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# Kinetic and product studies of the reactions of NO<sub>3</sub> with a series of unsaturated organic compounds

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**Abstract:** Rate coefficients for the reaction of NO<sub>3</sub> 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  $(5.7 \pm 1.2) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The experiments indicate that NO<sub>3</sub> 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<sub>3</sub> 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

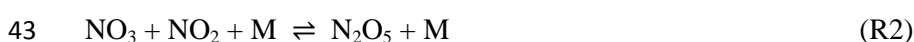
30 3-carene with the  $\text{NO}_3$  radical. Qualitative identification of an epoxide ( $\text{C}_{10}\text{H}_{16}\text{OH}^+$ ),  
31 caronaldehyde ( $\text{C}_{10}\text{H}_{16}\text{O}_2\text{H}^+$ ) and nitrooxy-ketone ( $\text{C}_{10}\text{H}_{16}\text{O}_4\text{NH}^+$ ) was achieved using  
32 PTR-TOF-MS and a reaction mechanism is proposed.

33 Keywords: rate coefficient,  $\text{NO}_3$  radical, products, terpene, OVOC

34

## 35 **Introduction**

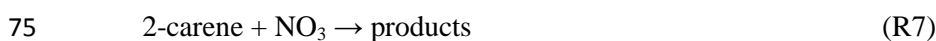
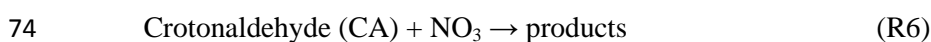
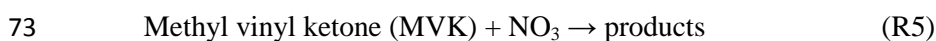
36 Although the hydroxyl radical (OH) is recognized as the dominant oxidant in the daytime, the  
37 NO<sub>3</sub> radical (NO<sub>3</sub>) is known to be the main oxidant of VOCs during the night (Atkinson 1991,  
38 Wayne et al. 1991). NO<sub>3</sub> is produced in the atmosphere via the reaction between O<sub>3</sub> and NO<sub>2</sub>,  
39 which can originate from combustion, biomass burning, lightning and bacterial sources  
40 (Brown et al. 2005, Aldener et al. 2006, Brown and Stutz 2012). During the night, NO<sub>3</sub> and  
41 NO<sub>2</sub> exist in thermal equilibrium with N<sub>2</sub>O<sub>5</sub>:



44 Oxidation by NO<sub>3</sub> is normally only significant during nighttime due to its rapid photolysis  
45 with a lifetime of ~5 s and the lifetime is significantly shorter in the presence of NO (in  
46 photochemical steady state with NO<sub>2</sub>) during daytime (Finlayson-Pitts and Pitts 2000),  
47 however, it has been shown that NO<sub>3</sub> can be an important daytime oxidant within the canopy  
48 in forested environments (Liebmann et al. 2019). Field measurements have reported NO<sub>3</sub>  
49 concentrations ranging from lower than the detection limit (10 pptv) to 800 pptv and N<sub>2</sub>O<sub>5</sub>  
50 concentrations could be as high as 10.9 ppbv dependent on local conditions (Brown and Stutz  
51 2012).

52 NO<sub>3</sub> is a major oxidant for a variety of VOCs and sulfur compounds, and is particularly  
53 reactive towards unsaturated biogenic VOCs (BVOC), including both isoprene  
54 (2-methyl-1,3-butadiene) and the monoterpenes (Wayne et al. 1991). Isoprene is the most  
55 abundant non-methane hydrocarbon in the atmosphere with annual global emissions of 500  
56 Tg (Guenther et al. 2006). Reactions of NO<sub>3</sub> with isoprene and monoterpenes could produce  
57 both nitrated compounds and secondary organic aerosol (SOA) in variable yields, some model  
58 studies have suggested that these reactions may be responsible for a large fraction of regional  
59 and global SOA (Griffin et al. 1999, Ng et al. 2008, Perring et al. 2009, Rollins et al. 2009).  
60 However, the nitrated compounds can be long-lived in the atmosphere acting as temporary  
61 reservoirs of odd nitrogen, which can then be transported downwind to remote regions where  
62 their decomposition, and subsequent NO<sub>x</sub> release, will influence the regional ozone  
63 production (Atlas 1988, Buhr et al. 1990, Aschmann et al. 2011, Suarez-Bertoa et al. 2012).

