

This article presents a nice and detailed investigation of the photolysis, ozonolysis and OH-reaction of a conjugated carbonyl nitrate produced in the oxidation of isoprene by NO₃ radical. The topic is of great importance to atmospheric chemistry since the formation and fate of organic nitrates play an outstanding role through their influence on the budget of NO_x over forested areas. The methods are appropriate and the analysis is sound (with some minor reservations as explained further below). The article is also very well-written, very clear, and appropriately illustrated. Although the focus is on a specific compound which in itself plays probably only a very minor role in the atmosphere, the results regarding the rates of photolysis and reaction with OH and O₃ are very likely valid to a broader class of compounds which are important intermediates in the oxidation of isoprene and (no doubt) many other compounds.

General comment

Among several interesting findings, this study provides sound evidence that the interaction between the two chromophores in a nitrooxy enal enhances its absorption cross section as well as its photolysis quantum yield, so much so that photolysis is their dominant sink in atmospheric conditions around mid-day. This view was proposed as a general trait for alpha- and beta-nitrooxy carbonyls (Muller et al., 2014), based on the laboratory observation of strongly enhanced photolysis rates (compared to nonconjugated carbonyls) for several keto-nitrates (Suarez-Bertoa et al., 2012) and for several compounds including ethanal nitrate, the simplest aldehyde nitrate (Muller et al., 2014). That this enhancement also exists for nitrooxy enals (or enones) was previously proposed, but lacked experimental proof, which is provided here. The conjugated nature of the compound under consideration is very important given the distinct features of photolysis parameters of enals or enones compared to other carbonyls, and I think this aspect should be acknowledged in the manuscript. Because of very low quantum yields (ca. 0.004), the photolysis of MACR and MVK is almost negligible in spite of their very high cross sections above 300 nm. The presence of the nitrate group is found to increase the quantum yield by two orders of magnitude, to a value of the order of unity (0.28-0.48 in this study). On top of that, the cross sections are also enhanced, as nicely shown in this work. Overall, the presence of the ONO₂ group has a much more dramatic impact for the photolysis rates of enals (or enones) than for other carbonyls. For this reason, I recommend that the studied compound should be referred to as an enal in the title and in the abstract.

We have changed to refer to this compound as “isoprene nitrooxy enal”, or “nitrooxy enal”, in the title, abstract and the rest of the manuscript.

In addition, the article presents an experimental determination of the OH- and O₃- reaction rates of the nitrooxy enal, thereby enabling the estimation of the relative contribution of photolysis and reaction with OH and O₃ to the total photochemical sink of this compound. Photolysis is found to be generally dominant during the day. The further degradation mechanism following photolysis or reaction with OH is also explored, and yields of different products are derived. Photolysis is believed to proceed in part C2 by O–NO₂ dissociation, as proposed in Muller et al. (2014), and for some part by C–CHO scission. Interpretation of the CIMS measurements and the derivation of yields is helped by kinetic modelling to account for the losses of the main observed products. The only reservation I have concerns the choice of photolysis rates for those products in this analysis

(see further below). But this is only a minor issue which should not affect the main conclusions of the study. I therefore recommend publication in ACP, after the authors take the above considerations into account, and address the following comments.

Minor comments

lines 71-78: The interaction between chromophores in nitrooxy carbonyls (i.e. also aldehydes) was found to enhance not only the cross sections but also the quantum yields (Muller et al., 2014). The combined effects on cross sections and quantum yields were observed for ethanal nitrate and for the sum of methyl vinyl ketone nitrate and methacrolein nitrate (MVKNO₃ + MACRNO₃) of which the measured temporal evolution in the experiment of Paulot et al. (2009) provided constraints on the photolysis parameters. A quantum yield of the order of unity was also proposed for the major nitrooxy enal produced in the oxidation of isoprene by NO₃. Its estimated photolysis rate was $5.6 \times 10^{-4} \text{ s}^{-1}$ for a solar zenith angle of 30 degrees, assuming a unity quantum yield and using the cross sections of MACR. As a consequence, photolysis was estimated to outrun OH-oxidation in atmospheric conditions.

