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# Photochemical Degradation of Isoprene-derived 4,1-Carbonyl Nitrate

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## Abstract

In isoprene-impacted environments, carbonyl nitrates are produced from $NO_3$-initiated isoprene oxidation, which constitutes a potentially important $NO_x$ reservoir. To better understand the fate of isoprene carbonyl nitrates, we synthesized a model compound, *trans*-4-nitrooxy-2-methyl-2-buten-1-al (4,1-isoprene carbonyl nitrate) and investigated its photochemical degradation process. The measured OH and $O_3$ oxidation rate constants for this carbonyl nitrate are $4.1(\pm0.7)\times10^{-11}$ $cm^3\,molecules^{-1}\,s^{-1}$ and $4.4(\pm0.3)\times10^{-18}$ $cm^3\,molecules^{-1}\,s^{-1}$. The UV absorption spectrum of the carbonyl nitrate was determined, and the result is consistent with TDDFT calculations. Based on its UV absorption cross section and photolysis frequency in a reaction chamber, we estimate that the ambient photolysis frequency for this compound is $3.1\times10^{-4}$ $s^{-1}$ for a solar zenith angle (SZA) of 45°. The fast photolysis rate and high reactivity toward OH lead to a lifetime of less than one hour for the carbonyl nitrate, with photolysis being a dominant daytime sink. The nitrate products derived from the OH oxidation and the photolysis of the isoprene carbonyl nitrate were identified with an iodide-based chemical ionization mass spectrometer. For the OH oxidation reaction, we quantified the yields of two nitrate products, MVK nitrate and ethanal nitrate, which together contributed to 37($\pm$5)% of the first-generation products.

## 1 Introduction

Over the past century, tropospheric ozone concentrations have increased from around 20 ppb to ~40 ppb, with urban-impacted concentrations often rising to 60-100 ppb (Parrish et al., 2014; Vingarzan, 2004), posing harmful effects on human health and crop yields (Lefohn and Foley,

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29    1993; Lippmann, 1989). Tropospheric ozone is catalytically produced in the chemical reactions

30    of nitrogen oxides ($NO_x \equiv NO + NO_2$) and volatile organic compounds (VOCs) (Haagen-Smit,

31    1952). $NO_2$ photolysis forms ozone (Blacet, 1952), and the ozone production rate is enhanced

32    when the $NO$-$NO_2$-$O_3$ cycle is coupled with the oxidation of VOCs (Chameides et al., 1988;

33    Chameides and Walker, 1973; Chameides et al., 1992). When $NO_x$ is incorporated into organic

34    molecules and forms organic nitrates ($RONO_2$), however, ozone formation is suppressed

35    (Roberts, 1990). Organic nitrates are a temporary $NO_x$ reservoir. Degradation of organic nitrates

36    can release $NO_2$ back into the atmosphere (Aschmann et al., 2011), and thus facilitate ozone

37    production. Organic nitrates in the gas phase can also adsorb onto atmospheric aerosols,

38    followed by condensed-phase hydrolysis (Rindelaub et al., 2015). This process removes the

39    reactive nitrogen from the atmosphere permanently, as the nitrooxy group is turned into the non-

40    volatile $NO_3^-$ ion (Darer et al., 2011; Hu et al., 2011). The relative importance of these parallel

41    nitrate sinks affects the availability of $NO_x$ and the ozone production rate in the troposphere.

42    Therefore, detailed understanding of the loss mechanisms of organic nitrates is crucial to

43    understanding the dynamics of ground-level ozone formation.

44    Modeling studies suggest that isoprene-derived organic nitrates have substantial influence on the

45    $NO_x$ cycle and tropospheric $O_3$ production (Horowitz et al., 2007; Mao et al., 2013; Paulot et al.,

46    2012; Wu et al., 2007). During the daytime, isoprene is lost rapidly to OH oxidation, forming

47    organic nitrates through the $RO_2 + NO$ reaction with a yield of 7-14% (Lockwood et al., 2010;

48    Patchen et al., 2007; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990;

49    Xiong et al., 2015). At night, reaction with $NO_3$ is a significant removal pathway for isoprene

50    (Brown et al., 2009; Starn et al., 1998), and organic nitrates constitute 65-70% of the oxidation

51    products (Perring et al., 2009; Rollins et al., 2009). While $NO_3$-initiated isoprene oxidation

52    contributes to a small fraction of isoprene loss, this reaction pathway could generate

53    approximately half of the isoprene-derived organic nitrates on a regional scale, due to its large

54    nitrate yield (Horowitz et al., 2007; Xie et al., 2013).

55    Fig.1 shows the formation pathways of organic nitrate products from $NO_3$-initiated oxidation of

56    isoprene, including hydroperoxy nitrate, carbonyl nitrate and hydroxy nitrate. Reactions for only

57    one of the nitrooxy peroxy radicals are shown for brevity. The hydroxy nitrates can be also

58    formed in the OH-initiated isoprene oxidation reactions, and their production and degradation

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59    have been studied extensively in both laboratory and field studies (Chen et al., 1998; Giacopelli

60    et al., 2005; Grossenbacher et al., 2004; Jacobs et al., 2014; Lee et al., 2014b; Lockwood et al.,

61    2010; Patchen et al., 2007; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson,

62    1990; Xiong et al., 2015). For the hydroperoxy nitrates, Schwantes et al. (2015) investigated

63    their production from the $RO_2 + HO_2$ reaction and identified the nitrooxy hydroxyepoxide

64    product from the OH oxidation of the isoprene hydroperoxy nitrate. For the isoprene carbonyl

65    nitrates, their formation has been quantified in an experimental study (Kwan et al., 2012), but

66    their sinks and fate can only be inferred from analog molecules, such as nitrooxy ketones, due to

67    lack of direct studies on these specific compounds. Suarez-Bertoa et al. (2012) conducted

68    kinetics experiments on three synthesized saturated nitrooxy ketones, and their results indicate

69    that photolysis is the dominant sink for these nitrate compounds. By comparing the published

70    UV absorption spectra of α-nitrooxy ketones with the UV spectra of the mono-functional nitrates

71    and ketones, Müller et al. (2014) suggested that the nitrooxy ketones have enhanced absorption

72    cross sections, which can facilitate the dissociation of the O−NO$_2$ bond. Like the nitrooxy

73    ketones discussed by Suarez-Bertoa et al. (2012) and Müller et al. (2014), the carbonyl nitrate

74    derived from NO$_3$ + isoprene oxidation has a chromophore, −C=C−C=O, at the β position of the

75    nitrate group, which may enhance the UV absorption cross section of the molecule and facilitate

76    its photolytic dissociation. However, since the five-carbon isoprene carbonyl nitrate (Fig. 1) is

77    unsaturated, it is expected to be lost rapidly to OH oxidation. To date, the relative importance of

78    the individual photochemical sinks for the unsaturated carbonyl nitrates is still unclear. To

79    answer this question, we synthesized a model compound for the five-carbon isoprene carbonyl

80    nitrates, and investigated its photochemical reactivities.

81    **2    Synthesis and characterization**

82    A model compound, 4,1-isoprene carbonyl nitrate (*trans*-2-methyl-4-nitrooxy-2-buten-1-al ) was

83    synthesized following the reaction scheme in Fig. 2. The nitrate was prepared by reacting AgNO$_3$

84    with the corresponding bromide (*trans*-4-bromo-2-methyl-2-buten-1-al) (Ferris et al., 1953),

85    which was synthesized following Gray (1981). The $^1$H and $^{13}$C NMR spectra of the synthesized

86    product are shown in Fig. S1 and Fig. S2. Its IR absorption spectrum is shown in Fig. S3.

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87 Shown in Fig. 3 are the UV absorption cross sections for the carbonyl nitrate, methacrolein

88 (MACR) and isopropyl nitrate, obtained in acetonitrile solvent. The absorption cross section of

89 the carbonyl nitrate is enhanced relative to that of MACR, but the two spectra have similar

90 features from 320 nm to 400 nm with peak absorption at 325 nm. This is probably because they

91 both contain the O=C–C=C chromophore. Below 320 nm the absorption of the carbonyl nitrate is

92 enhanced significantly in comparison with that of isopropyl nitrate. This observation is

93 consistent with reports from Müller et al. (2014) that molecules containing α,β-nitrooxy ketone

94 functionalities have enhanced UV absorption.

## 3 Methods

### 3.1 Setup for the kinetics chamber experiments

97 Three sets of reaction chamber experiments were conducted to determine the photolysis

98 frequency, OH oxidation rate constant and the $O_3$ oxidation rate constant for the carbonyl nitrate.

99 The experiments were performed in the 5500 L Purdue photochemical reaction chamber (Chen et

100 al., 1998). A chemical ionization mass spectrometer (CIMS) with $I^-$ as the reagent ion was used

101 to quantify the carbonyl nitrate and its nitrate degradation products (Xiong et al., 2015). The

102 chamber air was sampled into the CIMS through a 5.2 m long FEP tubing (0.8 cm ID, heated to

103 constant 50 °C). The photolysis frequenecy was obtained by measuring the loss of the carbonyl

104 nitrate inside the reaction chamber in the presence of UV radiation and propene as a radical

105 scavenger. When the UV lamps were turned off, the wall loss rate constant for the carbonyl

106 nitrate was dervied by observing its slow decay, with propene as an ozone and $NO_3$ scavenger.