64 To improve the representation of NO<sub>3</sub> oxidation of VOCs in tropospheric chemistry models,  
65 more kinetic studies of these reactions are needed. Especially since there are quite  
66 considerable discrepancies in measurements of NO<sub>3</sub> rate coefficients carried out in different  
67 laboratories. For example, even the reaction of NO<sub>3</sub> with isoprene, which has been studied  
68 extensively, remains quite uncertain, since reported rate constants span a range of a factor of 2  
69 as shown in IUPAC (Atkinson et al. 2006, Ammann et al. 2019). In this work, gas-phase rate  
70 coefficient measurements were made for the following reactions:



77 In addition, the experimental rate coefficients obtained for the different VOCs are discussed  
78 and compared with regard to their chemical structures. Besides that, some exploratory work is  
79 conducted regarding the products formed from the reaction of 2-carene and 3-carene with  
80 NO<sub>3</sub>, using PTR-TOF-MS. To the best of our knowledge, this work provides the first  
81 mechanistic study of the reaction of 2-carene with the NO<sub>3</sub> radical.

82

## 83 **Experimental methods**

### 84 **2.1 7300 L simulation chamber**

85 Experiments were carried out in the 7300 L CNRS-ICARE indoor simulation chamber at  
86 ambient temperature (298±2 K) and pressure (760 Torr ± 5 torr). This chamber and the  
87 associated technique have been described in detail in a previous study (Ren et al. 2019) and is  
88 thus described only briefly here. The chamber was made of Teflon foil and surrounded by  
89 opaque protection panels. Two Teflon fans were utilized to promote rapid mixing of the  
90 reactants. Dry and purified air (RH<1 %) was used as a bath gas in experiments and also to  
91 clean the chamber after each experiment. Known volumes of studied hydrocarbons were  
92 injected into a Pyrex impinger and driven into the chamber with a stream of purified air.

93 Concentrations were calculated using the ideal gas law, based on the volume and density of  
94 the sample that was injected and the volume of the chamber. In order to compensate for  
95 sampling flows and leaks and to avoid any ingress of outside air, 5 L/min of purified air was  
96 added continuously during the experiments to maintain a slight overpressure. SF<sub>6</sub> was used to  
97 determine the dilution rate in the chamber, which ranged from the (7-8)×10<sup>-6</sup> s<sup>-1</sup>.

98 A high-resolution proton transfer reaction time-of-flight mass spectrometer  
99 (IoniconAnalytik, PTR-TOF-MS 8000) with a hydronium ion (H<sub>3</sub>O<sup>+</sup>) ion source was  
100 employed to monitor the loss of the organic compounds in the chamber. The mass resolution  
101 of this instrument is >5000M/ΔM. The pressure in the PTR-TOF-MS drift tube was  
102 maintained at 2.1 mbar and drift voltage of 400 V was used to obtain an electric field, E/N, of  
103 98 Td. The sampling flow from the chamber to the PTR-TOF-MS was approximately 150 mL  
104 min<sup>-1</sup> through a 1 m long 1/8 inch OD Teflon tube, heated to 60 °C. The mass spectral data  
105 were analyzed by PTR-TOF Data Analyzer software (Müller et al. 2013). The detection  
106 sensitivities for the VOCs were derived from the slopes of the calibrations plots of the signal  
107 (in normalized counts per second, ncps) versus their corresponding mixing ratios (ppbv) as  
108 shown in Table 1. An in situ Fourier transform infrared spectrometry (FTIR, Nicolet 5700)  
109 coupled to a White-type multipass cell (143m optical path length) was also equipped to the  
110 simulation chamber, mainly for SF<sub>6</sub> detection. NO<sub>3</sub> radicals were generated from the thermal  
111 decomposition of N<sub>2</sub>O<sub>5</sub>.

112 Concentration ranges of the various chemicals of importance to these experiments are:  
113 [alkene]= (0.8 - 4.0) × 10<sup>12</sup> molecule cm<sup>-3</sup>, [N<sub>2</sub>O<sub>5</sub>] = (0.1 - 1.2) × 10<sup>11</sup> molecule cm<sup>-3</sup>,  
114 [NO<sub>2</sub>]=(2 - 5) × 10<sup>11</sup> molecule cm<sup>-3</sup>, [NO<sub>3</sub>] = (0.5 - 4.9) × 10<sup>10</sup> molecule cm<sup>-3</sup>.

