (Atkinson et al., 2006) value as $(6.5 \pm 1.3) \times 10^{-13}$ cm³/(molecule•sec) at 298 K. The recommended value of crotonaldehyde + NO₃ is $(5.7 \pm 1.2) \times 10^{-15}$ cm³/(molecule•sec), only taking into account the relative rate measurements.

The rate constant of methacrolein + NO₃ has been measured mainly by the relative method (Canosa-Mas et al., 1999; Chew et al., 1998; Kwok et al., 1996), only one study from Rudich et al. (1996) applied an absolute method and observed an upper limit of $< 8 \times 10^{-15}$ cm³/(molecule•sec). The value of this work agrees well with the studies using the relative method and hence we recommend a weighted average of $(3.3$

Table 3 – Kinetic results of this study and comparison with the literature for the reactions of NO₃ radical with isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), crotonaldehyde (CA), 2-carene and 3-carene.

	Technique	k (cm ³ /(molecule•sec))	T (K)	Reference
Isoprene	Relative, trans-2-butene	$(5.97 \pm 1.20) \times 10^{-13a}$	295 ± 1	Atkinson et al. (1984)
	Absolute, DF-MS	$(1.3 \pm 0.2) \times 10^{-12}$	298	Benter and Schindler (1988)
	Absolute, LIF	$(6.52 \pm 0.07) \times 10^{-13}$	297	Dlugokencky and Howard (1989)
	Relative, trans-2-butene	$(1.21 \pm 0.31) \times 10^{-12a}$	298 ± 2	Barnes et al. (1990)
	Absolute, DF-MS	$(7.8 \pm 0.6) \times 10^{-13}$	298	Wille et al. (1991)
	Absolute, PR-A	$(1.07 \pm 0.20) \times 10^{-12}$	295 ± 2	Ellermann et al. (1992)
	Relative, trans-2-butene	$(6.86 \pm 2.60) \times 10^{-13}$	298	Berndt and Böge (1997)
	Absolute, F-CIMS	$(7.3 \pm 0.2) \times 10^{-13}$	298 ± 2	Suh et al. (2001)
	Relative, trans-2-butene	$(5.3 \pm 1.1) \times 10^{-13a}$	296 ± 2	Stabel et al. (2005)
	Relative, 2-buten-1-ol	$(5.75 \pm 0.47) \times 10^{-13b}$		
	Relative, trans-2-butene	$(6.16 \pm 1.24) \times 10^{-13a}$	295 ± 2	Zhao et al. (2011)
	Relative	$(6.8 \pm 1.0) \times 10^{-13}$	297 ± 2	This work
	Recommended^{e,f}	$(6.6 \pm 0.8) \times 10^{-13}$		
MACR	Absolute, F-A	$< 8 \times 10^{-15}$	298	Rudich et al. (1996)
	Relative, propene	$(4.4 \pm 1.7) \times 10^{-15}$	296 ± 2	Kwok et al. (1996)
	Relative, propene	$(3.07 \pm 1.09) \times 10^{-15}$	298 ± 2	Chew et al. (1998)
	Relative, but-1-ene	$(3.50 \pm 1.06) \times 10^{-15}$		
	Relative, propene	$(3.7 \pm 1.0) \times 10^{-15}$	296 ± 2	Canosa-Mas et al. (1999)
	Relative	$(2.7 \pm 0.8) \times 10^{-15}$	298 ± 2	This work
	Recommended^e	$(3.3 \pm 0.9) \times 10^{-15}$		
CA	Relative, propene	$(5.15 \pm 2.58) \times 10^{-15c}$	298	Atkinson et al. (1987)
	Relative, propene	$(6.0 \pm 0.8) \times 10^{-15}$	297	Ullerstam et al. (2001)
	Absolute, DF-LIF	$(16.0 \pm 1.9) \times 10^{-15}$	298	Cabanas et al. (2001)
	Absolute, LIF	$(13.5 \pm 0.4) \times 10^{-15}$	298	Salgado et al. (2008)
	Relative	$(5.3 \pm 1.0) \times 10^{-15}$	298 ± 2	This work
	Recommended^{e,g}	$(5.7 \pm 1.2) \times 10^{-15}$		
MVK	Absolute, F-A	$\leq 1.2 \times 10^{-16}$	298	Rudich et al. (1996)
	Relative, propene	$< 6 \times 10^{-16}$	296 ± 2	Kwok et al. (1996)
	Relative, ethene	$(4.7 \pm 1.7) \times 10^{-16}$	296 ± 2	Canosa-Mas et al. (1999)
	Relative	$(1.3 \pm 0.6) \times 10^{-16}$	298 ± 2	This work
		Recommended^h	$(1.3 \pm 0.6) \times 10^{-16}$	
2-careneCarene	Absolute, DF-LIF	$(1.66 \pm 0.18) \times 10^{-11}$	298	Martínez et al. (1999)
	Relative, 2,3-dimethyl-2-butene	$(2.15 \pm 0.46) \times 10^{-11}$	295	Corchnoy and Atkinson (1990)
	Relative, 2-methyl-2-butene	$(1.87 \pm 0.27) \times 10^{-11}$		
	Relative	$(2.5 \pm 0.6) \times 10^{-11}$	296 ± 2	This work
	Recommended^{e,i}	$(1.8 \pm 0.6) \times 10^{-11}$		
3-Carene	Relative, 2-methyl-2-butene	$(1.01 \pm 0.35) \times 10^{-11d}$	295 ± 1	Atkinson et al. (1984)
	Relative, 2-methyl-2-butene	$(8.1 \pm 1.2) \times 10^{-12}$	298	Barnes et al. (1990)
	Relative	$(1.3 \pm 0.4) \times 10^{-11}$	297 ± 2	This work
	Recommended^{e,i}	$(8.7 \pm 0.5) \times 10^{-12}$		