107 The OH reaction rate constant and $O_3$ reaction rate constant were obtained using the relative rate

108 method  (Atkinson and Aschmann, 1985). Propene was used as the reference compound, and its

109 changing concentrations were measured using a GC-FID equipped with a 0.32 mm Rtx-Q-Bond

110 column. For the OH oxidation experiments, OH was generated through the photolysis of

111 isopropyl nitrite, which was synthesized follwoing Noyes (1933). NO was added to the chamber

112 to suppress the formation of $O_3$. In addition, two OH oxidation experiments were performed

113 without propene in order to quantify the oxidation products. For the OH-initiated oxidation

114 experiments, NO and $NO_2$ were measured using the Total REactive Nitrogen Instrument

115 (TRENI) (Lockwood et al., 2010). The ozonolysis experiments were performed in the dark, and

116    cyclohexane was added to the chamber as an OH scavenger. The initial conditions for the

117    experiments are listed in Table S1.

## 3.2    Computational methods

119    The theoretical UV absorption spectra of the carbonyl nitrate, MACR, and *n*-butyl nitrate in the

120    gas phase were calculated and analyzed, in four stages, using time-dependent density functional

121    theory (TDDFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Runge and Gross, 1984).

122    All calculations were carried out using the computational chemistry package Q-Chem 4.3 (Shao

123    et al., 2015). First, the structure of each molecule was optimized employing the long-range

124    corrected hybrid density functional ωB97X-D (Chai and Head-Gordon, 2008) with the 6-31+G*

125    basis set (Frisch et al., 1984). A high accuracy grid was employed. Second, frequencies

126    calculations were executed on the optimized structures to verify their accuracy. These were run

127    using the same setup described above. Third, after assuring the structures represented adequate

128    minima, the first ten singlet excited states of each molecule were computed with TDDFT, using

129    the same functional and basis set. Finally, a visual analysis of the molecular orbitals (MOs) was

130    carried out with the visualization software IQmol 2.7 (Gilbert, 2012).

## 4    Results

### 4.1    Absorption spectra and density functional calculations

133    Fig. 4 shows the TDDFT UV absorption spectra of the carbonyl nitrate, MACR, and *n*-butyl

134    nitrate. There are three groups of transitions in the simulated spectra.

135    Both MACR and the carbonyl nitrate show a relatively weak transition in the region around 330

136    nm, which corresponds to the first electronic transition, from the highest occupied molecular

137    orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), in both molecules. Fig. 5a

138    provides comparative information between the first electronic transition of the carbonyl nitrate

139    and the homologous excitation of MACR. As shown in Fig. 5a the character of the molecular

140    orbitals involved in this transition is similar in both cases, indicating that the aldehyde group is

141    involved in the first electronic excitation of the carbonyl nitrate.

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142   Fig. 5b shows the information corresponding to the second electronic transition of the carbonyl

143   nitrate and the homologous excitation of *n*-butyl nitrate. Both transitions are found in the region

144   around 255 nm, and they are 3 orders of magnitude darker than those at 330 nm. Inspection of

145   the character of the MOs involved in these processes reveals a correspondence between the

146   second electronic excitation of the carbonyl nitrate, HOMO−2 → LUMO+1, and the HOMO →

147   LUMO transition of *n*-butyl nitrate. As with the previous case, that observation confirms that the

148   nitrate group is involved in the second electronic excitation of the carbonyl nitrate, but at

149   wavelengths shorter than present at the Earth's surface. Fig. 5b also shows that in this case, the

150   local character of the MOs involved in the transition is even more pronounced, with bulky lobes

151   placed mainly over the nitrate group.

152   Even though the second electronic transition of carbonyl nitrate is not displayed in the

153   experimental spectra of Fig. 3, because its range covers from 280 nm to 410 nm, it is reasonable

154   to assume that it is caused by the local excitation of the nitrate group, based on the computational

155   results. Thus, it can be suggested that the experimental UV absorption spectra of isopropyl

156   nitrate is comparable to that of *n*-butyl nitrate simulated computationally. Thus it is possible that

157   the feature in the region around 280 nm of the carbonyl nitrate experimental spectrum of Fig. 3

158   could be caused by a broadening of the transition located around 255 nm.

159   The brightest transition in the modeled spectra of the carbonyl nitrate, 3 orders of magnitude

160   brighter than the ones at 330 nm, is located around 210 nm. There are two transitions in this

161   region and each one has a homologous excitation: the HOMO−1 → LUMO in carbonyl nitrate is

162   similar to HOMO−1 → LUMO in MACR, and the HOMO−5 → LUMO+1 in carbonyl nitrate is

163   related to the (mainly) HOMO−1 → LUMO transition of *n*-butyl nitrate. These transitions are

164   beyond the range of the experimental spectra on Fig. 3 and beyond the atmospherically relevant

165   absorption wavelengths.

166   **4.2   Photochemical sinks of 4,1-carbonyl nitrate**

167   Fig. 6 shows the first-order wall loss and photolysis loss of the carbonyl nitrate inside the

168   reaction chamber. The wall loss rate constant was $1.3(\pm0.1)\times10^{-5}$ s$^{-1}$, and the photolysis rate

169   constant was $3.0(\pm0.1)\times10^{-5}$ s$^{-1}$, after subtracting the wall loss rate constant from the first-order

170   decay rate constant measured for the photolysis experiments. It is worth mentioning that our

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171   reactant carbonyl nitrate has a *trans* configuration, and it may photo-isomerize into the *cis*

172   configuration, which would be detected at the same m/z by the CIMS. The cis-carbonyl nitrate

173   can either photo-dissociate or isomerize to re-form the *trans* isomer. Our previous work suggests

174   that the CIMS is 4 times more sensitive to the *cis* configuration than the *trans* configuration

175   (Xiong et al., 2015). If a significant amount of the *cis* isomer was present, the CIMS signal

176   should resemble a double exponential curve, because the *cis* isomer was being produced and

177   consumed simultaneously. In an extreme scenario with rapid *trans* → *cis* isomerization, the

178   CIMS signal should increase under radiation, due to the higher sensitivity of the *cis* isomer. For

179   our carbonyl nitrate photolysis experiments, a single exponential decay in the CIMS signal was

180   observed, indicating insignificant contribution from the *cis* isomer. Hence, our measured

181   photolysis frequency should well characterize the loss rate of the carbonyl nitrate inside the

182   reaction chamber.

183   Since the UV radiation inside the reaction chamber is different from the UV radiation in the

184   ambient environment (Fig. 7), $Cl_2$ was used as a reference compound to extrapolate the nitrate

185   photolysis rate from chamber radiation to solar radiation. The photolysis decay of $Cl_2$ in the

186   reaction chamber was measured with the CIMS (Neuman et al., 2010). Cyclohexane was added

187   to the chamber to scavenge the Cl atoms so that $Cl_2$ was not re-formed from Cl + Cl

188   recombination. The first-order photolysis rate constant for $Cl_2$ was $2.50(\pm0.04) \times 10^{-4}$ $s^{-1}$ (Fig.

189   S4).

190   The photolysis frequency (J) is the integrated product of quantum yield (Φ), absorption cross

191   section ($\sigma$, $cm^2$) and actinic flux (F, $cm^{-2}$ $s^{-1}$) across all wavelengths (Eq. 1). Therefore, the

192   photolysis frequencies for the carbonyl nitrate and $Cl_2$ in the reaction chamber can be compared

193   as in Eq. 2.

194   $J = \int \Phi_\lambda \sigma_\lambda F_\lambda d\lambda$                                       (Eq. 1)

195   $\dfrac{J_{Cl_2}^{chamber}}{J_{nitrate}^{chamber}} = \dfrac{\sum \varphi_{Cl_2} \sigma_{Cl_2} F_{chamber}}{\sum \varphi_{nitrate} \sigma_{nitrate} F_{chamber}}$                    (Eq. 2)

196   $J_{Cl_2}^{chamber}$ and $J_{nitrate}^{chamber}$ are the photolysis frequencies of $Cl_2$ and the carbonyl nitrate inside the

197   chamber. $\sigma_{Cl_2}$ and $\sigma_{nitrate}$ are the cross sections for $Cl_2$ and the carbonyl nitrate at each

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198    wavelength. $\sigma_{nitrate}$ was determined by this work (Fig. 3). $\sigma_{Cl_2}$ has been measured previously

199    and the IUPAC recommended values were used (Atkinson et al., 2007). $F_{chamber}$ is the

200    wavelength-dependent flux of photons inside the chamber. The radiation spectrum (Fig. 7) of the

201    chamber UV lamps (UVA 340) was obtained from the manufacturer (Q-lab), but the actual

202    absolute radiation intensity in the chamber is expected to differ from the manufacturer's

203    radiation spectrum by a scaling factor, because of the inverse-square dependence on distance,

204    and our specific multi-lamp geometry. When $Cl_2$ was used as a reference compound for the

205    nitrate photolysis rate, the scaling factors in Eq. 2 will cancel.

