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Kinetic and product studies of the reactions of NO_3 with a series of unsaturated organic compounds

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Abstract: Rate coefficients for the reaction of NO_3 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 $(6.6\pm0.8)\times10^{-13}$, $(1.8\pm0.6)\times10^{-11}$, $(8.7\pm0.5)\times10^{-12}$, $(1.24\pm1.04)\times10^{-16}$, $(3.3\pm0.9)\times10^{-15}$ and $(5.7\pm1.2)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The experiments indicate that NO_3 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 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. In addition, we investigated the product formation from the reactions of 2-carene and

3-carene with the NO_3 radical. Qualitative identification of an epoxide ($C_{10}H_{16}OH^+$), caronaldehyde ($C_{10}H_{16}O_2H^+$) and nitrooxy-ketone ($C_{10}H_{16}O_4NH^+$) was achieved using PTR-TOF-MS and a reaction mechanism is proposed.

Keywords: rate coefficient, NO_3 radical, products, terpene, OVOC

Introduction

Although the hydroxyl radical (OH) is recognized as the dominant oxidant in the daytime, the NO_3 radical (NO_3) is known to be the main oxidant of VOCs during the night (Atkinson 1991, Wayne et al. 1991). NO_3 is produced in the atmosphere via the reaction between O_3 and NO_2, which can originate from combustion, biomass burning, lightning and bacterial sources (Brown et al. 2005, Aldener et al. 2006, Brown and Stutz 2012). During the night, NO_3 and NO_2 exist in thermal equilibrium with N_2O_5:

$$NO_2 + O_3 \rightarrow NO_3 \qquad \text{(R1)}$$

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M \qquad \text{(R2)}$$

Oxidation by NO_3 is normally only significant during nighttime due to its rapid photolysis with a lifetime of ~5 s and the lifetime is significantly shorter in the presence of NO (in photochemical steady state with NO_2) during daytime (Finlayson-Pitts and Pitts 2000), however, it has been shown that NO_3 can be an important daytime oxidant within the canopy in forested environments (Liebmann et al. 2019). Field measurements have reported NO_3 concentrations ranging from lower than the detection limit (10 pptv) to 800 pptv and N_2O_5 concentrations could be as high as 10.9 ppbv dependent on local conditions (Brown and Stutz 2012).

NO_3 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 NO_3 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 NOx release, will influence the regional ozone production (Atlas 1988, Buhr et al. 1990, Aschmann et al. 2011, Suarez-Bertoa et al. 2012).

To improve the representation of NO_3 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 NO_3 rate coefficients carried out in different laboratories. For example, even the reaction of NO_3 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 (Atkinson et al. 2006, Ammann et al. 2019). In this work, gas-phase rate coefficient measurements were made for the following reactions:

Isoprene + NO_3 → products (R3)

Methacrolein (MACR) +NO_3 → products (R4)

Methyl vinyl ketone (MVK) + NO_3 → products (R5)

Crotonaldehyde (CA) + NO_3 → products (R6)

2-carene + NO_3 → products (R7)

3-carene +NO_3 → products (R8)

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 NO_3, using PTR-TOF-MS. To the best of our knowledge, this work provides the first mechanistic study of the reaction of 2-carene with the NO_3 radical.

Experimental methods

2.1 7300 L simulation chamber

Experiments were carried out in the 7300 L CNRS-ICARE indoor simulation chamber at ambient temperature (298±2 K) and pressure (760 Torr ± 5 torr). This chamber and the associated technique have been described in detail in a previous study (Ren 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 (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. SF_6 was used to determine the dilution rate in the chamber, which ranged from the (7-8)×10^{-6} s^{-1}.

A high-resolution proton transfer reaction time-of-flight mass spectrometer (IoniconAnalytik, PTR-TOF-MS 8000) with a hydronium ion (H_3O^+) ion source was employed to monitor the loss of the organic compounds in the chamber. The mass resolution of this instrument is >5000M/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^{-1} through a 1 m long 1/8 inch OD 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) coupled to a White-type multipass cell (143m optical path length) was also equipped to the simulation chamber, mainly for SF_6 detection. NO_3 radicals were generated from the thermal decomposition of N_2O_5.

Concentration ranges of the various chemicals of importance to these experiments are: [alkene]= (0.8 - 4.0) × 10^{12} molecule cm^{-3}, [N_2O_5] = (0.1 – 1.2) × 10^{11} molecule cm^{-3}, [NO_2]=(2 - 5) × 10^{11} molecule cm^{-3}, [NO_3] = (0.5 – 4.9) × 10^{10} molecule cm^{-3}.