On lines 73-80 of the revised manuscript, we have added more clarification on the results reported by the Muller et al. (2014) study, to indicate that the interaction between chromophores can enhance both cross section and quantum yield.

line 168: The error bar for the wall loss rate constant appears somewhat optimistic in view of the scatter shown on Fig. 6. How was it derived?

The reported error is the standard error (s) of the coefficient. For clarification, we now report the result with 95% confidence interval, using $t_{(N-2)} * s$ on lines 215-216.

line 175: "... cis isomer was present". I guess you mean "... was formed from the trans isomer", correct?

We have re-worded the reasoning for this part on line 226-238.

Figure 7. The caption should tell that the cross sections of the nitrate were obtained in acetonitrile.

We have included this information in the caption.

line 239: Is the factor 1.7 an average weighted by the irradiance spectrum?

The factor 1.7 is not a weighted average. It is calculated as the average ratio of gas-phase cross section divided by condensed-phase cross section at each wavelength. This is clarified on lines 296-298.

lines 393: Using the photorate of the 4,1-carbonyl nitrate to represent the photolysis loss of ethanal nitrate and the MVK nitrate is not appropriate as those compounds are not conjugated and their absorption cross sections are expected to be much lower in the relevant wavelength range (300-400 nm). For MVKNO₃, I recommend to use the cross sections of 3-nitrooxy-2-butanone which are known from Barnes et al. (1993), and a quantum yield of unity since this choice led to best results for MVKNO₃+MACRNO₃ evolution in Muller et al. (2014). For ethanal nitrate, the cross sections shown in Fig. 2 in Muller et al. (2014) could be used, as it was also found to give good results against Paulot et al. This update should decrease the calculated photolysis frequencies, especially for MVKNO₃. Note that the OH-reaction rate of MVKNO₃ according to Kwok and Atkinson (1995) is $1.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, which might not be entirely negligible.

We calculated the photolysis frequency of 3-nitrooxy-2-butanone using the cross section reported by Barnes et al. (1993) and a unity quantum yield. The result, $4.5\text{E-}6 \text{ s}^{-1}$ is used as a surrogate for the photolysis frequency of MVKNO₃. We calculated the MVKNO₃ + OH rate constant as $1.78\text{E-}12 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, based on Kwok and Atkinson (1995). We corrected the MVKNO₃ yield using these updated loss rates on lines 468-481.

We calculated that the photolysis frequency for ethanal nitrate is $1.69\text{E-}5 \text{ s}^{-1}$, using the cross section recommended by Muller et al (2014) and a unity quantum yield. This information is added on lines 464-466.

line 494: As far as photolysis is concerned, I don't really see why unsaturated ketones would be much different from unsaturated aldehydes. The absorption cross sections and quantum yields of MVK and MACR are very similar.

The unsaturated ketones and aldehydes are expected to have similar photochemical properties, given their similar structures, but the ketones may not be as reactive to OH as the aldehydes. We have made the clarification on lines 583-587.

Technical corrections

line 106 "derived"

line 213: "were known" -> "are known"

line 214: "we calculated" -> "we calculate"

line 220: "introduced" → "introduce"

line 226: "we calculated that lambda0 was..." → "we calculate that lambda should be..."

line 273: "multiplying by..."

The above corrections have been made.

References

Barnes, I., Becker, K. H., and Zhu, T.: Near UV absorption spectra and photolysis products of difunctional organic nitrates: Possible importance as NO_x reservoirs, *Journal of Atmospheric Chemistry*, 17, 353-373, 10.1007/bf00696854, 1993.

Kwok, E. S. C., and Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update, *Atmospheric Environment*, 29, 1685-1695, [http://dx.doi.org/10.1016/1352-2310\(95\)00069-B](http://dx.doi.org/10.1016/1352-2310(95)00069-B), 1995.

Müller, J. F., Peeters, J., and Stavrakou, T.: Fast photolysis of carbonyl nitrates from isoprene, *Atmospheric Chemistry and Physics*, 14, 2497-2508, 10.5194/acp-14-2497-2014, 2014.

The manuscript, "Photochemical degradation of isoprene-derived 4,1-carbonyl nitrate" by Xiong et al. reports on the photolysis rate of the trans-4-1 carbonyl nitrate derived in the atmosphere from the NO₃ radical oxidation of isoprene. The manuscript is well written and describes a great deal of well-thought-out work. The main implication of this work is that this conformer of isoprene carbonyl nitrate will have a short lifetime in the atmosphere due mainly to photolysis, with non-negligible contribution from OH oxidation. The work also identifies some of the major byproducts of OH oxidation and photolysis of this compound, thereby improving our understanding of isoprene photochemistry. The work should be published in ACP with a few minor clarifications.