206    The Cl-Cl bond dissociation energy is 243 kJ/mol (Luo, 2007a), equivalent to a photon at 492

207    nm. Since $Cl_2$ has only one bond, it has unity quantum yield below 492 nm and zero quantum

208    yield above 492 nm. The emission spectrum of the UV lamps for the reaction chamber is

209    centered from 300 nm to 400 nm (Fig. 7). Hence, $\varphi_{Cl_2} = 1$ in Eq. 2, at all wavelengths. For the

210    carbonyl nitrate, however, its quantum yield is affected by the bond dissociation energy,

211    intramolecular vibrational energy redistribution and relaxation of the excited molecule from

212    collisions, so an average effective quantum yield ($\varphi_{nitrate}^{eff}$) is assumed, and Eq. 2 becomes Eq. 3.

213    Since the photolysis rates, absorption cross sections and chamber radiation spectrum were known,

214    we calculated that $\varphi_{nitrate}^{eff}$ was 0.48.

215    $$\frac{J_{Cl_2}^{chamber}}{J_{nitrate}^{chamber}} = \frac{\sum \sigma_{Cl_2} F_{chamber}}{\varphi_{nitrate}^{eff} \sum \sigma_{nitrate} F_{chamber}} \qquad \text{(Eq. 3)}$$

216    The effective quantum yield of 0.48 indicates that when the carbonyl nitrates absorbs a photon

217    inside the reaction chamber, the probability (averaged across the absorption wavelengths) for it

218    to dissociate is 48%. However, the probability for nitrate photolysis is not equal at all

219    wavelengths, the low energy photons (long wavelength) being less likely to induce photo-

220    dissociation. Hence, we introduced a threshold wavelength $\lambda_0$, for which the carbonyl nitrate has

221    unity quantum yield below $\lambda_0$ and zero quantum yield above $\lambda_0$. Although this approach accounts

222    for the energy difference of photons with different wavelengths, it is still a very rough

223    estimation. Using the threshold wavelength, the effective quantum yield can be expressed by Eq.

224    4 and Eq. 5, where $\varphi(\lambda)$ is the quantum yield of the carbonyl nitrate, and $F(\lambda)$ is the chamber

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225    photon flux (Fig. 7), as a function of the wavelength λ. Solving for the unknown $\lambda_0$ in Eq. 5, we

226    calculated that $\lambda_0$ was 347 nm.

227    $$\varphi(\lambda) = \begin{cases} 1 \ (\lambda \leq \lambda_0) \\ 0 \ (\lambda > \lambda_0) \end{cases}$$    (Eq. 4)

228    $$\frac{\sum_\lambda F(\lambda) \cdot \varphi(\lambda)}{\sum_\lambda F(\lambda)} = 0.48$$    (Eq. 5)

229    The solar radiation spectrum was calculated with the TUV model (Madronich and Flocke, 1998).

230    By assuming that the carbonyl nitrate has zero quantum yield above 347 nm and unity quantum

231    yield below 347 nm, its photolysis frequency is $2.6 \times 10^{-4}$ $s^{-1}$ for a solar zenith angle (SZA) of

232    45°, and $3.7 \times 10^{-4}$ $s^{-1}$ for SZA of 0°. It is worth mentioning that the condensed-phase and gas-

233    phase absorption spectra should be different, because the solvent molecules affect the

234    polarization and dipole moment of the solute (Bayliss and McRae, 1954; Braun et al., 1991;

235    Linder and Abdulnur, 1971). Although we were unable to measure the gas-phase cross section of

236    the carbonyl nitrate, we could assess the uncertainty caused by using the condensed-phase

237    spectrum in our calculation, by comparing the gas-phase and condensed-phase spectra of MACR

238    and isopropyl nitrate (Fig. S5a). On average, the gas-phase absorption cross sections of MACR

239    and isopropyl nitrate are 1.7 times those in the solution phase (Fig. S5b). For the carbonyl nitrate,

240    if the gas-phase cross section is assumed to be 1.7 times that of the solution-phase cross section,

241    the calculated effective quantum yield becomes 0.28, leading to a threshold wavelength ($\lambda_0$) of

242    336 nm. Using this set of cross section and quantum yields, we calculated that the nitrate

243    photolysis frequency was $3.1 \times 10^{-4}$ $s^{-1}$ for SZA of 45°, and $4.6 \times 10^{-4}$ $s^{-1}$ for SZA of 0°, which are

244    19% and 24% larger than results obtained using the condensed-phase cross section. The

245    calculated ambient photolysis frequency is not affected as significantly by the change in the

246    absorption cross section, because it is constrained by the measured photolysis frequency in the

247    reaction chamber. When a larger cross section is applied, a smaller quantum yield is derived, and

248    the calculated ambient photolysis frequency, being the integrated product of the cross section,

249    quantum yield and radiation, will not increase as much as the cross section. In addition to the

250    cross section, our treatment of the wavelength-dependent quantum yield can also introduce

251    uncertainty to the calculated results. If a constant effective quantum yield is used in the

252    calculation, the ambient photolysis frequency is $2.0 \times 10^{-4}$ $s^{-1}$ for SZA of 45°, and $2.8 \times 10^{-4}$ $s^{-1}$ for

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253   SZA of 0°, which are 23% and 24% lower than assuming a threshold wavelength. Therefore, our

254   calculated ambient photolysis frequency, based on condensed-phase absorption cross section and

255   a threshold energy for unity quantum yield, has an uncertainty of 25%.  Since we believe that the

256   cross sections are indeed larger in the gas phase, our best estimate is $3.1 \times 10^{-4}\,\text{s}^{-1}$ for SZA=45°.

257   Fig. 8 shows the results for the relative rate experiments for the OH-initiated and $O_3$-initiated

258   oxidation of the carbonyl nitrate, with propene as the reference compound. The loss of the

259   carbonyl nitrate to wall uptake and photolysis is corrected when comparing the oxidative loss of

260   the nitrate to that of propene, using the same method as Hallquist et al. (1997). The OH and $O_3$

261   oxidation rate constants for propene are $3.0(\pm0.5) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Klein et al., 1984;

262   Zellner and Lorenz, 1984) and $1.00(\pm0.06) \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Herron and Huie, 1974;

263   Treacy et al., 1992). These are the IUPAC preferred rate constants for T=298K

264   (http://iupac.pole-ether.fr/). Hence, the OH and $O_3$ oxidation rate constants for the isoprene

265   carbonyl nitrate are, based on the results from the relative rate experiments, $4.1(\pm0.7) \times 10^{-11}$ cm$^3$

266   molecules$^{-1}$ s$^{-1}$ and $4.4(\pm0.3) \times 10^{-18}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ respectively, at 295 K.

267   The OH oxidation rate constant for the carbonyl nitrate can be estimated through the structure-

268   activity-relationship (SAR) approach proposed by Kwok and Atkinson (1995). The rate constant

269   for OH addition to the double bond can be calculated as k(-CH=CH), which is $8.69 \times 10^{-11}$ cm$^3$

270   molecules$^{-1}$ s$^{-1}$, multiplied by the two correction factors C(-CHO) and C(-CH$_2$ONO$_2$), which are

271   0.34 and 0.47 respectively. The resulting OH addition rate constant is $1.39 \times 10^{-11}$ cm$^3$

272   molecules$^{-1}$ s$^{-1}$. The rate constant for H abstraction from the –CHO group is $1.61 \times 10^{-11}$ cm$^3$

273   molecules$^{-1}$ s$^{-1}$, after multiplying a correction factor of 1 for having a double bond at its α

274   position. The rate constant for H abstraction from the methylene group is $3.7 \times 10^{-14}$ cm$^3$

275   molecules$^{-1}$ s$^{-1}$, calculated by multiplying the base rate constant for methylene groups, which is

276   $9.34 \times 10^{-13}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, by the correction factors of the nitrate group and the double

277   bond, which are 0.04 and 1, respectively. OH addition to the nitrate group has a rate constant of

278   $4.4 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, after taking account of the enhancement factor of 1.23 for the

279   methylene group. H abstraction from the methyl group has a rate constant of $1.36 \times 10^{-13}$ cm$^3$

280   molecules$^{-1}$ s$^{-1}$. By summing up the rate constants for all these reaction pathways, the SAR-

281   derived OH oxidation rate constant for the 4,1-carbonyl nitrate rate constant is $3.1 \times 10^{-11}$ cm$^3$

282   molecules$^{-1}$ s$^{-1}$, approximately 30% lower than the experimental measurement. The dominant

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283     reaction channels are OH addition to the double bond and H abstraction from the aldehyde

284     group. Contributions from the other reaction pathways are small (<3%).

285     The relative importance of the three photochemical sinks, photolysis, OH oxidation and $O_3$

286     oxidation, depends on the solar radiation and the concentrations of OH and $O_3$. To better

287     illustrate their relative contributions, observations of OH and $O_3$ from previous field campaigns

288     were used to calculate the loss rates of the carbonyl nitrate. The local solar radiation was

289     calculated with the TUV model (Madronich and Flocke, 1998), which was then used to derive

290     the photolysis frequency. The calculated results (Fig. 9) suggest that photolysis is a significant

291     degradation pathway for the carbonyl nitrate, which can dominate over OH oxidation toward

292     mid-day. When the solar radiation intensity is small (such as 6:00 AM for the 1999 SOS

293     campaign), OH oxidation is likely the dominant sink. Due to the fast photolysis and high

294     reactivity toward OH, the photochemical lifetime of the carbonyl nitrate can be as short as less

295     than one hour.