^a Values from the literatures recalculated by $k_{\text{trans-2-butene}} = (3.90 \pm 0.78) \times 10^{-13}$ (IUPAC).

^b Values from the literatures recalculated by $k_{\text{2-buten-1-ol}} = (3.23 \pm 0.12) \times 10^{-13}$ (Zhao et al., 2011).

^c Values from the literatures recalculated by $k_{\text{propene}} = (9.50 \pm 5.50) \times 10^{-15}$ (IUPAC).

^d Values from the literatures recalculated by $k_{\text{2-methyl-2-butene}} = (9.37 \pm 0.33) \times 10^{-12}$ (Calvert et al., 2000).

^e Recommended value weighted average in Eqs. (3) and (4).

^f Recommended value included all the literatures excluded Benter and Schindler, 1988; Barnes et al., 1990; and Ellermann et al., 1992.

^g Recommended value included all the literatures excluded Cabanas et al., 2001 and Salgado et al., 2008.

^h Recommended value was the one obtained in this work.

ⁱ Recommended value included all the literature data.

DF-MS: discharge flow system and mass spectrometer; LIF: laser induced fluorescence; DF-LIF: discharge flow system and laser induced fluorescence; PR-A: pulse radiolysis combined with kinetic spectroscopy in the visible; F-CIMS: flow tube and chemical ionization mass spectrometer; F-A: flow tube coupled to a diode laser absorption system; CRDS: cavity ring-down spectroscopy; IUPAC: International Union of Pure and Applied Chemistry; T: temperature.

The uncertainties of the literature data of k were revised by including the quoted uncertainties in the rate constant of references by using the propagation of uncertainty in Eq. (2).

$\pm 0.9) \times 10^{-15}$ cm³/(molecule•sec), which is in good agreement with IUPAC value $(3.4 \pm 0.6) \times 10^{-15}$ cm³/(molecule•sec) at 298 K. The rate constant of methyl vinyl ketone reaction with NO₃ radical in this work is in the range of upper limit value of Rudich et al. (1996), but lower than that of Canosa-Mas et al. (1999) and Kwok et al. (1996) who used relative

method. Hence we recommend a preferred value as $(1.3 \pm 0.6) \times 10^{-16}$ cm³/(molecule•sec) obtained in this work.

As shown in Table 3, rate constants of the NO₃ reactions with both 2-carene and 3-carene have been measured using the relative method with 2-methyl-2-butene (Atkinson et al., 1984; Barnes et al., 1990; Corchnoy and Atkinson, 1990)