2.2 Relative rate kinetic studies

Rate coefficients were determined by following the simultaneous decays of the studied VOCs and reference compounds from their reaction with NO_3 and other loss processes (wall loss, dilution):

NO_3 + VOC → Products $k_{3\text{-}8}$

NO_3 + References → Products k_{ref}

VOC/Reference → wall loss/ dilution k_d

$k_{3\text{-}8}$ and k_{ref} are the rate coefficient for the reactions of NO_3 with the studied VOCs

including isoprene, mehacrolein, 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 N_2O_5, the SF_6 and VOCs were introduced into the chamber and kept for one hour to quantify k_d. The dilution rate was followed by monitoring SF_6 throughout the experiment period using the long-path Fourier transform infrared spectrometer equipped to the chamber (2) sufficient N_2O_5 was continually introduced to the chamber from a stream of purified air, such that a measureable consumption of VOCs occurred on a reasonable timescale (30 mins to 1 hour). 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 NO_3 and non-reactive loss, it can be shown that:

$$\ln\frac{[VOC]_0}{[VOC]_t} - k_d * t = \frac{k_{3-8}}{k_{ref}} * \left(\ln\frac{[ref]_0}{[ref]_t} - k_d * t\right) \qquad \text{Eq.1}$$

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 $\ln\frac{[VOC]_0}{[VOC]_t} - k_d * t$ against $\ln\frac{[ref]_0}{[ref]_t} - k_d * t$ should be straight lines of slope $\frac{k_{3-8}}{k_{ref}}$, with zero intercept.

2.3 Chemicals

The sources of chemicals used and their purities are: isoprene (99%), methacrolein (95%), methyl vinyl ketone (99%), crotonaldehyde (≥ 99.5%), 2-carene (97%), 3-carene (≥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.

N_2O_5 was synthesized in a vacuum line by the reaction of NO_2 with excess O_3 through reactions R1 and R2 (Zhou et al. 2017). In the first stage of synthesis, NO_2 was produced from the reaction of NO and O_3 in a glass tube. The mixture of NO_2 and O_3 were then flushed into a bulb (1 L) where NO_3 and N_2O_5 are formed. At the end of the synthesis, N_2O_5 crystals were collected in a cold trap (190 K). N_2O_5 crystals were then purified by trap-to-trap distillation under a flow of O_2/O_3, which could be kept for several weeks in a cold trap

maintained 190 K.

Results and discussion

3.1 Rate constants of NO_3 reaction with studied VOCs

The rate coefficients for isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene reaction with NO_3 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 to 4.1× 10^{12} molecule cm^{-3} as shown in Table 2. The recommended rate constants for the reaction of reference compounds with NO_3] at 298 K are: $k_{2\text{-methyl propanal}}$ = (1.17±0.23)×10^{-14} (Calvert et al. 2011), $k_{\text{methyl methacrylate}}$=(2.98±0.35)×$10^{-15}$ (Zhou et al. 2017), $k_{1,3\text{-cyclohexadiene}}$ = (1.15±0.35)×10^{-11} (Calvert et al. 2000), $k_{\alpha\text{-cedrene}}$ = (8.20±0.73)×10^{-12} (Calvert et al. 2000), $k_{\text{methyl acrylate}}$ = (1.10±0.55)×10^{-16} (Calvert et al. 2011) and $k_{\text{cyclohexene}}$ = (5.90±1.77)×10^{-13} (Calvert et al. 2000). Unit in cm^3 $molecule^{-1}$ s^{-1}.

Figure 1 and 2 show straight lines of $\ln\frac{[VOC]_0}{[VOC]_t} - k_d * t$ as a function of $\ln\frac{[ref]_0}{[ref]_t} - k_d * t$ with zero intercept. It can be observed that all individual experiments are in good agreement. The rate coefficient ratio of $\frac{k}{k_{ref}}$ was expected from the linear fitting of Figure 1 and Figure 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, $\frac{k}{k_{ref}}$, obtained for the studied VOCs are shown in Table 2. The quoted uncertainties on the $\frac{k}{k_{ref}}$ are 2 times the standard deviation in the least-squares fit of $\ln\frac{[VOC]_0}{[VOC]_t} - k_d * t$ vs $\ln\frac{[ref]_0}{[ref]_t} - k_d * t$, and then multiplied 2.9 as the Student *t*-distribution contribution due to the limited number of measurements. The rate constants obtained for the studied VOCs, $k_{3\text{-}8}$, 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):

$$\frac{k}{k_{\mathrm{ref}}} k_{\mathrm{ref}} \sqrt{\left[\frac{\sigma_{k_{\mathrm{ref}}}}{k_{\mathrm{ref}}}\right]^2 + \left[\frac{\sigma_{\frac{k}{k_{\mathrm{ref}}}}}{\frac{k}{k_{\mathrm{ref}}}}\right]^2} \qquad \text{Eq.2}$$