### 296     4.3    Degradation products of the 4,1-carbonyl nitrate

### 297     4.3.1   OH oxidation

298     The products from the OH-initiated oxidation of the 4,1-carbonyl nitrate were observed by the

299     CIMS. The change in the CIMS signals before and after the reaction are illustrated in Fig. 10,

300     along with assignment of some of the molecular structures based on the molecular weight and

301     likely chemistry. The OH-initiated oxidation reaction can proceed through two channels: H

302     abstraction from the aldehyde group and OH addition to the double bond.

303     For the H abstraction pathway, a peroxyacyl nitrate (PAN) product was observed at m/z 349 (Fig.

304     10), which can be formed as shown in Fig. 11. The first-order dissociation rate constant for the

305     PAN compound was determined at room temperature (295 K) using the following method. A

306     100 L Teflon bag containing the air mixture of approximately 1 ppm isopropyl nitrite and 30 ppb

307     4,1-carbonyl nitrate was irradiated, and the PAN compound was formed from OH and $NO_2$

308     (produced through the photolysis of isopropyl nitrite) reaction with the 4,1-carbonyl nitrate.

309     After 5 min reaction time, the bag was removed from the UV radiation, and NO was injected into

310     the bag to around 4 ppm in concentration. The bag was then sampled simultaneously by the

311     CIMS, which monitored the decrease in the signal of the PAN compound, and by the TRENI,

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312    which monitored the concentrations of NO and $NO_2$. The PAN dissociation reaction is a

313    reversible process, where the dissociation products, peroxyacyl (PA) radical and $NO_2$, can re-

314    combine to form PAN. With the addition of the large amount of NO, PA radicals are

315    predominantly consumed by the irreversible PA + NO reaction, leading to the decay of the PAN

316    compound. The apparent PAN dissociation rate constant can be described by Eq. 6 (Shepson et

317    al., 1992), where k is the first-order loss rate constant measured by the CIMS (Fig. S6), $k_{PAN}$ is

318    the real PAN dissociation rate constant, [NO] and [$NO_2$] are the concentrations for NO and $NO_2$,

319    and $k_{NO}$ and $k_{NO2}$ are the rate constants for PA + NO and PA + $NO_2$ reactions. Since the rate

320    constants $k_{NO}$ and $k_{NO2}$ for the carbonyl nitrate-derived PA radical are unknown, the IUPAC

321    recommended rate constants for the peroxyacetyl radicals ($CH_3C(O)O_2$) are used, with $k_{NO}$ =

322    $2.0 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and $k_{NO2}$ = $8.9 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The PAN dissociation

323    rate constant, after correcting for the competing PA + NO and PA + $NO_2$ reactions using Eq. 6, is

324    $5.7(\pm 0.8) \times 10^{-4}$ $s^{-1}$, based on three experimental trials. In addition to dissociation, the PAN

325    compound in the 100 L bag could also undergo wall loss. This loss rate was estimated by

326    multiplying the wall loss rate of the carbonyl nitrate in the 5500 L chamber by a factor of 16,

327    which is the square diffusion distance of the chamber relative to that of the 100 L bag, assuming

328    the PAN compound and the isoprene carbonyl nitrate have similar diffusion and adsorption

329    coefficients. Considering the uncertainty in wall loss rate, the PAN dissociation rate constant is

330    $5.7(+0.8/-2.8) \times 10^{-4}$ $s^{-1}$. Previous studies of the dissociation rate constants for peroxyacyl nitrates

331    have reported results ranging from $1.6 \times 10^{-4}$ $s^{-1}$ to $6.0 \times 10^{-4}$ $s^{-1}$ at 298 K (Bridier et al., 1991;

332    Grosjean et al., 1994; Kabir et al., 2014; Roberts and Bertman, 1992). Our result is consistent

333    with previous work.

334    $$k = k_{PAN}(1 - \frac{1}{1+\frac{k_{NO}[NO]}{k_{NO_2}[NO_2]}})$$                    (Eq. 6)

335    Since our OH oxidation experiments were conducted in the presence of high NO concentration, a

336    significant fraction of the PA radicals from the H abstraction reaction channel were expected to

337    react with NO to form alkoxy radicals. Based on the product observed at m/z 321, a reaction

338    scheme (Fig. 11) is proposed, where the alkoxy radical dissociates into $CO_2$ and an alkyl radical,

339    which is further oxidized to form a C4 dinitrate (m/z 321, Fig. 10), along with ethanal nitrate

340    (m/z 232, Fig. 10).

341     For the OH addition pathway, OH can add to the C2 and the C3 position of the 4,1-isoprene

342     carbonyl nitrate, but the less substituted C3 position should be preferential (Peeters et al., 2007).

343     For the C2 addition, the expected nitrate products are C5 dinitrate and ethanal nitrate (Fig. 12a),

344     as observed at m/z 351 and m/z 232 (Fig. 10). $NO_2$ could potentially be released with the

345     concurrent formation of a C4 di-aldehyde (Fig. 12a). The CIMS signal for this compound at m/z

346     229 did not increase (Fig. 10), but the CIMS sensitivity for this compound could be relatively

347     low. For the C3 addition, the expected nitrate products are C5 dinitrate, MVK nitrate and ethanal

348     nitrate (Fig. 12b), observed at m/z 351, m/z 276 and m/z 232 (Fig. 10). The C2 and C3 OH

349     addition pathway would lead to two C5 dinitrate isomers, but they were detected at the same

350     mass by the CIMS.

351     Using a GC-ECD/CIMS method similar to the one described by Xiong et al. (2015), the CIMS

352     sensitivities of the nitrate products were determined relative to the CIMS sensitivity of the 4,1-

353     carbonyl nitrate. The setup was modified to operate the GC separation under pressure lower than

354     1 atm (Fig. S7), which helped to lower the elution temperature. A Teflon bag filled with the 4,1-

355     carbonyl nitrate, isopropyl nitrite, and NO was irradiated to generate the OH oxidation products.

356     The mixture of the 4,1-carbonyl nitrate and its products were then cryo-focused and separated on

357     the GC column, and eluent species were detected by the ECD and the CIMS simultaneously. We

358     were able to quantify the MVK nitrate and the ethanal nitrate using this method, assuming

359     identical ECD sensitivities for nitrates. The other products shown in Fig. 10, however, were not

360     detected with simultaneous good signal-to-noise ratio on the ECD and the CIMS. The

361     ECD/CIMS chromatograms are shown in Fig. 13. We determined that the reaction of the 4,1-

362     carbonyl nitrate and the reagent ion $I^-$ could form $NO_3^-$, but the same reaction did not occur for

363     the MVK nitrate and the ethanal nitrate (Fig. 13). Formation of $NO_3^-$ from $I^-$ reaction with

364     organic nitrates has not been reported previously. Since $I^-$ is a poor nucleophile, it is unclear if

365     this reaction proceeds by $S_N2$ substitution. Using the same $I^-$ ionization method, Wang et al.

366     (2014) observed $NO_3^-$ signal equivalent to a $NO_3 + N_2O_5$ concentration of 200-1000 ppt during a

367     field study in Hong Kong. Through interference tests, the authors attributed 30-50% of the

368     observed $NO_3^-$ signal to the interference from peroxyacetyl nitrate and $NO_2$. Since $I^-$ reaction

369     with the carbonyl nitrate can also generate $NO_3^-$, organic nitrates ($RONO_2$) could be a potential

370     source of interference for $NO_3 + N_2O_5$ measurement with the $I^-$ ionization method.

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371  For the GC-ECD/CIMS calibration, 9 trials were conducted at three different pressures. The

372  results are summarized in Table S2. The relative CIMS sensitivities for the 4,1-carbonyl nitrate,

373  ethanal nitrate and MVK nitrate are 1:15(±3):34(±3) respectively. The absolute CIMS sensitivity

374  of the 4,1-carbonyl nitrate was determined with standard gas samples prepared following Xiong

375  et al. (2015), and the result was used to calculate the absolute sensitivities for the ethanal nitrate

376  and the MVK nitrate. The ethanal nitrate and the MVK nitrate both have the $-ONO_2$ group at the

377  $\beta$ position of the acidic H, so their CIMS sensitivities are comparable. For the MVK nitrate, the

378  electron-withdrawing ketone group can further enhance its gas-phase acidity and its affinity to

379  bind with $I^-$. Hence, the CIMS sensitivity for the MVK nitrate is greater than for the ethanal

380  nitrate. For the 4,1-carbonyl nitrate, its low CIMS sensitivity can be caused by the *trans-$\delta$*

381  configuration of the $-ONO_2$ group and the $-CHO$ group. Our previous studies on isoprene-

382  derived hydroxynitrates suggested that the CIMS sensitivity for the $\beta$ isomer is 8 times greater

383  than for the *trans-$\delta$* isomer (Xiong et al., 2015). Lee et al. (2014a) also reported the $\beta$ isomer

384  sensitivity being over 16 times greater than the *trans-$\delta$* isomer sensitivity, using iodide as the

385  reagent ion. Hence, our calibration results, with the sensitivity for the ethanal nitrate 15 times

386  greater than the sensitivity for the 4,1-carbonyl nitrate, is consistent with previous work.