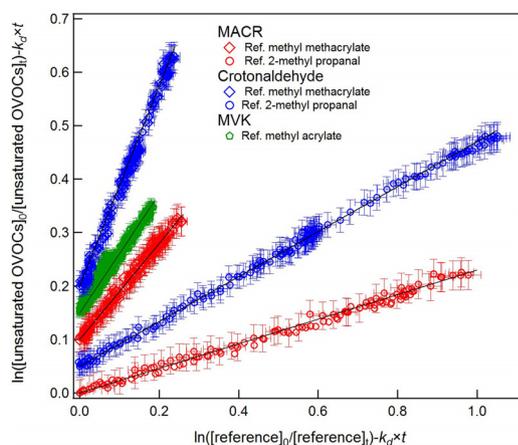


Fig. 2 – Plots of relative kinetic data obtained from the NO_3 reaction with methyl vinyl ketone using methyl acrylate as the reference, and NO_3 radical reaction with methacrolein and crotonaldehyde using methyl methacrylate, 2-methyl propanal as the reference. Note: crotonaldehyde with reference 2-methyl propanal, methacrolein with reference methyl methacrylate, methyl vinyl ketone with reference methyl acrylate and crotonaldehyde with reference methyl methacrylate were shifted on the y-axis 0.05, 0.1, 0.15 and 0.2 respectively for clarity. $[\text{unsaturated VOCs}]_0$: initial concentration of VOCs; $[\text{unsaturated OVOCs}]_t$: the concentration of VOCs at time t ; OVOCs: oxygenated volatile organic compounds.

and 2,3-dimethyl-2-butene (Corchnoy and Atkinson, 1990) as reference compounds. For the reaction of $\text{NO}_3 + 3\text{-carene}$, Barnes et al. (1990) measured a lower value than Atkinson et al. (1984), whereas a higher value was obtained in this work. Hence, we recommended the weighted average as $(8.7 \pm 0.5) \times 10^{-12} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$ by taking into account of all three measurements. For the reaction of $\text{NO}_3 + 2\text{-carene}$, however Martínez et al. (1999) measured the rate constant that was $\sim 30\%$ lower than other studies, we recommend the weighted average as $(1.8 \pm 0.6) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$ by taking into account all the measurements of Corchnoy and Atkinson (1990), Martínez et al. (1999) and this work.

2.3. Reactivity of unsaturated VOCs toward to NO_3 radical

The reaction of NO_3 radicals with unsaturated VOCs can proceed by two main pathways: addition to an unsaturated bond and H-atom abstraction. Canosa-Mas et al. (1988) and Wayne et al. (1991) have shown that both the addition and H-atom abstraction rate coefficients of OH radical and NO_3 radical reaction with alkynes and aliphatic aldehydes correlate. D'Anna et al. (2001) updated these relationships for addition as: $\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) + (22.7 \pm 2.5)$ and we updated the relationship for H-abstraction from alkanes based on the recent data of Zhou et al. (2019) giving: $\log(k_{\text{NO}_3}) = (1.78 \pm 0.57) \times \log(k_{\text{OH}}) + (4.26 \pm 6.59)$ as shown in Fig. 3. The data points of isoprene, 2-carene and 3-carene, as shown in Fig. 3, fall close to the correlation line for the addition reaction. This implies that the reaction of NO_3 radical with isoprene, 2-carene and 3-carene proceed mainly through the addition on the $\text{C}=\text{C}$ double bond. However, the data points of methacrolein, crotonaldehyde and methyl vinyl ketone fall close to the correlation line for abstraction reaction, even those which contain an olefinic bond. Martínez et al. (1999) investigated the reaction of NO_3 with a

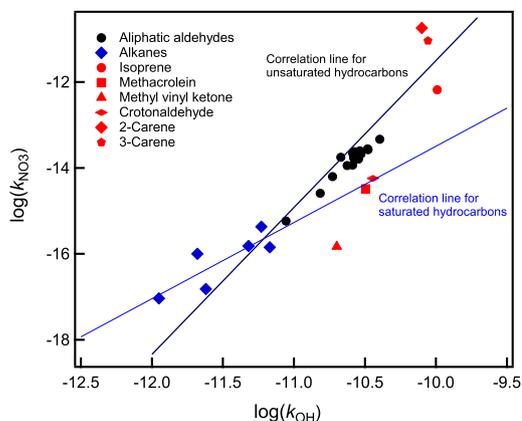


Fig. 3 – Linear free energy plot for the reactions of OH and NO_3 radicals with a series of 15 aliphatic aldehydes and studied unsaturated VOCs. The correlation line for addition is given by: $\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) + (22.7 \pm 2.5)$ from D'Anna et al. (2001) and the correlation line for H-atom abstraction is given by: $\log(k_{\text{NO}_3}) = (1.78 \pm 0.57) \times \log(k_{\text{OH}}) + (4.26 \pm 6.59)$ from the updated alkane data of Zhou et al., 2019. k_{NO_3} : rate coefficient of NO_3 reaction with VOCs; k_{OH} : rate coefficient of OH reaction with VOCs.