## 115 **2.2 Relative rate kinetic studies**

116 Rate coefficients were determined by following the simultaneous decays of the studied VOCs  
117 and reference compounds from their reaction with NO<sub>3</sub> and other loss processes (wall loss,  
118 dilution):



122 k<sub>3-8</sub> and k<sub>ref</sub> are the rate coefficient for the reactions of NO<sub>3</sub> with the studied VOCs

123 including isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde, 2-carene, 3-carene and  
124 reference compounds (cyclohexene, methyl methacrylate, 2-methyl propanal, methyl acrylate,  
125 1,3-cyclohexadiene,  $\alpha$ -cedrene), respectively.  $k_d$  is the non-reactive loss rate of studied VOCs  
126 and reference compounds.

127 The typical experimental procedure consisted of (1) prior to injection of  $N_2O_5$ , the  $SF_6$   
128 and VOCs were introduced into the chamber and kept for one hour to quantify  $k_d$ . The  
129 dilution rate was followed by monitoring  $SF_6$  throughout the experiment period using the  
130 long-path Fourier transform infrared spectrometer equipped to the chamber (2) sufficient  
131  $N_2O_5$  was continually introduced to the chamber from a stream of purified air, such that a  
132 measureable consumption of VOCs occurred on a reasonable timescale (30 mins to 1 hour).  
133 The decays of both the studied VOCs and reference compounds were continuously monitored  
134 using PTR-TOF-MS.

135 Assuming that the VOCs and reference compounds were lost only by reaction with  $NO_3$   
136 and non-reactive loss, it can be shown that:

$$137 \quad \ln \frac{[VOC]_0}{[VOC]_t} - k_d * t = \frac{k_{3-g}}{k_{ref}} * (\ln \frac{[ref]_0}{[ref]_t} - k_d * t) \quad \text{Eq.1}$$

138 Where  $[VOC]_0$ ,  $[VOC]_t$  and  $[ref]_0$ ,  $[ref]_t$  are the corresponding concentrations of VOCs and  
139 reference compounds at initial time and time t. Hence, plots of  $\ln \frac{[VOC]_0}{[VOC]_t} - k_d * t$  against  $\ln \frac{[ref]_0}{[ref]_t}$   
140  $- k_d * t$  should be straight lines of slope  $\frac{k_{3-g}}{k_{ref}}$ , with zero intercept.

### 141 2.3 Chemicals

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

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

152 maintained 190 K.

## 153 **Results and discussion**

### 154 **3.1 Rate constants of NO<sub>3</sub> reaction with studied VOCs**

155 The rate coefficients for isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde,  
156 2-carene and 3-carene reaction with NO<sub>3</sub> radical were obtained in the 7300 L ICARE  
157 simulation chamber using references including cyclohexene, 2-methyl propanal, methyl  
158 methacrylate, methyl acrylate, 1,3-cyclohexadiene and  $\alpha$ -cedrene. The concentration of VOCs  
159 ranged from 0.8 to  $4.1 \times 10^{12}$  molecule cm<sup>-3</sup> as shown in Table 2. The recommended rate  
160 constants for the reaction of reference compounds with NO<sub>3</sub> ] at 298 K are:  $k_{2\text{-methyl propanal}} =$   
161  $(1.17 \pm 0.23) \times 10^{-14}$  (Calvert et al. 2011),  $k_{\text{methyl methacrylate}} = (2.98 \pm 0.35) \times 10^{-15}$  (Zhou et al. 2017),  
162  $k_{1,3\text{-cyclohexadiene}} = (1.15 \pm 0.35) \times 10^{-11}$  (Calvert et al. 2000),  $k_{\alpha\text{-cedrene}} = (8.20 \pm 0.73) \times 10^{-12}$  (Calvert  
163 et al. 2000),  $k_{\text{methyl acrylate}} = (1.10 \pm 0.55) \times 10^{-16}$  (Calvert et al. 2011) and  $k_{\text{cyclohexene}} =$   
164  $(5.90 \pm 1.77) \times 10^{-13}$  (Calvert et al. 2000). Unit in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