387  With the CIMS sensitivities determined, the yield of the MVK nitrate and the ethanal nitrate

388  from the OH-initiated oxidation of 4,1-carbonyl nitrate was obtained by comparing the formation

389  of the products relative to the loss of the reactant (Fig. 14). The ethanal nitrate was corrected for

390  loss to OH oxidation and photolysis, using the method described by Tuazon et al. (1984). The

391  applied ethanal nitrate + OH rate constant was $3.4 \times 10^{-12} \, cm^3 \, molecules^{-1} \, s^{-1}$, calculated using the

392  structure-reactivity relationship proposed by Kwok and Atkinson (1995). The photolysis

393  frequency of the isoprene carbonyl nitrate was applied to account for the photolytic loss of

394  ethanal nitrate inside the chamber, because the $\beta$-ketone group is known to enhance the

395  absorption cross section of the nitrate (Müller et al., 2014). For the MVK nitrate, no OH loss

396  correction was applied, because MVK nitrate is saturated and is not expected to undergo

397  significant loss to OH. However, its loss to wall uptake and photolysis loss was corrected,

398  following the same method as used for the ethanal nitrate. The MVK nitrate loss rates for wall

399  uptake and photolysis inside the chamber were set the same as those for the 4,1-carbonyl nitrate,

400  because MVK nitrate is also a ketone nitrate, which is prone to photolysis loss, and it has a

401  molecular weight close to that of the 4,1-carbonyl nitrate. The apparent yield is 24.5% for MVK

402    nitrate and 8.08% for ethanal nitrate. Considering the uncertainties in the sensitivities of MVK

403    nitrate and ethanal nitrate (Table S2), the MVK nitrate yield is 24(±3)%, and the ethanal nitrate

404    yield is 8(±2)%. The fractional inlet sampling loss for the three nitrates was determined by

405    comparing the CIMS signals of sampling through the 5.2 m long 50°C tubing and through a 20

406    cm room temperature tubing. By correcting for the inlet sampling loss, the MVK nitrate yield is

407    24(±5)%, and the ethanal nitrate yield is 8(±3)%. For the two OH oxidation experiments, the

408    first-order loss rate of the 4,1-carbonyl nitrate was $3 \times 10^{-4}\,\text{s}^{-1}$ (Fig. S8). Since the total wall

409    uptake and photolysis loss rate for 4,1-isoprene carbonyl nitrate was $4.3 \times 10^{-5}\,\text{s}^{-1}$,

410    approximately 85% of the 4,1-carbonyl nitrate was lost to OH oxidation. After correcting for this

411    factor, the MVK nitrate yield is 28(±5)%, and the ethanal nitrate yield is 9(±3)%.

### 4.3.2  Photolysis

413    Previous work on acetaldehyde suggests that at 313 nm the dominant photolysis reaction is

414    dissociation of the C−CHO bond, forming a formyl radical (•CHO) (Blacet and Loeffler, 1942).

415    At shorter wavelength (265 nm), the reaction can proceed by intramolecular rearrangement

416    forming $CH_4$ and CO (Blacet and Loeffler, 1942). For compounds with longer carbon chain

417    length, such as propyl- and butyl- aldehydes, the photo-dissociation reaction can produce alkenes

418    and smaller aldehydes at 238 nm and 187 nm (Blacet and Crane, 1954). Since the UV radiation

419    that reaches the earth's surface is mostly above 300 nm, the formyl radical pathway is expected

420    to be the most important photolysis reaction for alkyl aldehydes (Shepson and Heicklen, 1982).

421    For the isoprene carbonyl nitrate, the C−CHO bond is strengthened by the delocalized electrons

422    from the vinyl and the carbonyl groups, leading to a bond dissociation energy of 413 kJ/mol, as

423    measured for acrolein, which is larger than the C−CHO bond dissociation energy of acetaldehyde

424    (355 kJ/mol) (Wiberg et al., 1992). In comparison, the O−$NO_2$ bond dissociation energy is 175

425    kJ/mol (Luo, 2007b), much lower than the dissociation energy of the C−CHO bond. Hence,

426    dissociation of the weak O−$NO_2$ bond may be an important reaction pathway for the carbonyl

427    nitrate. This process likely involves the absorption of a photon by the C=C−C=O chromophore,

428    followed by intramolecular energy redistribution to deposit energy into the O−$NO_2$ bond prior to

429    dissociation. This reaction step would generate $NO_2$ and an alkoxy radical, which upon reaction

430    with $O_2$ forms a conjugated dialdehyde.

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431    Fig. 15 shows the CIMS spectra before and after the photolysis of the isoprene carbonyl nitrate.

432    Cyclohexane was used as the OH scavenger for this experiment. The CIMS signal for the

433    dialdehyde, which is the O−NO$_2$ bond dissociation product (reaction mechanism shown in Fig.

434    16), did not increase significantly. This may be because the CIMS was not sensitive to the

435    dialdehyde, and/or the dialdehyde underwent rapid secondary reactions, rendering its steady-state

436    concentration below the CIMS detection limit. Alternatively, it is possible that the alkoxy radical

437    derived from O−NO$_2$ bond dissociation undergoes a 1,5-H shift reaction (Fig. 16), rendering the

438    formation of the dialdehyde an insignificant pathway. The resulting alkyl radical can

439    immediately form a peroxy radical, which may follow the H shift mechanism proposed by

440    Peeters et al. (2009) and form a hydroperoxy aldehyde (HPALD) compound, as observed at m/z

441    257 by the CIMS (Fig. 15). When the peroxy radical reacts with NO or RO$_2$, the resulting alkoxy

442    radical will form a hydroxy dialdehyde (Fig. 16) with m/z ratio at 241, which was also observed

443    by the CIMS (Fig. 14). It is worth noting that we also observed CIMS signals for the

444    deprotonated ions derived from the HPALD compound (m/z 129 and m/z 147) and the hydroxy

445    dialdehyde (m/z 113 and m/z 131). The proton transfer reaction between the iodide ion and

446    alcohols/peroxides have not been observed previously, but it is possible that the conjugated

447    structures help stabilize the charge and hence make the proton transfer reaction a viable reaction

448    channel.

449    The product at m/z 276 has the molecular weight of MVK nitrate. In the presence of OH

450    scavenger, however, the reaction is unlikely to proceed by the OH-initiated oxidation pathway to

451    form MVK nitrate. Instead, we hypothesize that the isoprene carbonyl nitrate could dissociate via

452    the C−CHO bond, which, following reaction with O$_2$ and HO$_2$, would form a vinyl

453    hydroperoxide with the same molecular weight as MVK nitrate. Vinyl hydroperoxides are

454    known to be a reactive intermediate from the intramolecular H shift of Criegee biradical, which

455    can decompose into OH and alkoxy radicals (Kroll et al., 2002). However, the un-energized

456    vinyl hydroperoxides should have a lifetime long enough to be detected by mass spectrometers

457    (Liu et al., 2015). In fact, theoretical calculations suggest that at 25 °C vinyl hydroperoxide has a

458    lifetime of 58 hours (Richardson, 1995). Therefore, the product at m/z 276 is likely the vinyl

459    hydroperoxide. For the OH oxidation product experiments, however, we attributed m/z 276 to

460    MVK nitrate only, because RO$_2$ + NO reaction (forming MVK nitrate) should dominate over

461    RO$_2$ + HO$_2$ reaction (forming vinyl hydroperoxide), in the presence of high NO concentration.

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462  Based on the CIMS spectra of the photolysis products, we conclude that the photolysis of the

463  isoprene carbonyl nitrate leads to the dissociation of both the $O-NO_2$ and the $C-CHO$ bonds. A

464  reaction scheme is proposed in Fig. 16. Future studies are needed to evaluate the relative

465  importance of these two processes.

466  **5   Conclusions and future work**

467  An isoprene-derived carbonyl nitrate model compound was synthesized to study its

468  photochemical degradation chemistry in the atmosphere. The UV absorption spectrum of this

469  compound has contributions from both the $C=C-C=O$ and the $-ONO_2$ chromophores, as is

470  confirmed by theoretical calculations, but absorption in the actinic region involves a transition

471  involving the carbonyl group. The combination of the $C=C-C=O$ and the $-ONO_2$ chromophores

472  enhances the UV cross section of this molecule relative to alkyl nitrates, making photolysis its

473  dominant daytime sink. The photochemical lifetime of the carbonyl nitrate can be less than one

474  hour, due to its rapid photolysis loss, together with high reactivity toward OH and $O_3$. The OH

475  and $O_3$ oxidation rate constants for the 4,1-isoprene carbonyl nitrate obtained in this study were

476  both smaller than the reported rate constants for the $\delta$-isoprene hydroxy nitrates (Jacobs et al.,

477  2014; Lee et al., 2014b). This could be because the oxidation by either OH or $O_3$ would break the

478  resonance structure of the $C=C-C=O$ moiety, thus increasing the activation energy.