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:

$k_{average}=(w_1k_1 + w_2k_2 + \ldots)/(w_1+w_2+\ldots)$, where $w_1=1/\sigma_1$, etc. Eq.3

The error, $\sigma_{average}$, was given by:

$\sigma_{av}=2*(1/ {}_1+1/\sigma_2+ \ldots)^{-0.5}$ Eq.4

3.2 Comparison with the literature

Table 3 summarizes the rate constants measured by this work with data from the literature for the reactions of the NO_3 radical with isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene and 3-carene. As shown in Table 3, the kinetics of the isoprene reaction with NO_3 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) and 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) and 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 NO_3

may result from its reaction with NO_2, alkyl and peroxy radicals in these experiments. As a result, we recommend a weighted rate constant of isoprene + NO_3 of $(6.6\pm0.8)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} 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 $(6.5\pm1.3)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The recommended value of crotonaldehyde + NO_3 is $(5.7\pm1.2)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, only taking into account the relative rate measurements.

The rate constant of methacrolein + NO_3 has been measured mainly by the relative method (Kwok et al. 1996, Chew et al. 1998, Canosa-Mas et al. 1999), only one study from Rudich et al. (1996) applied an absolute method and observed an upper limit of $<8\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. The value of this work agrees well with the studies using the relative method and hence we recommend a weighted average of $(3.3\pm0.9)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, which is in good agreement with IUPAC value $(3.4\pm0.6)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The rate constant of methyl vinyl ketone reaction with NO_3 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 $(1.3\pm0.6)\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} obtained in this work.

As shown in Table 3, rate constants of the NO_3 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) and 2,3-dimethyl-2-butene (Corchnoy and Atkinson 1990) as reference compounds. For the reaction of NO_3 + 3-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 $(8.7\pm0.5)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} by taking into account of all three measurements. For the reaction of NO_3 + 2-carene, however Martínez et al. (1999) measured the rate constant that was ~30% lower than other studies, we recommend the weighted average as $(1.8\pm0.6)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} by taking into account all the measurements of Corchnoy and Atkinson (1990), Martínez et al. (1999) and this work.

3.3 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: $\log(k_{NO3}) = (3.43\pm0.24) \times \log(k_{OH}) + (22.7\pm2.5)$ and we updated the relationship for H-abstraction from alkanes based on the recent data of Zhou et al. (2019) giving: $\log(k_{NO3}) = (1.78\pm0.57) \times \log(k_{OH}) + (4.26\pm6.59)$ as shown in Figure 3. The data points of isoprene, 2-carene and 3-carene, as shown in Figure 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 C=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 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 donator inductive effect of the alkyl chain around the C=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 C=C and a C=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 [$(3.4\pm1.0)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, (Calvert et al. 2000)] and propene [$(9.50\pm5.50)\times10^{-15}$ cm^3

molecule^{-1} s^{-1}, IUPAC http://iupac.pole-ether.fr/#] with NO_3, respectively. This indicates a strong electron-withdrawing effect of the C=O group in the α position, which strongly deactivates the NO_3 addition on the C=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 $–CH_3$ group attached to the C=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 ($5.7\pm1.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1}) is slightly faster than the reaction of methacrolein with the NO_3 radical ($3.3\pm0.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1}). The structure of methacrolein and crotonaldehyde differs in that the $-CH_3$ in methacrolein is closer to the C=O group than in crotonaldehyde, which may decrease the electron-donating affection of $–CH_3$ to the C=C double bond.

3.4 Products investigation of 2-carene & 3-carene reaction with NO_3 radical and proposed reaction mechanism

The product formation from the reactions of 2-carene and 3-carene with the NO_3 radical were conducted in the 7300 L simulation chamber under ambient temperature and pressure. As shown in Figure 4a and 4c, 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 N_2O_5 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 Figure 4, the m/z 153.127, 169.122 and 215.115 according to $C_{10}H_{16}OH^+$, $C_{10}H_{16}O_2H^+$ and $C_{10}H_{16}O_4NH^+$, respectively, were identified as the products. Figures 4b and 4d demonstrate the linearity of product formation vs the reactant consumption, indicating that the $C_{10}H_{16}OH^+$, $C_{10}H_{16}O_2H^+$ are primary products from the 2-carene/3-carene reaction with NO_3 radical.