165 Figure 1 and 2 show straight lines of  $\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d * t$  as a function of  $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d * t$  with zero  
166 intercept. It can be observed that all individual experiments are in good agreement. The rate  
167 coefficient ratio of  $\frac{k}{k_{ref}}$  was expected from the linear fitting of Figure 1 and Figure 2, which  
168 was fitted using the protocol of Brauers and Finlayson-Pitts (1997) by taking into account  
169 errors on both abscissa and ordinate scales. These errors were estimated from the calibration  
170 curve before the experiments. The relative rate ratios,  $\frac{k}{k_{ref}}$ , obtained for the studied VOCs are  
171 shown in Table 2. The quoted uncertainties on the  $\frac{k}{k_{ref}}$  are 2 times the standard deviation in  
172 the least-squares fit of  $\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d * t$  vs  $\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} - k_d * t$ , and then multiplied 2.9 as the  
173 Student *t*-distribution contribution due to the limited number of measurements. The rate  
174 constants obtained for the studied VOCs,  $k_{3-8}$ , according to different reference compounds are  
175 also shown in Table 2. The uncertainties for *k* combined the precision of our measured values  
176 with the quoted uncertainties in the rate constant of references by using the following  
177 propagation of uncertainty (Zhou et al. 2017):



$$178 \quad \frac{k}{k_{\text{ref}}} k_{\text{ref}} \sqrt{\left[\frac{\sigma k_{\text{ref}}}{k_{\text{ref}}}\right]^2 + \left[\frac{\sigma \frac{k}{k_{\text{ref}}}}{\frac{k}{k_{\text{ref}}}}\right]^2} \quad \text{Eq.2}$$

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

$$184 \quad k_{\text{average}} = (w_1 k_1 + w_2 k_2 + \dots) / (w_1 + w_2 + \dots), \text{ where } w_1 = 1/\sigma_1, \text{ etc.} \quad \text{Eq.3}$$

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

$$186 \quad \sigma_{\text{av}} = 2 * (1/\sigma_1 + 1/\sigma_2 + \dots)^{-0.5} \quad \text{Eq.4}$$

### 187 3.2 Comparison with the literature

188 Table 3 summarizes the rate constants measured by this work with data from the  
 189 literature for the reactions of the  $\text{NO}_3$  radical with isoprene, methacrolein, methyl vinyl  
 190 ketone, crotonaldehyde, 2-carene and 3-carene. As shown in Table 3, the kinetics of the  
 191 isoprene reaction with  $\text{NO}_3$  radical has been studied extensively using both absolute and  
 192 relative methods. We recalculate the values for the studies of Atkinson et al. (1984), Barnes et  
 193 al. (1990) and Stabel et al. (2005) using more recent recommended reference values  
 194 (trans-2-butene and 2-buten-1-ol) from IUPAC (Atkinson et al. 2006) and Zhao et al. (2011).  
 195 Although the rate coefficient obtained in this work is in good agreement with most of  
 196 previous studies, a larger difference is observed compared with the work of Benter and  
 197 Schindler (1988), Barnes et al. (1990) and Ellermann et al. (1992). With the exception of  
 198 Barnes et al. (1990), both Benter and Schindler (1988) and Ellermann et al. (1992) applied  
 199 absolute method using DF-MS (discharge flow system and mass spectrometer and PR-A  
 200 (pulse radiolysis combined with kinetic spectroscopy in the visible). As shown in Table 3,  
 201 higher values were also observed for crotonaldehyde for two absolute determinations  
 202 (Cabañas et al. 2001, Salgado et al. 2008) compared with the relative measurements  
 203 [(Atkinson et al. 1987, Ullerstam et al. 2001) and this work]. As mentioned by Zhao et al.  
 204 (2011), Canosa-Mas et al. (1988) and Wille et al. (1991), additional removal of VOCs may  
 205 occur due to its side reactions initiated by F atoms / OH radicals or additional loss of  $\text{NO}_3$

206 may result from its reaction with NO<sub>2</sub>, alkyl and peroxy radicals in these experiments. As a  
207 result, we recommend a weighted rate constant of isoprene + NO<sub>3</sub> of  $(6.6\pm 0.8)\times 10^{-13}$  cm<sup>3</sup>  
208 molecule<sup>-1</sup> s<sup>-1</sup> based on all the studies except Benter and Schindler (1988), Barnes et al. (1990)  
209 and Ellermann et al. (1992), which is in good agreement with IUPAC (Atkinson et al. 2006)  
210 value as  $(6.5\pm 1.3)\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. The recommended value of  
211 crotonaldehyde + NO<sub>3</sub> is  $(5.7\pm 1.2)\times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, only taking into account the  
212 relative rate measurements.