479  Using the iodide-based CIMS, we identified the first-generation nitrate products from the OH-

480  initiated oxidation of the synthesized carbonyl nitrate, including mononitrate, dinitrate and

481  nitrooxy peroxyacyl nitrate. Two of the products, the MVK nitrate and the ethanal nitrate, were

482  quantified, which contributed to 37($\pm$5)% of the total products. The CIMS spectra of the nitrate

483  photolysis products suggest that both the $C-CHO$ bond and the $O-NO_2$ bond dissociate in the

484  reaction. Since photolysis is a significant sink for the carbonyl nitrate, it is important for future

485  studies to investigate the relative importance of the two reaction pathways, in order to fully

486  understand the fate of $NO_x$ in isoprene-rich atmospheres. Dissociation of the $O-NO_2$ bond may

487  afford highly oxidized alcohol and hydroperoxide, which can potentially undergo uptake into the

488  particle phase and facilitate the formation of secondary organic aerosols. The $C-CHO$

489  dissociation pathway may form a vinyl hydroperoxide product.

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490 The $NO_3$-initiated isoprene oxidation can produce a series of carbonyl nitrates. The 1,4-carbonyl

491 nitrate, which is the dominant isomer, is expected to have similar photolysis reactivity as the 4,1-

492 carbonyl nitrate studied in this work, because they both have the $O=C-C=C-C$ chromophore and

493 the $-ONO_2$ chromophore, which would enhance the molecular absorption cross section. The

494 influence of the unsaturated ketone functionality on nitrate photolysis is still unclear, and future

495 studies are needed to understand how the different conjugated structures can affect the

496 photochemical processes.

497 The experiments in this work were conducted in the presence of relatively high NO

498 concentration. In the ambient environment, organic nitrates produced in the high $NO_x$ regime can

499 undergo photochemical degradation in the low NO regime, due to the wide span of ambient $NO_x$

500 concentrations (Su et al., 2015; Xiong et al., 2015). Crounse et al. (2012) proposed that under

501 low NO conditions, the oxidation of methacrolein (MACR) can regenerate OH radicals and form

502 a lactone that is prone to reactive uptake onto the aerosol phase. Since the 4,1-carbonyl nitrate

503 has a structure similar to that of MACR, it might also undergo similar reaction in the clean

504 environment. Further experimental work is needed to investigate how the photochemical

505 oxidation process of the carbonyl nitrate can influence the formation of OH radicals and growth

506 of secondary organic aerosols.

507 **Acknowledgement**

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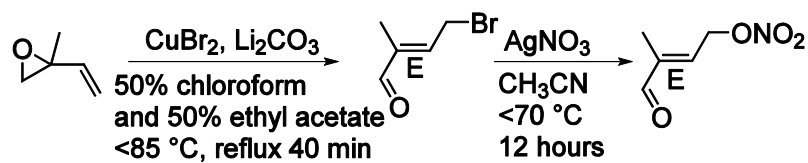804

805    **List of Figures**
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846    Figure 1. Organic nitrates produced from $NO_3$-initiated isoprene oxidation.

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851    Figure 2. The synthesis route for the 4,1-isoprene carbonyl nitrate.

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855    Figure 3. UV absorption cross section of the carbonyl nitrate, MACR and isoproyl nitrate. The

856    spectra were obtained in acetonitrile solvent.

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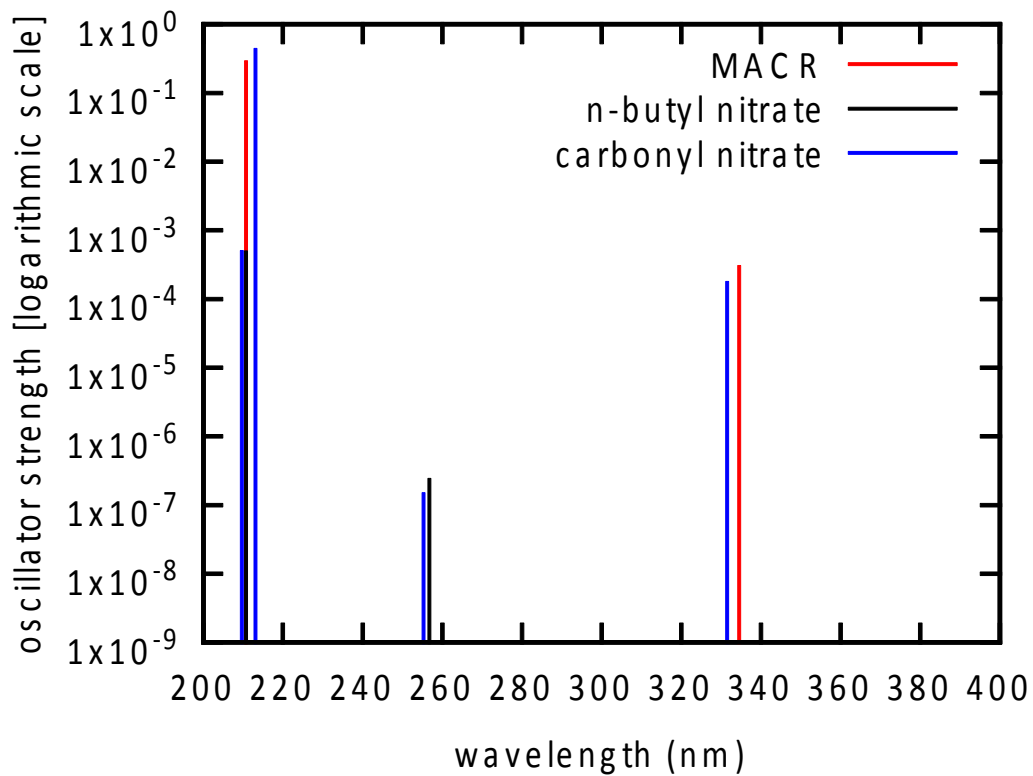


858

859   Figure 4. Theoretical absorption spectra of the carbonyl nitrate, MACR, and *n*-butyl nitrate in the

860   gas phase.

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862

(a) First excitation in carbonyl nitrate
331.51 nm ≈ 3.7404 eV
HOMO → LUMO
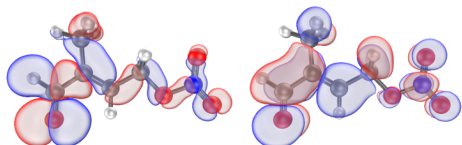
(b) Second excitation in carbonyl nitrate
255.27 nm ≈ 4.8575 eV
HOMO−2 → LUMO+1
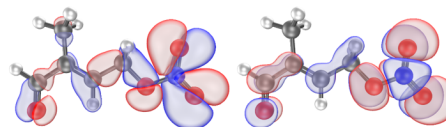
Homologous excitation in MACR
334.54 nm ≈ 3.7066 eV
HOMO → LUMO
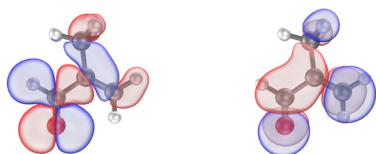
Homologous excitation in *n*-butyl nitrate
256.76 nm ≈ 4.8295 eV
HOMO → LUMO
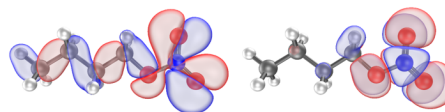


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864 Figure 5. Molecular orbital analysis of the first (a) and second (b) electronic excitation of the

865 carbonyl nitrate. The blue and red colors represent the opposite phases of molecular orbitals.

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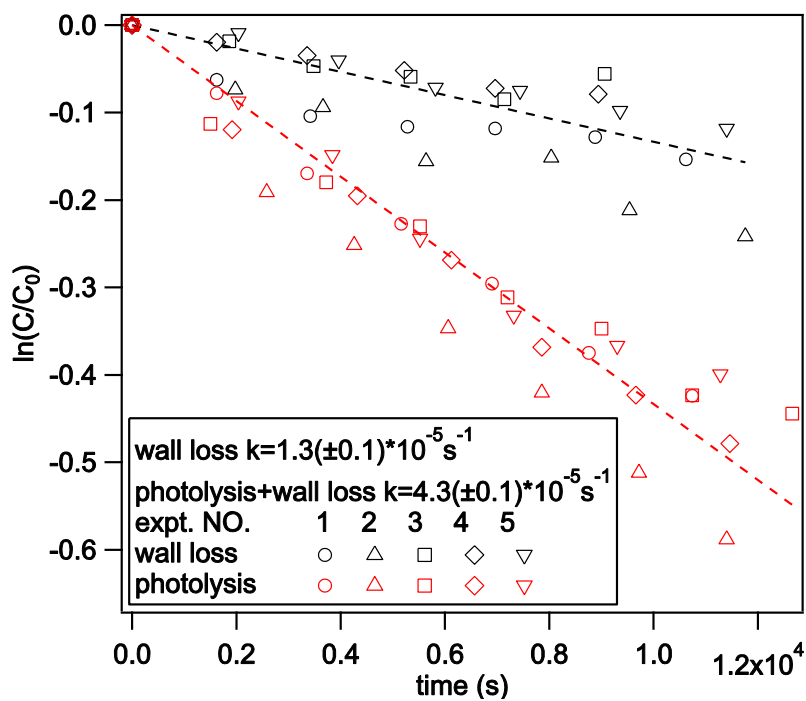
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869    Figure 6. Wall loss and photolysis loss of the carbonly nitrate in the reaction chamber.