Several studies (Griffin et al. 1999, Hallquist et al. 1999, Colville and Griffin 2004, Fry et al. 2014) have investigated the products and aerosol formation from the reaction of 3-carene with the NO_3 radical and identified the end products 2,2-dimethyl-3-(2-oxopropyl)cyclo-propaneacetaldehyde (by analogy, here known as caronaldehyde, $C_{10}H_{16}O_2$, 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 NO_3 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 NO_3 and which was attributed to the epoxide, $C_{10}H_{16}O$. The epoxide formation from NO_3 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 NO_3 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 ($C_{10}H_{16}O_4N$) 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 NO_3 radical (Barnes et al. 1990), as shown in Figure 5, we were able to propose a reaction mechanism for 2-carene/3-carene reaction with NO_3 radical as below: the reaction proceeds mainly through NO_3 addition to the C=C bond to form two nitrooxy alkyl radicals, which can either react with O_2 to form an RO_2 radical (nitrooxy-peroxy radical) or lose NO_2 to form an epoxide $C_{10}H_{16}O$ via reactions R7a/ R8a or R7b/ R8b in Figure 5, respectively. Then the nitrooxy-peroxy radical (RO_2) can either react with NO_2 to form a nitrooxy-peroxy nitrate or other RO_2 radicals to form an RO radical (nitrooxy-alkoxy radical), hydroxy-nitrate and nitrooxy-ketone $C_{10}H_{16}O_4N$ through reactions R7c/ R8c or R7d/ R8d in Figure 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 it in this work using low reactant concentrations. As shown in Figure 5, nitrooxy-ketone $C_{10}H_{16}O_4N$ could also be formed through the reaction R7e/ R8e, as RO radical (nitrooxy-alkoxy radical) reaction with O_2. However, the RO radical (nitrooxy-alkoxy radical) could also form caronaldehyde $C_{10}H_{16}O_2$ by losing NO_2 via reactions R7f/ R8f in Figure 5.

To our best knowledge, there are no previous product and mechanism studies for the reaction of 2-carene with NO_3. 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 Figure 4, the

formation yield of identified products, nitrooxy-ketone ($C_{10}H_{16}O_4N$), caronaldehyde ($C_{10}H_{16}O_2$) and epoxide ($C_{10}H_{16}O$), are different between the 2-carene and 3-carene reactions with NO_3, which may relate to their different reactivity toward NO_3 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 understand the reaction of NO_3 with 2-carene/3-carene in the atmosphere.

Conclusion and Atmospheric Implications

The first objective of our study was to establish accurate rate coefficients of the reaction of the NO_3 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 $(6.6\pm0.8)\times10^{-13}$, $(1.8\pm0.6)\times10^{-11}$, $(8.7\pm0.5)\times10^{-12}$, $(1.24\pm1.04)\times10^{-16}$, $(3.3\pm0.9)\times10^{-15}$ and $(5.7\pm1.2)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, respectively at 295±2 K and 760 Torr. Hence, these lifetimes were estimated assuming an NO_3 concentration of 5×10^8 molecule cm^{-3} (Atkinson 1991) in the following equation: $\tau_{NO3} = \frac{1}{[NO_3]*k_{VOC}}$. The atmospheric lifetimes of studied VOCs depending on their reaction with OH, O_3 and Cl were also calculated using the following oxidant concentrations: [OH] = 1×10^6 molecule cm^{-3} (Spivakovsky et al. 2000), [O_3] = 7×10^{11} molecule cm^{-3} (Monks et al. 2009) and [Cl] = 1×10^4 molecule cm^{-3} (Wingenter et al. 1996) and the rate constants from the literature (Calvert et al. 2000, Suh and Zhang 2000, Cabañas et al. 2001, Timerghazin and Ariya 2001, Ullerstam et al. 2001, Sato et al. 2004, Calvert et al. 2011, Chen et al. 2015, Ren et al. 2017). The calculated lifetimes are shown in Table 4. It is clear that the calculated tropospheric lifetimes of these VOCs with respect to the NO_3 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 hours to months. The reaction of NO_3 may be more important than other oxidants to 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 NO_3 will contribute significantly at night when the NOx 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: $\frac{1}{\tau_{eff}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{NO3}} + \frac{1}{\tau_{O3}}$.

The reactivity of studied VOCs toward NO_3 was also discussed. The experiments indicate that NO_3 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 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 C=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 ($C_{10}H_{16}O_4N$) and caronaldehyde ($C_{10}H_{16}O_2$) 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.

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