series of monoterpenes and concluded that their room temperature rate constant depends on the number and the structure of alkyl substituents around the olefinic bond. In this work, the rate constants of 3-carene and 2-carene reaction with NO_3 radical were determined to be ~ 16 and ~ 30 times larger than isoprene, respectively. By analogy to their reaction with ozone (as shown in Table 4), the additional steric effects of 3-carene than 2-carene could be the reason for its lower rate constants than 3-carene. As discussed by Chen et al. (2015), the reduction in rate coefficient for 3-carene arises from two hypotheses: (1) the conformational constraints of a C6-ring system containing two sp^2 hybridized carbons could decrease its reactivity; (2) the bridgehead carbon is out of the plane of the C6-ring similar to α -pinene and camphene, which may cause additional steric effects. However, a higher donor inductive effect of the alkyl chain around the $\text{C}=\text{C}$ bond should also be considered for the higher rate constant of 2-carene reaction with NO_3 radical than 3-carene.

Methacrolein and methyl vinyl ketone are the main products from the oxidation of isoprene in the atmosphere, which both contain one $\text{C}=\text{C}$ and a $\text{C}=\text{O}$ group. However, the rate coefficients of methacrolein and methyl vinyl ketone with NO_3 are at least one order magnitude lower than the reaction with their non-carbonyl analogues isobutene $((3.4 \pm 1.0) \times 10^{-13} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$, Calvert et al., 2000) and propene $((9.50 \pm 5.50) \times 10^{-15} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$, IUPAC, <http://iupac.pole-ether.fr/#>) with NO_3 , respectively. This indicates a strong electron-withdrawing effect of the $\text{C}=\text{O}$ group in the α position, which strongly deactivates the NO_3 addition on the $\text{C}=\text{C}$ bond (Kerdouci et al., 2012) as well as for other electrophilic addition reactions such as ozonolysis (McGillen et al., 2011). Conversely, the electron-donating inductive effect of the $-\text{CH}_3$ group attached to the $\text{C}=\text{C}$ bond in methacrolein increases its reactivity relative to that of methyl vinyl ketone (Canosa-Mas et al., 1999). As shown in Table 3, the reaction of crotonaldehyde with NO_3 radical $((5.7 \pm 1.2) \times 10^{-15} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$) is slightly faster than the reaction of methacrolein with the NO_3 radical $((3.3 \pm 0.9) \times 10^{-15} \text{ cm}^3/(\text{molecule}\cdot\text{sec})$). The structure of methacrolein and crotonaldehyde differs in that the $-\text{CH}_3$ in

Table 4 – Summary of rate constants and estimated atmospheric lifetimes of studied VOCs with respect to their reactions with OH, NO₃, O₃, and Cl at 298 ± 2 K and atmospheric pressure.

VOCs	Rate constant (cm ³ /(molecule•sec))				Lifetime (hr)			
	NO ₃ ^b	OH (× 10 ⁻¹¹)	O ₃ (× 10 ⁻¹⁸)	Cl (× 10 ⁻¹⁰)	τ _{NO₃}	τ _{OH}	τ _{O₃}	τ _{Cl}
Isoprene	6.6 × 10 ⁻¹³	10.2 ^c	11.3 ^e	4.00 ^h	0.84	2.7	35	69
Methacrolein	3.3 × 10 ⁻¹⁵	3.20 ^d	0.71 ^e	3.30 ⁱ	170	8.7	559	84
Methyl vinyl ketone	1.5 × 10 ⁻¹⁶	2.00 ^d	4.50 ^e	0.99 ^j	3736	13.9	88	281
Crotonaldehyde	5.7 × 10 ⁻¹⁵	3.60 ^d	1.58 ^f	2.20 ^j	98	7.7	251	126
2-Carene	1.8 × 10 ⁻¹¹	7.95 ^c	239 ^g	5.80 ^k	0.03	3.5	1.7	48
3-Carene	9.1 × 10 ⁻¹²	8.78 ^c	38.0 ^g	5.20 ^k	0.06	3.2	10	53

Assuming [OH] = 1 × 10⁶ molecules/cm³ (Spivakovsky et al., 2000), [NO₃] = 5 × 10⁸ molecules/cm³ (Atkinson et al., 1991), [O₃] = 7 × 10¹¹ molecules/cm³ (Monks et al., 2009) and [Cl] = 1 × 10⁴ molecules/cm³ (Wingenter et al. 1996)

^b Rate constants from this work.