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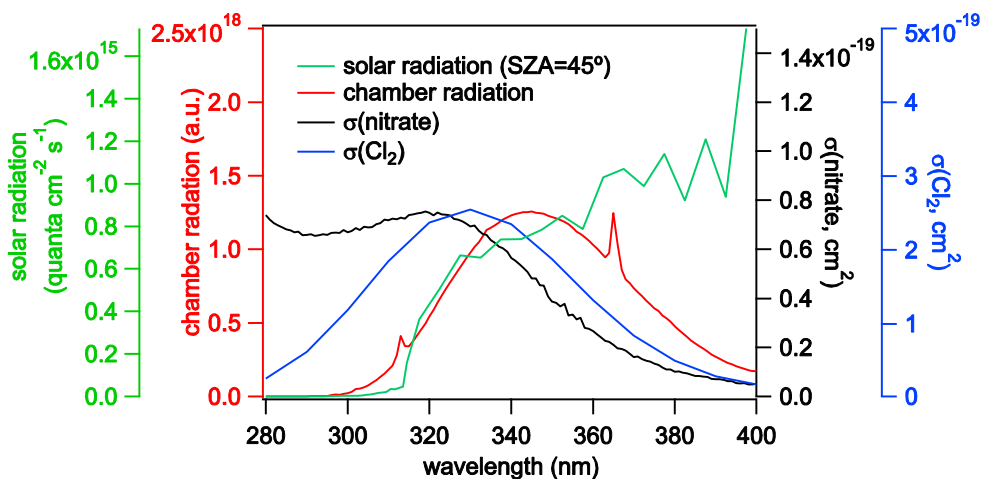


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873    Figure 7. The radiation spectra of the chamber (red) and the sun (green, SZA=45° as an example),

874    and the absorption spectra of the carbonyl nitrate (black) and chlorine (blue).

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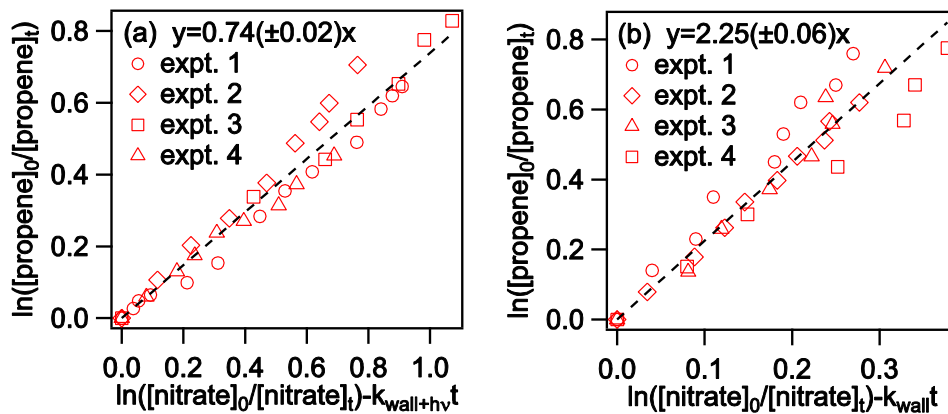


877

878    Figure 8. The first-order loss of propene relative to that of the carbonyl nitrate for OH-initiated (a)

879    and $O_3$-initiated (b) oxidation reactions.

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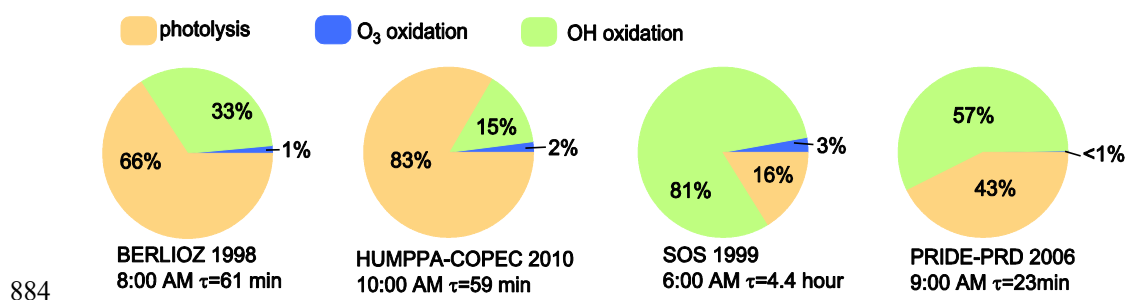
Figure 9. The relative contributions of photolysis (orange), OH oxidation (green) and $O_3$ oxidation (blue) to the photochemical decay of the carbonyl nitrate, calculated based on measured OH and $O_3$ concentrations for the following field studies: BERLIOZ 1998 study at Pabstthum, Germany (Platt et al., 2002; Mihelcic et al., 2003), HUMPPA-COPEC 2010 study at Hyytiälä, Finland, SOS 1999 study at Nashville, US (Roberts et al., 2002; Martinez et al., 2003) and PRIDE-PRD 2006 study at Guangzhou, China (Lu et al., 2012).

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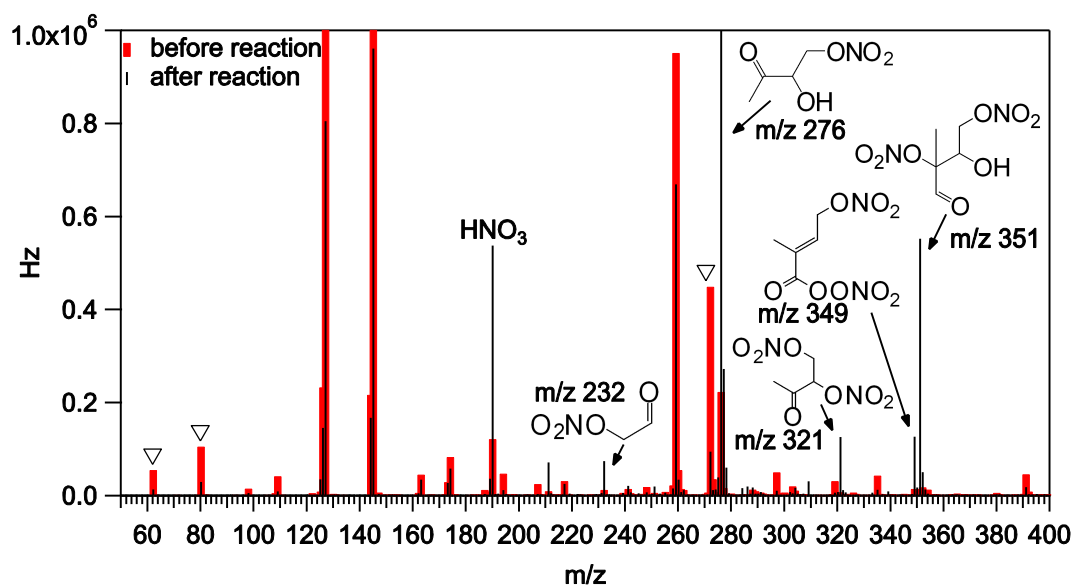
893

894 Figure 10. The CIMS spectra before (red) and after (black) the OH + carbonyl nitrate oxidation

895 reaction. The inverted triangles show the decreases in CIMS signals for the carbonyl nitrate (m/z

896 272) and the $NO_3^-$ fragments (m/z 62, water cluster at m/z 80) derived from the carbonyl nitrate
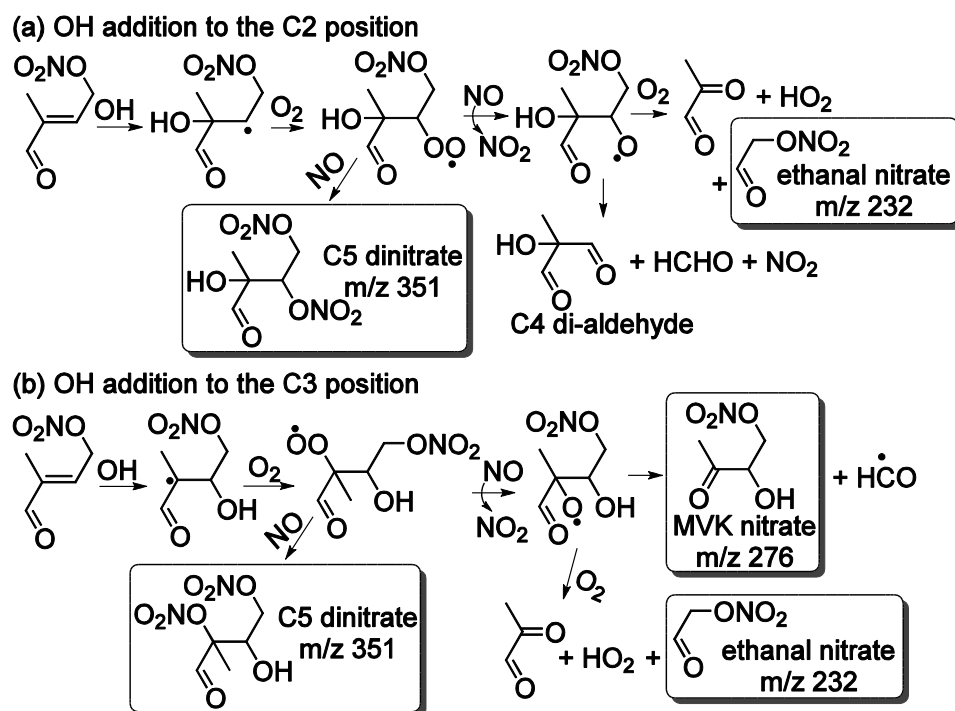
897 (Fig. 11).