213 The rate constant of methacrolein + NO<sub>3</sub> has been measured mainly by the relative  
214 method (Kwok et al. 1996, Chew et al. 1998, Canosa-Mas et al. 1999), only one study from  
215 Rudich et al. (1996) applied an absolute method and observed an upper limit of  $<8\times 10^{-15}$  cm<sup>3</sup>  
216 molecule<sup>-1</sup> s<sup>-1</sup>. The value of this work agrees well with the studies using the relative method  
217 and hence we recommend a weighted average of  $(3.3\pm 0.9)\times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is  
218 in good agreement with IUPAC value  $(3.4\pm 0.6)\times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. The rate  
219 constant of methyl vinyl ketone reaction with NO<sub>3</sub> radical in this work is in the range of upper  
220 limit value of Rudich et al. (1996), but lower than that of Canosa-Mas et al. (1999) and Kwok  
221 et al. (1996) who used relative method. Hence we recommend a preferred value as  
222  $(1.3\pm 0.6)\times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained in this work.

223 As shown in Table 3, rate constants of the NO<sub>3</sub> reactions with both 2-carene and  
224 3-carene have been measured using the relative method with 2-methyl-2-butene (Atkinson et  
225 al. 1984, Barnes et al. 1990, Corchnoy and Atkinson 1990) and 2,3-dimethyl-2-butene  
226 (Corchnoy and Atkinson 1990) as reference compounds. For the reaction of NO<sub>3</sub> + 3-carene,  
227 Barnes et al. (1990) measured a lower value than Atkinson et al. (1984), whereas a higher  
228 value was obtained in this work. Hence we recommended the weighted average as  
229  $(8.7\pm 0.5)\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> by taking into account of all three measurements. For the  
230 reaction of NO<sub>3</sub> + 2-carene, however Martínez et al. (1999) measured the rate constant that  
231 was ~30% lower than other studies, we recommend the weighted average as  $(1.8\pm 0.6)\times 10^{-11}$   
232 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> by taking into account all the measurements of Corchnoy and Atkinson  
233 (1990), Martínez et al. (1999) and this work.

### 234 3.3 Reactivity of unsaturated VOCs toward to NO<sub>3</sub> radical

235 The reaction of NO<sub>3</sub> radicals with unsaturated VOCs can proceed by two main pathways:  
236 addition to an unsaturated bond and H-atom abstraction. Canosa-Mas et al. (1988) and Wayne  
237 et al. (1991) have shown that both the addition and H-atom abstraction rate coefficients of OH  
238 radical and NO<sub>3</sub> radical reaction with alkynes and aliphatic aldehydes correlate. D'Anna et al.  
239 (2001) updated these relationships for addition as:  $\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) +$   
240  $(22.7 \pm 2.5)$  and we updated the relationship for H-abstraction from alkanes based on the recent  
241 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  
242 in Figure 3. The data points of isoprene, 2-carene and 3-carene, as shown in Figure 3, fall  
243 close to the correlation line for the addition reaction. This implies that the reaction of NO<sub>3</sub>  
244 radical with isoprene, 2-carene and 3-carene proceed mainly through the addition on the C=C  
245 double bond. However, the data points of methacrolein, crotonaldehyde and methyl vinyl  
246 ketone fall close to the correlation line for abstraction reaction, even those which contain an  
247 olefinic bond. Martínez et al. (1999) investigated the reaction of NO<sub>3</sub> with a series of  
248 monoterpenes and concluded that their room temperature rate constant depends on the  
249 number and the structure of alkyl substituents around the olefinic bond. In this work, the rate  
250 constants of 3-carene and 2-carene reaction with NO<sub>3</sub> radical were determined to be  $\approx 16$  and  
251  $\approx 30$  times larger than isoprene, respectively. By analogy to their reaction with ozone (as  
252 shown in Table 4), the additional steric effects of 3-carene than 2-carene could be the reason  
253 for its lower rate constants than 3-carene. As discussed by Chen et al. (2015), the reduction in  
254 rate coefficient for 3-carene arises from two hypotheses: (1) the conformational constraints of  
255 a C<sub>6</sub>-ring system containing two sp<sup>2</sup> hybridized carbons could decrease its reactivity; (2) the  
256 bridgehead carbon is out of the plane of the C<sub>6</sub>-ring similar to  $\alpha$ -pinene and camphene, which  
257 may cause additional steric effects. However, a higher donor inductive effect of the alkyl  
258 chain around the C=C bond should also be considered for the higher rate constant of 2-carene  
259 reaction with NO<sub>3</sub> radical than 3-carene.