^c Rate constants from Calvert et al. (2002).

^d Rate constants from Calvert et al. (2011).

^e Rate constants from Ren et al. (2017).

^f Rate constant from Sato et al. (2004).

^g Rate constants from Chen et al. (2015).

^h Rate constant from Suh et al. (2000).

ⁱ Rate constants from Canosa-Mas et al. (2001).

^j Rate constant from Ullerstam et al. (2001).

^k Rate constants from Timerghazin and Ariya (2001).

[X]: concentration of the X species; τ_{NO₃}, τ_{OH}, τ_{O₃} and τ_{Cl}: lifetimes of the studied VOCs with respect to the reactions with NO₃, OH, O₃ and Cl, respectively.

methacrolein is closer to the C=O group than in crotonaldehyde, which may decrease the electron-donating affection of -CH₃ to the C=C double bond.

2.4. Products investigation of 2-carene and 3-carene reaction with NO₃ radical and proposed reaction mechanism

The product formation from the reactions of 2-carene and 3-carene with the NO₃ radical were conducted in the 7300 L simulation chamber under ambient temperature and pressure. As shown in Fig. 4a and c, the 2-carene or 3-carene were introduced into the chamber first, and kept for two hours to inspect the wall-loss/dilution rate. Then N₂O₅ was injected continually for 15 min twice during the experiment in order to initiate the reaction. The possible products were detected using PTR-TOF-MS. As shown in Fig. 4, the *m/z* (mass-to-charge ratio) 153.127, 169.122 and 215.115 according to C₁₀H₁₆OH⁺, C₁₀H₁₆O₂H⁺ and C₁₀H₁₆O₄NH⁺, respectively, were identified as the products. Fig. 4b and d demonstrates the linearity of product formation vs the reactant consumption, indicating that the C₁₀H₁₆OH⁺, C₁₀H₁₆O₂H⁺ are primary products from the 2-carene/3-carene reaction with NO₃ radical.

Several studies (Colville and Griffin, 2004; Fry et al., 2014; Griffin et al., 1999; Hallquist et al., 1999) have investigated the products and aerosol formation from the reaction of 3-carene with the NO₃ radical and identified the end products 2,2-dimethyl-3-(2-oxopropyl)cyclo-propaneacetaldehyde (by analogy, here known as caronaldehyde, C₁₀H₁₆O₂, molar yields of 2%–3%), carbonyls (estimated molar yield of 20%–30%) and nitrates (66%–74%). By assuming the same sensitivity to 2-carene/3-carene in the PTR-TOF-MS, the caronaldehyde (*m/z* 169.122) formation yield was estimated as ~1% and ~0.3%, respectively, for 2-carene and 3-carene reaction with NO₃ radical. In this work, the *m/z* 153.127 was also detected by PTR-TOF-MS from the reaction system of 2-carene/3-carene with NO₃ and which was attributed to the epoxide, C₁₀H₁₆O. The epoxide formation from NO₃ addition to alkenes has been reported for several compounds, e.g. α-pinene, 2-butene, 2,3-dimethyl-2-butene (Benter et al., 1994; Wängberg et al., 1997), where formation yields generally range from 3% ± 0.5% to 20% ± 10% under atmospheric conditions. The epoxide formation

yields from the reactions of 2-carene and 3-carene with NO₃ were estimated to be ~3.6% and ~10.6%, respectively, by assuming same detection sensitivity as 2-carene and 3-carene in PTR-TOF-MS. Some organic nitrates such as nitrooxy-ketone (C₁₀H₁₆O₄N) were also detected in PTR-TOF-MS in *m/z* 215.115.