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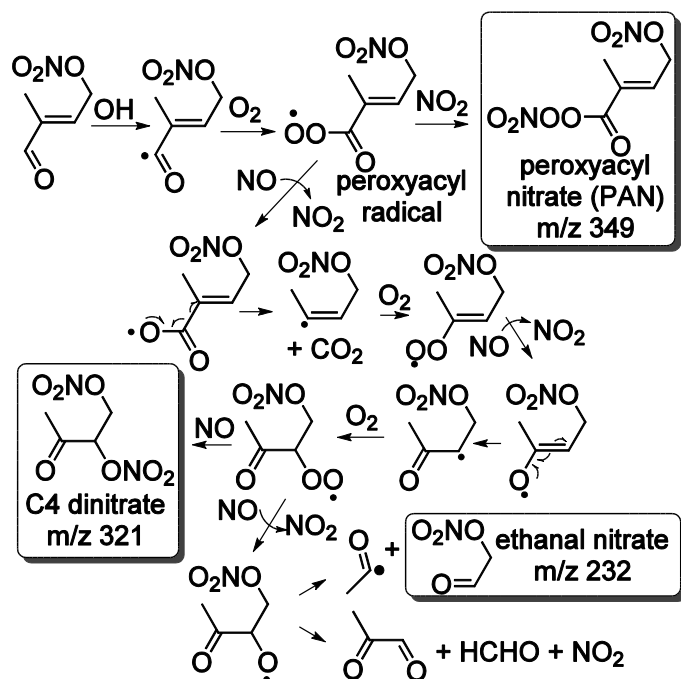
900

901 Figure 11. A proposed reaction mechanism for the H abstraction pathway for the OH + carbonyl

902 nitrate oxidation reaction. The compounds in boxes are proposed products as observed by the
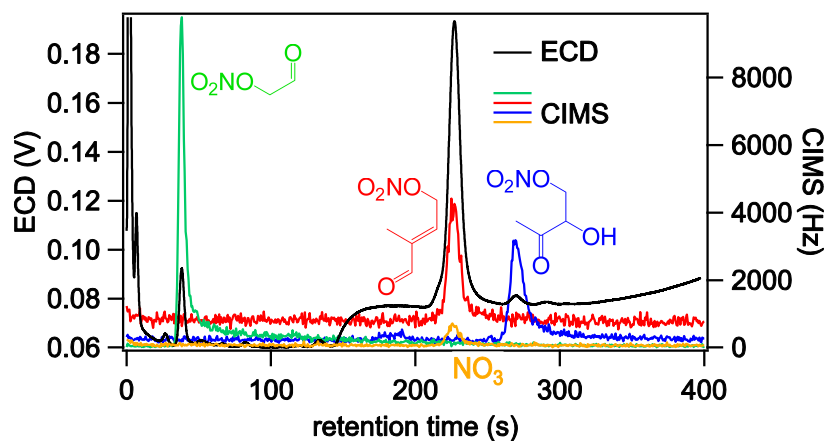
903 CIMS (Fig. 8).

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Figure 12. Proposed reaction mechanisms for OH addition to the C2 (a) and C3 (b) position of the carbonyl nitrate. The compounds in boxes are proposed products as observed by the CIMS (Fig. 8).
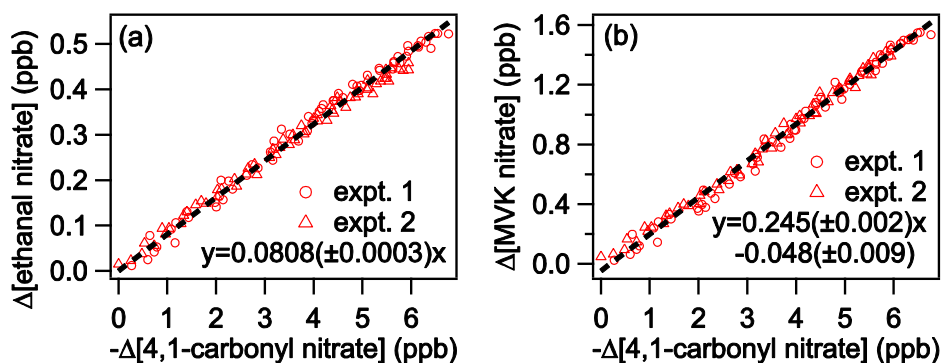
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914     Figure 13. The GC-ECD/CIMS spectra for the carbonyl nitrate (red), MVK nitrate (blue) and

915     ethanal nitrate (green). The reaction of iodide with the carbonyl nitrate generated $NO_3^-$ ion

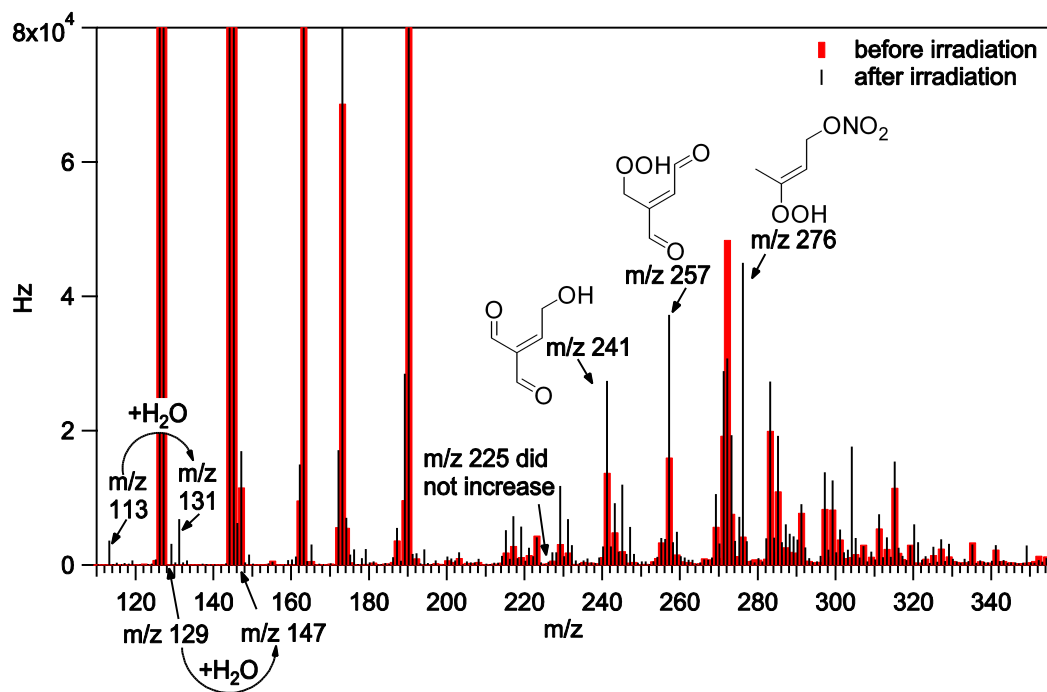916     (orange). The ECD chromatogram is shown in black.

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919



920     Figure 14. The formation of ethanal nitrate (a) and MVK nitrate (b) relative to the loss of the

921     isoprene carbonyl nitrate for the OH + carbonyl nitrate oxidation experiments.
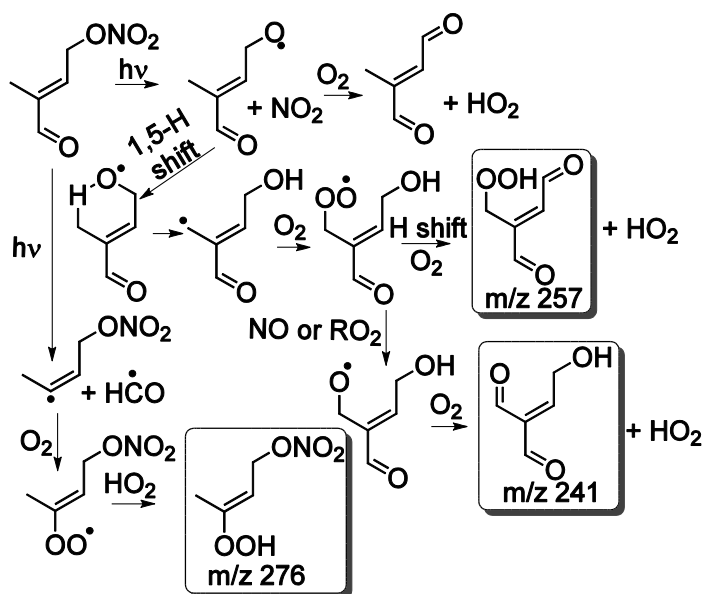
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923

924    Figure 15. CIMS spectra before (red) and after (black) the photolysis of the isoprene carbonyl

925    nitrate.

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929    Figure 16. A proposed reaction mechanisms for the carbonyl nitrate photolysis reaction. The

930    compounds in boxes are proposed products as observed by the CIMS (Fig. 13).

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