260 Methacrolein and methyl vinyl ketone are the main products from the oxidation of  
261 isoprene in the atmosphere, which both contain one C=C and a C=O group. However, the rate  
262 coefficients of methacrolein and methyl vinyl ketone with NO<sub>3</sub> are at least one order  
263 magnitude lower than the reaction with their non-carbonyl analogues isobutene  
264  $[(3.4 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ , (Calvert et al. 2000)] and propene  $[(9.50 \pm 5.50) \times 10^{-15} \text{ cm}^3$

265 molecule<sup>-1</sup> s<sup>-1</sup>, IUPAC <http://iupac.pole-ether.fr/#>] with NO<sub>3</sub>, respectively. This indicates a  
266 strong electron-withdrawing effect of the C=O group in the α position, which strongly  
267 deactivates the NO<sub>3</sub> addition on the C=C bond (Kerdouci et al. 2012) as well as for other  
268 electrophilic addition reactions such as ozonolysis (McGillen et al. 2011). Conversely, the  
269 electron-donating inductive effect of the –CH<sub>3</sub> group attached to the C=C bond in  
270 methacrolein increases its reactivity relative to that of methyl vinyl ketone (Canosa-Mas et al.  
271 1999). As shown in Table 3, the reaction of crotonaldehyde with NO<sub>3</sub> radical ( $5.7 \pm 1.2 \times 10^{-15}$   
272 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) is slightly faster than the reaction of methacrolein with the NO<sub>3</sub> radical  
273 ( $3.3 \pm 0.9 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). The structure of methacrolein and crotonaldehyde differs  
274 in that the –CH<sub>3</sub> in methacrolein is closer to the C=O group than in crotonaldehyde, which  
275 may decrease the electron-donating affection of –CH<sub>3</sub> to the C=C double bond.

#### 276 **3.4 Products investigation of 2-carene & 3-carene reaction with NO<sub>3</sub> radical and** 277 **proposed reaction mechanism**

278 The product formation from the reactions of 2-carene and 3-carene with the NO<sub>3</sub> radical were  
279 conducted in the 7300 L simulation chamber under ambient temperature and pressure. As  
280 shown in Figure 4a and 4c, the 2-carene or 3-carene were introduced into the chamber first,  
281 and kept for two hours to inspect the wall-loss/ dilution rate. Then N<sub>2</sub>O<sub>5</sub> was injected  
282 continually for 15 min twice during the experiment in order to initiate the reaction. The  
283 possible products were detected using PTR-TOF-MS. As shown in Figure 4, the m/z 153.127,  
284 169.122 and 215.115 according to C<sub>10</sub>H<sub>16</sub>OH<sup>+</sup>, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>H<sup>+</sup> and C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>NH<sup>+</sup>, respectively,  
285 were identified as the products. Figures 4b and 4d demonstrate the linearity of product  
286 formation vs the reactant consumption, indicating that the C<sub>10</sub>H<sub>16</sub>OH<sup>+</sup>, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>H<sup>+</sup> are  
287 primary products from the 2-carene/3-carene reaction with NO<sub>3</sub> radical.

288 Several studies (Griffin et al. 1999, Hallquist et al. 1999, Colville and Griffin 2004, Fry et al.  
289 2014) have investigated the products and aerosol formation from the reaction of 3-carene with  
290 the NO<sub>3</sub> radical and identified the end products  
291 2,2-dimethyl-3-(2-oxopropyl)cyclo-propaneacetaldehyde (by analogy, here known as  
292 caronaldehyde, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>, molar yields of 2-3%), carbonyls (estimated molar yield of 20-30%)  
293 and nitrates (66-74%). By assuming the same sensitivity to 2-carene/3-carene in the  
294 PTR-TOF-MS, the caronaldehyde (m/z 169.122) formation yield was estimated as ~ 1% and