Minor questions/comments/suggestions: I disagree with the "double" and "single" exponential discussion (lines 175-178). That a double exponential will be observed if large amounts of cis is present is unconvincing without additional information and likely cannot be concluded without knowing the isomerization rate. What is the chamber residence time? A cis-trans equilibrium at some point will be reached. If the rate at which this occurs is instantaneous (or at least much faster than residence time), a single exponential will always be observed because the CIMS only ever sees a mixture of the two isomers. Would you expect a significant difference in the photolysis rate of cis versus trans? If not, does it matter which isomer you are measuring? All that matters for this part of the experiment is the decay rate. If photo lifetime of cis versus trans is very different, you would have to qualify that the 1.3e-5 sec⁻¹ rate is some average of the two isomers.

The chamber is operated in a static rather than dynamic mode. The duration of each experiment is about 3 hours. If a cis-trans equilibrium is established instantaneously, a single exponential will be observed. However, we don't expect the cis and trans isomer to differ in photolysis frequency, given they both have the nitroxy enal structure. Therefore, the measured decay rate should represent the photolysis frequency of the trans precursor in the reaction chamber. We have added this discussion to lines 226-238.

It would be helpful to know which compounds whose structures are drawn in figures 10 and 15, as well as those boxed in figures 11 and 12 are observed by both GC and CIMS. The CIMS captures signal at nominal masses, therefore, to infer not only molecular composition (C_xH_yO_z) but molecular structure (i.e. identifying functional groups) would impart a certain amount of uncertainty. If only the CIMS without GC is used to infer a compound identity (such as dinitrates which I imagine do not survive GC column), this is worth clarifying. Also, how well can you distinguish MVK nitrate from MACR nitrate with GC /CIMS?

The compounds that were observed by both GC and CIMS are now indicated in blue. The structures proposed in figures 10-12 and 15-16 are inferred based on nominal masses. We have added this information to the captions of these graphs.

We are unclear how well the GC/CIMS can distinguish MVK nitrate from MACR nitrate. For this work, we do not expect to have MACR nitrate in the system, because the nitroxy enal has a secondary carbon at its C3 position, and the OH oxidation reaction cannot add a functional group at this position while still maintaining it as a secondary carbon as in MACR nitrate. Therefore, we infer m/z 276 to be MVK nitrate. We have added this discussion to lines 409-412.

Given CIMS observations of boxed compounds in figures 12 and 16, can you infer branching ratios of OH oxidation paths (a versus b in figure 12) and the two photolysis paths (figure 16).

The branching ratios for the OH oxidation cannot be obtained because the products from H-abstraction pathway were not quantified. For the OH addition pathway, we did quantify two of the products. However, ethanal nitrate is produced from both H abstraction and OH addition pathways (including both (a) and (b) pathways). MVK nitrate is produced in pathway (b) only, but it has ethanal nitrate as byproduct (along with C5 dinitrate), which makes it impossible to determine the branching ratio for pathway (b). We have added this discussion to lines 491-497.

For photolysis pathways, we cannot determine the branching ratio because the photolysis products were identified, but not quantified. This is clarified on lines 549-552.

How were the spectra in figure 3 obtained? Are they of three different samples, one containing pure carbonyl nitrate in solvent, the second pure MACR, and the third pure isopropyl nitrate? If the spectra are of one mixture containing all three compounds, how were the spectra distinguished or attributed to a particular compound?

The spectra were obtained with three different samples, each one containing one pure solute in the acetonitrile solvent. This is clarified on line 99-100.

Is each a simulated or calculated spectrum from the observed (the sum of the three spectra shown in figure 3). This needs to be better explained, in particular, for the discussion on lines 142 to 165. This discussion tries to establish that the excitation features of carbonyl nitrate is well understood, that the one near 255 nm is from the nitrate group C2 and the one near 330 nm is from the aldehyde group. However, there are some aspects of this discussion that are difficult to follow, hence, the argument is not as convincing as can be. For instance, figure 3 shows isopropyl nitrate along with MACR and carbonyl nitrate, whereas figure 4 shows n-butyl nitrate. Explain why the combination of these 3 compounds was chosen for this part of the study...similarity in structure, overlapping functional groups, etc. Figure 4 and 5 involve calculations...why not include isopropyl nitrate as well? It would make comparison simpler and argument more convincing.