According to the product formation and a generalized reaction mechanism applicable to monoalkenes, dialkenes, and monoterpenes reactions with NO₃ radical (Barnes et al., 1990), as shown in Fig. 5, we were able to propose a reaction mechanism for 2-carene/3-carene reaction with NO₃ radical as below: the reaction proceeds mainly through NO₃ addition to the C=C bond to form two nitrooxy alkyl radicals, which can either react with O₂ to form an RO₂ radical (nitrooxy-peroxy radical) or lose NO₂ to form an epoxide C₁₀H₁₆O via reactions R7a/R8a or R7b/R8b in Fig. 5, respectively. Then the nitrooxy-peroxy radical (RO₂) can either react with NO₂ to form a nitrooxy-peroxy nitrate or other RO₂ radicals to form a RO radical (nitrooxy-alkoxy radical), hydroxy-nitrate and nitrooxy-ketone C₁₀H₁₆O₄N through reactions R7c/R8c or R7d/R8d in Fig. 5, respectively. As reported by Hallquist et al. (1999), the nitrooxy-peroxy nitrate are quite unstable and can only be detected in the beginning of reaction, which could explain why it was not detected in this work using low reactant concentrations. As shown in Fig. 5, nitrooxy-ketone C₁₀H₁₆O₄N could also be formed through the reaction R7e/R8e, as RO radical (nitrooxy-alkoxy radical) reaction with O₂. However, the RO radical (nitrooxy-alkoxy radical) could also form caronaldehyde C₁₀H₁₆O₂ by losing NO₂ via reactions R7f/R8f in Fig. 5.

To our best knowledge, there are no previous product and mechanism studies for the reaction of 2-carene with NO₃. It should be noted that, because of the lack of standards, all product formation yields from our work are based on the assumption of the same sensitivity of product peaks as 2-carene and 3-carene in PTR-TOF-MS. However, as shown in Fig. 4, the formation yield of identified products, nitrooxy-ketone (C₁₀H₁₆O₄N), caronaldehyde (C₁₀H₁₆O₂) and epoxide (C₁₀H₁₆O), are different between the 2-carene and 3-carene reactions with NO₃, which may relate to their different reactivity toward NO₃ radical as discussed in previous section, however, a difference in sensitivity for these species cannot be ruled out. Hence, more studies should be conducted to better un-