295 ~ 0.3%, respectively, for 2-carene and 3-carene reaction with NO<sub>3</sub> radical. In this work, the  
296 m/z 153.127 was also detected by PTR-TOF-MS from the reaction system of  
297 2-carene/3-carene with NO<sub>3</sub> and which was attributed to the epoxide, C<sub>10</sub>H<sub>16</sub>O. The epoxide  
298 formation from NO<sub>3</sub> addition to alkenes has been reported for several compounds, e.g.  
299 α-pinene, 2-butene, 2,3-Dimethyl-2-butene (Benter et al. 1994, Wängberg et al. 1997), where  
300 formation yields generally range from 3±0.5% to 20±10% under atmospheric conditions. The  
301 epoxide formation yields from the reactions of 2-carene and 3-carene with NO<sub>3</sub> were  
302 estimated to be ~ 3.6% and ~10.6%, respectively, by assuming same detection sensitivity as  
303 2-carene and 3-carene in PTR-TOF-MS. Some organic nitrates such as nitrooxy-ketone  
304 (C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>N) were also detected in PTR-TOF-MS in m/z 215.115.

305 According to the product formation and a generalized reaction mechanism applicable to  
306 monoalkenes, dialkenes, and monoterpenes reactions with NO<sub>3</sub> radical (Barnes et al. 1990), as  
307 shown in Figure 5, we were able to propose a reaction mechanism for 2-carene/3-carene  
308 reaction with NO<sub>3</sub> radical as below: the reaction proceeds mainly through NO<sub>3</sub> addition to the  
309 C=C bond to form two nitrooxy alkyl radicals, which can either react with O<sub>2</sub> to form an RO<sub>2</sub>  
310 radical (nitrooxy-peroxy radical) or lose NO<sub>2</sub> to form an epoxide C<sub>10</sub>H<sub>16</sub>O via reactions R7a/  
311 R8a or R7b/ R8b in Figure 5, respectively. Then the nitrooxy-peroxy radical (RO<sub>2</sub>) can either  
312 react with NO<sub>2</sub> to form a nitrooxy-peroxy nitrate or other RO<sub>2</sub> radicals to form an RO radical  
313 (nitrooxy-alkoxy radical), hydroxy-nitrate and nitrooxy-ketone C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>N through reactions  
314 R7c/ R8c or R7d/ R8d in Figure 5, respectively. As reported by Hallquist et al. (1999), the  
315 nitrooxy-peroxy nitrate are quite unstable and can only be detected in the beginning of  
316 reaction, which could explain why it was not detected in this work using low reactant  
317 concentrations. As shown in Figure 5, nitrooxy-ketone C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>N could also be formed  
318 through the reaction R7e/ R8e, as RO radical (nitrooxy-alkoxy radical) reaction with O<sub>2</sub>.  
319 However, the RO radical (nitrooxy-alkoxy radical) could also form caronaldehyde C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>  
320 by losing NO<sub>2</sub> via reactions R7f/ R8f in Figure 5.

321 To our best knowledge, there are no previous product and mechanism studies for the reaction  
322 of 2-carene with NO<sub>3</sub>. It should be noted that, because of the lack of standards, all product  
323 formation yields from our work are based on the assumption of the same sensitivity of  
324 product peaks as 2-carene and 3-carene in PTR-TOF-MS. However, as shown in Figure 4, the

325 formation yield of identified products, nitrooxy-ketone ( $C_{10}H_{16}O_4N$ ), caronaldehyde  
326 ( $C_{10}H_{16}O_2$ ) and epoxide ( $C_{10}H_{16}O$ ), are different between the 2-carene and 3-carene reactions  
327 with  $NO_3$ , which may relate to their different reactivity toward  $NO_3$  radical as discussed in  
328 previous section, however, a difference in sensitivity for these species cannot be ruled out.  
329 Hence, more studies should be conducted to better understand the reaction of  $NO_3$  with  
330 2-carene/3-carene in the atmosphere.