The calculation was performed for each spectrum separately. In Fig. 3, we compared isopropyl nitrate and MACR with isoprene nitrooxy enal, because MACR has the enal structure, and isopropyl nitrate has the nitrooxy group, and the combination of these two compounds resembles the nitrooxy enal studied in this work. This explanation was added to lines 102-105 of the revised manuscript.

To better compare the measured UV spectra with the calculated spectra, we have now added calculations for isopropyl nitrate in section 3.2 and 4.1 of the revised manuscript.

Figure 4 is described as an absorption spectrum. But it looks very different from figure 3. Figure 4 looks more like band strength or absorption lines. Is it possible to simulate actual absorption spectra (one for MACR, one for carbonyl nitrate, one for n-butyl nitrate) given data shown in figure 4 under conditions similar to those in figure 3 and compare that result to figure 3? Would provide stronger support to TDDFT calculation.

Fig. 4 shows the theoretical gas phase absorption spectra of the nitrooxy enal, MACR, isopropyl nitrate, and n-butyl nitrate. To accurately capture the broadening of these lines in TDDFT, it is required to consider the effect of the chromophore's vibrational degrees of freedom and/or to include a condensed phase environment that surrounds the chromophore. However, explicit modeling of broadening either due to vibronic interactions or solvent effects is computationally challenging. We believe the analysis of this kind is beyond the scope of the present work. It is also possible to artificially broaden stick spectra with Gaussian or Lorentzian envelopes, to represent collision broadening. However, we do not think that such artificial broadening would provide any additional information, while the presented stick theoretical spectra provide adequate support for our arguments. This discussion is added to lines 165-170.

Lines 142-144, reads as if authors are saying there is a transition for n-butyl nitrate near 330 nm when there is not. Please re-word.

We have re-worded the sentence to refer the 330 nm transition as a transition for the nitrooxy enal only on line 180-182.

Lines 148-149..."...Earth's surface..." what is the significance of this statement? Figure 5 and lines 159-165. What is the relevance of including the excitation feature near 210 nm (figure 4) when there is no experimental data (figure 3) to compare against. This spectral region is also "beyond atmospheric relevance" as authors note.

The theoretical calculations suggest that the nitrooxy group has an electronic transition at 210 nm and 255 nm, but both wavelengths are outside the solar radiation spectrum near the surface. Therefore, we speculate that the isoprene nitrooxy enal absorbs photons primarily through the transition of the enal chromophore, instead of the nitrooxy functionality, and the dissociation of the O-NO₂ bond likely results from intramolecular energy redistribution. This discussion is added to line 207-212.

Including those transitions gives a clear picture of how the theoretical spectrum of the nitrooxy enal is a function of both nitrooxy absorption and absorption of the enal group, through the comparison with the absorption of the alkyl nitrates and MACR. While though they might not seem directly relevant to the experimental data, they show internal consistency of the simulated spectra. This discussion is further clarified on line 198-200.

Figure 1. Is the reaction between the NO₃ radical and nitroxy peroxy radical the only route to the alkoxy radical, hence carbonyl nitrate? Isn't reaction with RO₂ more likely than NO₃ to generate the alkoxy given abundance of RO₂ in most BVOC rich region? At the very least, RO₂ should be included. Rollins et al 2009 ACP (www.atmos-chemphys.net/9/6685/2009/).

We have now included RO₂ as a second reactant to form nitrooxy alkoxy radicals in Fig. 1.

Application to field observation was demonstrated in figure 9. Out of curiosity, is there direct observation of isoprene carbonyl nitrate from the field using CIMS+GC? Spectrum or chromatogram or time series or diel average? How abundant is isoprene carbonyl nitrate considering it is produced at night when loss rate is presumably slow? How well can the CIMS distinguish C₅H₇NO₄ from potential interference due to the isotope of the signal at m/z 271. Do you have carbonyl nitrate + NO₃ oxidation results, similar to those of OH and photolysis shown here? These would be nice additions to this work, but perhaps saving for separate manuscript.