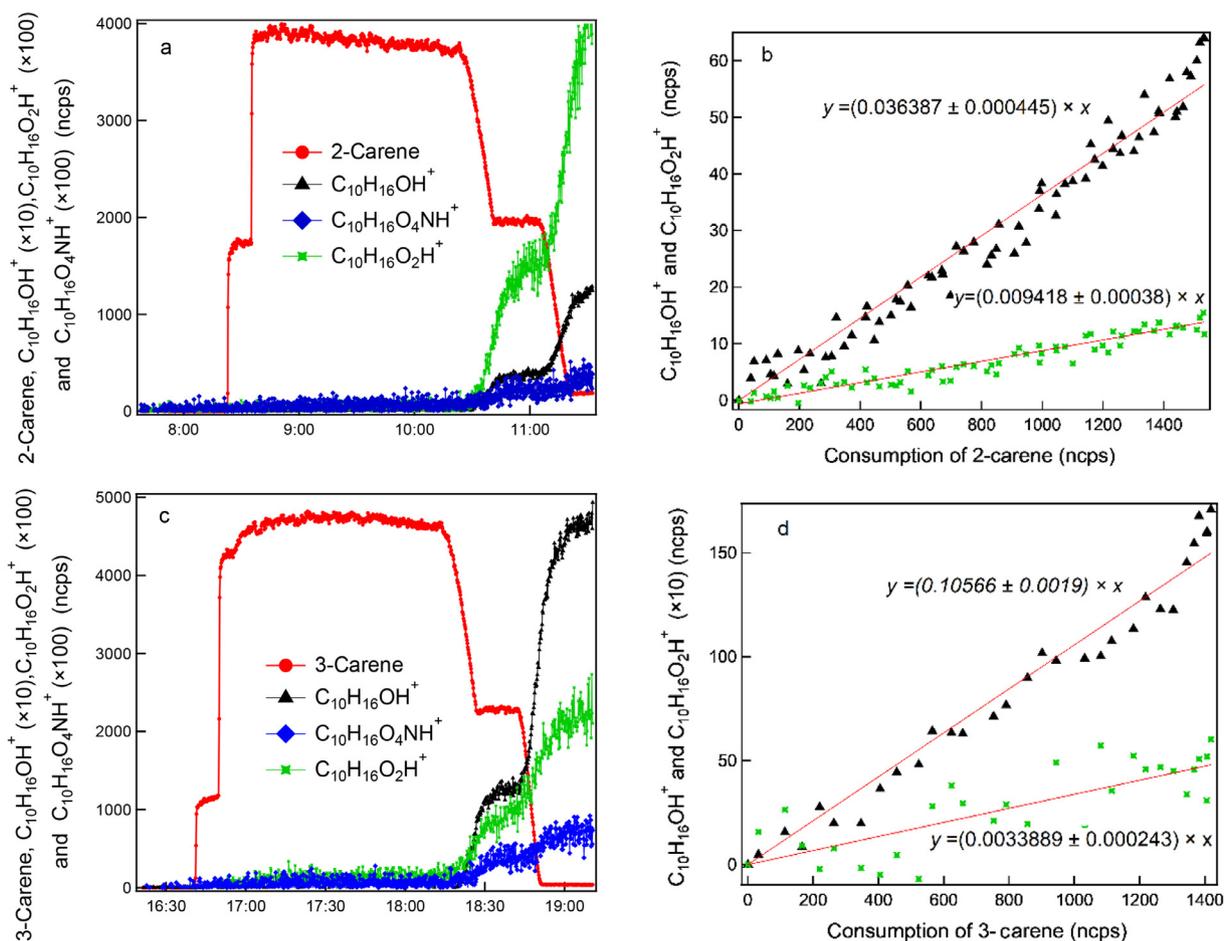


Fig. 4 – Time profile of 2-carene/3-carene (m/z 137.133), epoxide (C₁₀H₁₆OH⁺, m/z 153.127), nitrooxy-ketone (C₁₀H₁₆O₄NH⁺, m/z 215.115) and caronaldehyde (C₁₀H₁₆O₂H⁺, m/z 169.122) measured by PTR-TOF-MS upon introduction of (a) 2-carene and (c) 3-carene, and plots show product formation as function of (b) 2-carene and (d) 3-carene consumption.

understand the reaction of NO₃ with 2-carene/3-carene in the atmosphere.

3. Conclusions and atmospheric implications

The first objective of our study was to establish accurate rate coefficients of the reaction of the NO₃ radical with a series of unsaturated VOCs in order to better define their atmospheric lifetimes. Recommended rate coefficients are provided for isoprene, 2-carene, 3-carene, methyl vinyl ketone (MVK), methacrolein (MACR) and crotonaldehyde (CA), as $(6.6 \pm 0.8) \times 10^{-13}$, $(1.8 \pm 0.6) \times 10^{-11}$, $(8.7 \pm 0.5) \times 10^{-12}$, $(1.24 \pm 1.04) \times 10^{-16}$, $(3.3 \pm 0.9) \times 10^{-15}$ and $(5.7 \pm 1.2) \times 10^{-15}$ cm³/(molecule•sec), respectively at 295 ± 2 K and 760 Torr. Hence, these lifetimes (τ_{NO_3}) were estimated assuming an NO₃ concentration of 5×10^8 molecule/cm³ (Atkinson, 1991) in the following equation: $\tau_{\text{NO}_3} = \frac{1}{[\text{NO}_3] \times k_{\text{VOC}}}$ (where k_{VOC} is the rate coefficient recommended from this work). The atmospheric lifetimes of studied VOCs depending on their reaction with OH, O₃ and Cl were also calculated using the following oxidant concentrations: [OH] = 1×10^6 molecule/cm³ (Spivakovskiy et al., 2000), [O₃] = 7×10^{11} molecule/cm³ (Monks et al., 2009) and [Cl] = 1×10^4 molecule/cm³ (Wingenter et al., 1996) and the rate constants from the literature (Cabañas et al., 2001; Calvert et al., 2000; Calvert et al., 2011; Chen et al.,

2015; Ren et al., 2017; Sato et al., 2004; Suh and Zhang, 2000; Timerghazin and Ariya, 2001; Ullerstam et al., 2001). The calculated lifetimes are shown in Table 4. It is clear that the calculated tropospheric lifetimes of these VOCs with respect to the NO₃ reaction vary from a few minutes (isoprene, 2-carene and 3-carene) to few months (methyl vinyl ketone). The atmospheric lifetimes for studied VOCs due to reaction with OH radicals are roughly a few hours. Lifetimes with respect to ozone are longer, ranging from ~1.7 hr to months. The reaction of NO₃ may be more important than other oxidants for the overall loss of isoprene, 2-carene and 3-carene, assuming that the oxidant concentrations employed in these calculations are representative of typical tropospheric conditions. In addition, the reaction of NO₃ will contribute significantly at night when the NO_x emissions are high. Based on our measurements, we expect the overall atmospheric lifetimes of the studied VOCs with respect to all these oxidants are few minutes to a few days using the following equation:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} \quad (16)$$

where τ_{eff} , τ_{OH} , τ_{Cl} and τ_{O_3} are effective lifetime and those with respect to reactions with OH, Cl and ozone, respectively.