331

### 332 **Conclusion and Atmospheric Implications**

333 The first objective of our study was to establish accurate rate coefficients of the reaction of  
334 the  $NO_3$  radical with a series of unsaturated VOCs in order to better define their atmospheric  
335 lifetimes. Recommended rate coefficients are provided for isoprene, 2-carene, 3-carene,  
336 methyl vinyl ketone (MVK), methacrolein (MACR) and crotonaldehyde (CA), as  
337  $(6.6\pm 0.8)\times 10^{-13}$ ,  $(1.8\pm 0.6)\times 10^{-11}$ ,  $(8.7\pm 0.5)\times 10^{-12}$ ,  $(1.24\pm 1.04)\times 10^{-16}$ ,  $(3.3\pm 0.9)\times 10^{-15}$  and  
338  $(5.7\pm 1.2)\times 10^{-15}$   $cm^3$  molecule $^{-1}$  s $^{-1}$ , respectively at  $295\pm 2$  K and 760 Torr. Hence, these  
339 lifetimes were estimated assuming an  $NO_3$  concentration of  $5 \times 10^8$  molecule  $cm^{-3}$  (Atkinson  
340 1991) in the following equation:  $\tau_{NO_3} = \frac{1}{[NO_3]*k_{VOC}}$ . The atmospheric lifetimes of studied  
341 VOCs depending on their reaction with OH,  $O_3$  and Cl were also calculated using the  
342 following oxidant concentrations:  $[OH] = 1 \times 10^6$  molecule  $cm^{-3}$  (Spivakovsky et al. 2000),  
343  $[O_3] = 7 \times 10^{11}$  molecule  $cm^{-3}$  (Monks et al. 2009) and  $[Cl] = 1 \times 10^4$  molecule  $cm^{-3}$   
344 (Wingenter et al. 1996) and the rate constants from the literature (Calvert et al. 2000, Suh and  
345 Zhang 2000, Cabañas et al. 2001, Timerghazin and Ariya 2001, Ullerstam et al. 2001, Sato et  
346 al. 2004, Calvert et al. 2011, Chen et al. 2015, Ren et al. 2017). The calculated lifetimes are  
347 shown in Table 4. It is clear that the calculated tropospheric lifetimes of these VOCs with  
348 respect to the  $NO_3$  reaction vary from a few minutes (isoprene, 2-Carene and 3-Carene) to few  
349 months (methyl vinyl ketone). The atmospheric lifetimes for studied VOCs due to reaction  
350 with OH radicals are roughly a few hours. Lifetimes with respect to ozone are longer, ranging  
351 from  $\sim 1.7$  hours to months. The reaction of  $NO_3$  may be more important than other oxidants  
352 to for the overall loss of isoprene, 2-carene and 3-carene, assuming that the oxidant  
353 concentrations employed in these calculations are representative of typical tropospheric

354 conditions. In addition, the reaction of NO<sub>3</sub> will contribute significantly at night when the  
355 NO<sub>x</sub> emissions are high. Based on our measurements, we expect the overall atmospheric  
356 lifetimes of the studied VOCs with respect to all these oxidants are few minutes to a few days

357 using the following equation:  $\frac{1}{\tau_{eff}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}}$ .

358 The reactivity of studied VOCs toward NO<sub>3</sub> was also discussed. The experiments indicate that  
359 NO<sub>3</sub> radical reactions with all the studied unsaturated VOCs proceed through addition to the  
360 olefinic bond, however, it indicates that the introduction of a carbonyl group into unsaturated  
361 VOCs can deactivate the neighboring olefinic bond towards reaction with the NO<sub>3</sub> radical,  
362 which is to be expected since the presence of these electron-withdrawing substituents will  
363 reduce the electron density in the π orbitals of the alkenes, and will therefore reduce the rate  
364 coefficient of these electrophilic addition reactions. The different steric and inductive effects  
365 of the alkyl chain around the C=C bond were considered for the different rate constants of  
366 2-carene and 3-carene reaction with NO<sub>3</sub>.

367 In addition, the product formation from the reaction of 2-carene and 3-carene with NO<sub>3</sub>  
368 radical were also investigated. Epoxide, nitrooxy ketone (C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>N) and caronaldehyde  
369 (C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>) were identified for both reaction systems. In the atmosphere, the epoxide could  
370 react with OH and NO<sub>3</sub> radicals and the atmospheric fate of caronaldehyde is expected to be  
371 reaction with OH and photolysis (Hallquist et al. 1997). Secondary organic aerosol (SOA) has  
372 been observed in the reaction of NO<sub>3</sub> with 3-carene in the simulation chamber with  
373 mass-based yields of up to 72 % (Griffin et al. 1999, Hallquist et al. 1999) and organonitrates  
374 comprised 56% of the aerosol mass. Hence, more work on the identification of organonitrates  
375 SOA formation from reaction system of 2-carene and 3-carene with NO<sub>3</sub> radical would be  
376 desirable.

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384

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