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

Yangang Ren¹, Max McGillen^{1,3}, Ibrahim Ouchen², Veronique Daële¹ and Abdelwahid Mellouki^{1*}

¹ Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS (UPR 3021), Observatoire des Sciences de l'Univers en région Centre (OSUC), 1C Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

² Earth Sciences Department, Scientific Institute, Mohammed V- University, Rabat 10106, Morocco

³ Le Studium Loire Valley Institute for Advanced Studies, Orléans 45071, France.

*Corresponding author: A. Mellouki (mellouki@cnrs-orleans.fr)

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⁻¹ s⁻¹, 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

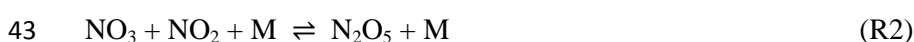
30 3-carene with the NO_3 radical. Qualitative identification of an epoxide ($\text{C}_{10}\text{H}_{16}\text{OH}^+$),
31 caronaldehyde ($\text{C}_{10}\text{H}_{16}\text{O}_2\text{H}^+$) and nitrooxy-ketone ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{NH}^+$) was achieved using
32 PTR-TOF-MS and a reaction mechanism is proposed.

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

34

35 **Introduction**

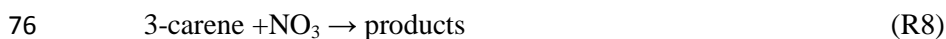
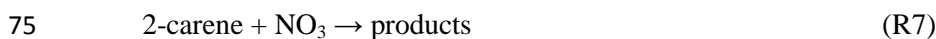
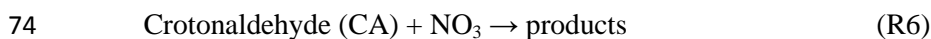
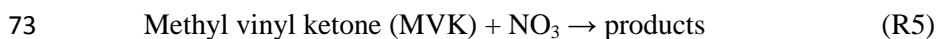
36 Although the hydroxyl radical (OH) is recognized as the dominant oxidant in the daytime, the
37 NO₃ radical (NO₃) is known to be the main oxidant of VOCs during the night (Atkinson 1991,
38 Wayne et al. 1991). NO₃ is produced in the atmosphere via the reaction between O₃ and NO₂,
39 which can originate from combustion, biomass burning, lightning and bacterial sources
40 (Brown et al. 2005, Aldener et al. 2006, Brown and Stutz 2012). During the night, NO₃ and
41 NO₂ exist in thermal equilibrium with N₂O₅:



44 Oxidation by NO₃ 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 NO₂) during daytime (Finlayson-Pitts and Pitts 2000),
47 however, it has been shown that NO₃ can be an important daytime oxidant within the canopy
48 in forested environments (Liebmann et al. 2019). Field measurements have reported NO₃
49 concentrations ranging from lower than the detection limit (10 pptv) to 800 pptv and N₂O₅
50 concentrations could be as high as 10.9 ppbv dependent on local conditions (Brown and Stutz
51 2012).

52 NO₃ 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 NO₃ 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_x 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 NO₃ 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 NO₃ rate coefficients carried out in different
67 laboratories. For example, even the reaction of NO₃ 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 NO₃, 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 NO₃ 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. SF₆ was used to
97 determine the dilution rate in the chamber, which ranged from the (7-8)×10⁻⁶ s⁻¹.

98 A high-resolution proton transfer reaction time-of-flight mass spectrometer
99 (IoniconAnalytik, PTR-TOF-MS 8000) with a hydronium ion (H₃O⁺) 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⁻¹ 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 SF₆ detection. NO₃ radicals were generated from the thermal
111 decomposition of N₂O₅.

112 Concentration ranges of the various chemicals of importance to these experiments are:
113 [alkene]= (0.8 - 4.0) × 10¹² molecule cm⁻³, [N₂O₅] = (0.1 - 1.2) × 10¹¹ molecule cm⁻³,
114 [NO₂]=(2 - 5) × 10¹¹ molecule cm⁻³, [NO₃] = (0.5 - 4.9) × 10¹⁰ molecule cm⁻³.

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 NO₃ and other loss processes (wall loss,
118 dilution):



122 k₃₋₈ and k_{ref} are the rate coefficient for the reactions of NO₃ 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, α -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:

$$137 \quad \ln \frac{[VOC]_0}{[VOC]_t} - k_d * t = \frac{k_{3-8}}{k_{ref}} * (\ln \frac{[ref]_0}{[ref]_t} - k_d * t) \quad \text{Eq.1}$$

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 $\frac{k_{3-8}}{k_{ref}}$, 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 NO₃ reaction with studied VOCs**

155 The rate coefficients for isoprene, methacrolein, methyl vinyl ketone, crotonaldehyde,
156 2-carene and 3-carene reaction with NO₃ 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 α -cedrene. The concentration of VOCs
159 ranged from 0.8 to 4.1×10^{12} molecule cm⁻³ as shown in Table 2. The recommended rate
160 constants for the reaction of reference compounds with NO₃] 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 cm³ molecule⁻¹ s⁻¹.