The reactivity of studied VOCs toward NO₃ was also discussed. The experiments indicate that NO₃ radical reactions with all the studied unsaturated VOCs proceed through addition to the olefinic bond, however, it indicates that the in-

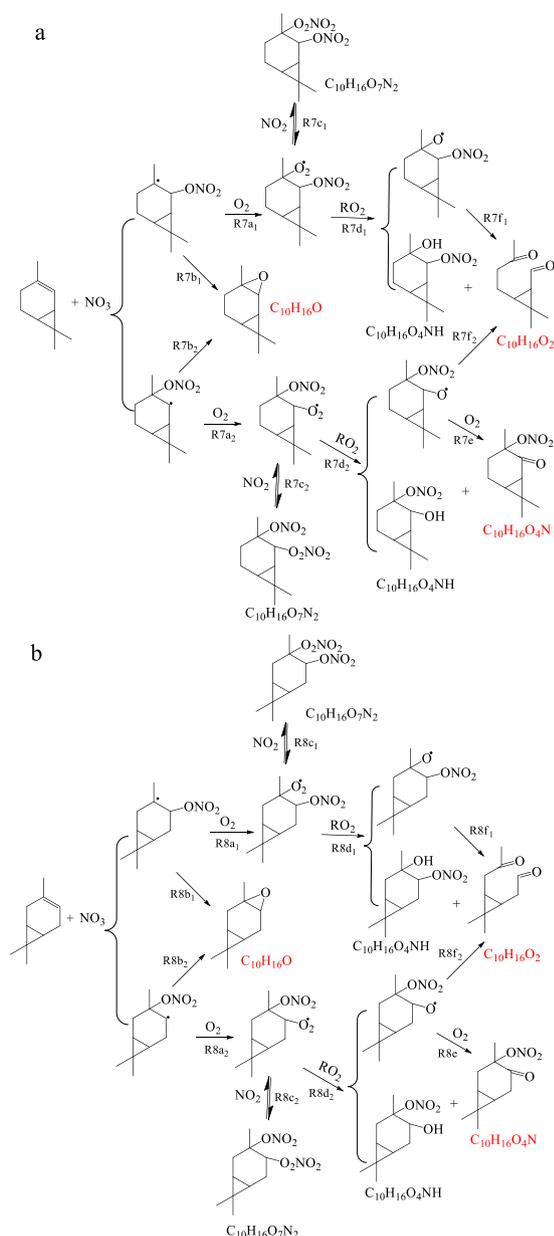


Fig. 5 – Proposed reaction mechanism of 2-carene (a) and 3-carene (b) reaction with NO_3 radical under the condition of this work: in the absence of NO and in excess of 2-carene/3-carene. The products identified in PTR-TOF-MS of this work were highlighted in red. RO_2 : peroxy radical. R7a_1 , R7a_2 , R7b_1 , R7b_2 , R7c_1 , R7c_2 , R7d_1 , R7d_2 , R7e , R7f_1 , R7f_2 , R8a_1 , R8a_2 , R8b_1 , R8b_2 , R8c_1 , R8c_2 , R8d_1 , R8d_2 , R8e , R8f_1 , and R8f_2 refer to reaction numbers as shown in the text.

roduction of a carbonyl group into unsaturated VOCs can deactivate the neighboring olefinic bond towards reaction with the NO_3 radical, which is to be expected since the presence of these electron-withdrawing substituents will reduce the electron density in the π orbitals of the alkenes, and will therefore reduce the rate coefficient of these electrophilic addition reactions. The different steric and inductive effects of the alkyl chain around the $\text{C}=\text{C}$ bond were considered for the different rate constants of 2-carene and 3-carene reaction with NO_3 .

In addition, the product formation from the reaction of 2-carene and 3-carene with NO_3 radical were also investigated. Epoxide, nitrooxy ketone ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{N}$) and caronaldehyde ($\text{C}_{10}\text{H}_{16}\text{O}_2$) were identified for both reaction systems. In the atmosphere, the epoxide could react with OH and NO_3 radicals and the atmospheric fate of caronaldehyde is expected to be reaction with OH and photolysis (Hallquist et al., 1997). Secondary organic aerosol (SOA) has been observed in the reaction of NO_3 with 3-carene in the simulation chamber with mass-based yields of up to 72% (Griffin et al., 1999; Hallquist et al., 1999) and organonitrates comprised 56% of the aerosol mass. Hence, more work on the identification of organonitrates SOA formation from reaction system of 2-carene and 3-carene with NO_3 radical would be desirable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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