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_{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, σ_{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 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 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 NO_3

206 may result from its reaction with NO₂, alkyl and peroxy radicals in these experiments. As a
207 result, we recommend a weighted rate constant of isoprene + NO₃ of $(6.6\pm 0.8)\times 10^{-13}$ cm³
208 molecule⁻¹ s⁻¹ 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 $(6.5\pm 1.3)\times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K. The recommended value of
211 crotonaldehyde + NO₃ is $(5.7\pm 1.2)\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, only taking into account the
212 relative rate measurements.

213 The rate constant of methacrolein + NO₃ 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 $< 8\times 10^{-15}$ cm³
216 molecule⁻¹ s⁻¹. The value of this work agrees well with the studies using the relative method
217 and hence we recommend a weighted average of $(3.3\pm 0.9)\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, which is
218 in good agreement with IUPAC value $(3.4\pm 0.6)\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K. The rate
219 constant of methyl vinyl ketone reaction with NO₃ 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 $(1.3\pm 0.6)\times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ obtained in this work.

223 As shown in Table 3, rate constants of the NO₃ 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 NO₃ + 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 $(8.7\pm 0.5)\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ by taking into account of all three measurements. For the
230 reaction of NO₃ + 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 cm³ molecule⁻¹ s⁻¹ 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 NO₃ radical

235 The reaction of NO₃ 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 NO₃ 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 ± 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 NO₃
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 NO₃ 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 NO₃ radical were determined to be ≈ 16 and
251 ≈ 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 C₆-ring system containing two sp² hybridized carbons could decrease its reactivity; (2) the
256 bridgehead carbon is out of the plane of the C₆-ring similar to α -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 NO₃ 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 NO₃ 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⁻¹ s⁻¹, IUPAC <http://iupac.pole-ether.fr/#>] with NO₃, respectively. This indicates a
266 strong electron-withdrawing effect of the C=O group in the α position, which strongly
267 deactivates the NO₃ 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 –CH₃ 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 NO₃ radical ($5.7 \pm 1.2 \times 10^{-15}$
272 cm³ molecule⁻¹ s⁻¹) is slightly faster than the reaction of methacrolein with the NO₃ radical
273 ($3.3 \pm 0.9 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹). The structure of methacrolein and crotonaldehyde differs
274 in that the –CH₃ in methacrolein is closer to the C=O group than in crotonaldehyde, which
275 may decrease the electron-donating affection of –CH₃ to the C=C double bond.

276 **3.4 Products investigation of 2-carene & 3-carene reaction with NO₃ radical and** 277 **proposed reaction mechanism**

278 The product formation from the reactions of 2-carene and 3-carene with the NO₃ 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 N₂O₅ 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 C₁₀H₁₆OH⁺, C₁₀H₁₆O₂H⁺ and C₁₀H₁₆O₄NH⁺, 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 C₁₀H₁₆OH⁺, C₁₀H₁₆O₂H⁺ are
287 primary products from the 2-carene/3-carene reaction with NO₃ 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 NO₃ radical and identified the end products
291 2,2-dimethyl-3-(2-oxopropyl)cyclo-propaneacetaldehyde (by analogy, here known as
292 caronaldehyde, C₁₀H₁₆O₂, 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 NO₃ 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 NO₃ and which was attributed to the epoxide, C₁₀H₁₆O. The epoxide
298 formation from NO₃ 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 NO₃ 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 (C₁₀H₁₆O₄N) 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 NO₃ 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 NO₃ radical as below: the reaction proceeds mainly through NO₃ addition to the
309 C=C bond to form two nitrooxy alkyl radicals, which can either react with O₂ to form an RO₂
310 radical (nitrooxy-peroxy radical) or lose NO₂ to form an epoxide C₁₀H₁₆O via reactions R7a/
311 R8a or R7b/ R8b in Figure 5, respectively. Then the nitrooxy-peroxy radical (RO₂) can either
312 react with NO₂ to form a nitrooxy-peroxy nitrate or other RO₂ radicals to form an RO radical
313 (nitrooxy-alkoxy radical), hydroxy-nitrate and nitrooxy-ketone C₁₀H₁₆O₄N 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 C₁₀H₁₆O₄N could also be formed
318 through the reaction R7e/ R8e, as RO radical (nitrooxy-alkoxy radical) reaction with O₂.
319 However, the RO radical (nitrooxy-alkoxy radical) could also form caronaldehyde C₁₀H₁₆O₂
320 by losing NO₂ 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 NO₃. 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 ± 2 K and 760 Torr. Hence, these
339 lifetimes were estimated assuming an NO_3 concentration of 5×10^8 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 ~ 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 NO₃ will contribute significantly at night when the
355 NO_x 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 NO₃ was also discussed. The experiments indicate that
359 NO₃ 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 NO₃ 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 NO₃.

367 In addition, the product formation from the reaction of 2-carene and 3-carene with NO₃
368 radical were also investigated. Epoxide, nitrooxy ketone (C₁₀H₁₆O₄N) and caronaldehyde
369 (C₁₀H₁₆O₂) were identified for both reaction systems. In the atmosphere, the epoxide could
370 react with OH and NO₃ 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 NO₃ 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 NO₃ radical would be
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384

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