To date there is no report on field observations of isoprene carbonyl nitrates using CIMS or GC method. One of the challenges for this type of measurement might be that when iodide-based CIMS is used, the isoprene nitrooxy enal can react with iodide and form NO₃⁻, instead of nitrate-iodide cluster, and the nitrooxy enal could be detected as NO₃ and N₂O₅ radicals. In addition, iodide-based CIMS is most sensitive to species with acidic hydrogens, which the enal nitrate does not have. Brown et al. (2009) observed NO₃ + isoprene chemistry in Northeast US in the 2004 NEAQS study, and they estimated that the total concentrations of the isoprene-derived nitrate could reach 500 ppt. The carbonyl nitrates are expected to contribute a significant fraction to the total organic nitrates estimated by Brown et al. (2009), but the exact amount cannot be obtained without direct measurement of the carbonyl nitrates. This discussion is added to lines 434-440.

Our CIMS has unit mass resolution. For this work, we used pure isoprene nitrooxy enal as the precursor, which did not introduce much interference at m/z 271. This is clarified on lines 122-124.

Since this work is focused on the photochemistry of the nitrooxy enal, which describes the loss-dominant processes after sunrise, we did not include experiments concerning NO₃ oxidation. This is clarified on lines 116-118 of the revised manuscript.

Figure 4. Many have a difficult time distinguishing red from blue. May help to choose different color scheme. Also, are vertical lines necessary to show this data? The three lines at 210 nm are difficult to distinguish from one another. Perhaps use markers instead? Also, change "1×10^{exponent}" to just "10^{exponent}"

Fig. 4 was updated including the changes suggested by the reviewer.

The wall loss rate constant is fairly high compared to the photolysis rate constant. What is the residence time in the 5.2 m long tubing? Is laminar flow maintained? Also, curious if heating the inlet to 50 degC can induce cis-trans isomerization.

The wall loss and photolysis rate constants were obtained with repeated experiments. The radiation inside the chamber is approximately 10% of solar radiation. Therefore, our photolysis rate constant is small, making the wall loss rate constant high compared with photolysis frequency. This information is added to line 218-220.

The residence time in the tubing is around 5 s, and laminar flow is maintained. We have conducted inlet tests for the heated tubing, and we do not expect significant isomerization inside our sampling line. This information is added to line 125-131.

Line 235. Why is there no gas phase spectrum? Is it technically challenging? If so, it would be helpful for community to know.

We were concerned about potentially large wall loss of the organic nitrate inside a small UV cell. Hence, the measurements were performed with nitrate solutions. This is clarified on line 100-102.

Reference

Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dubé, W. P., Atlas, E., Weber, R. J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S. A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 3027-3042, 10.5194/acp-9-3027-2009, 2009.

1 Photochemical Degradation of Isoprene-derived **4,1-Carbonyl** 2 **Nitrate**4,1-Nitrooxy Enal

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9 **Abstract**

10 In isoprene-impacted environments, carbonyl nitrates are produced from NO₃-initiated isoprene
11 oxidation, which constitutes a potentially important NO_x reservoir. To better understand the fate
12 of isoprene carbonyl nitrates, we synthesized a model compound, *trans*-4-nitrooxy-2-methyl-2-
13 buten-1-al (4,1-isoprene carbonyl nitrate, or 4,1-isoprene nitrooxy enal) and investigated its
14 photochemical degradation process. The measured OH and O₃ oxidation rate constants (298 K) for
15 this ~~carbonyl nitrate~~nitrooxy enal are $4.1(\pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $4.4(\pm 0.3) \times 10^{-18} \text{ cm}^3$
16 $\text{molecules}^{-1} \text{ s}^{-1}$, respectively. ~~Its~~The UV absorption spectrum ~~of the carbonyl nitrate~~ was
17 determined, and the result is consistent with TDDFT calculations. Based on its UV absorption
18 cross section and photolysis frequency in a reaction chamber, we estimate that the ambient
19 photolysis frequency for this compound is $3.1(\pm 0.8) \times 10^{-4} \text{ s}^{-1}$ for a solar zenith angle (SZA) of 45°.
20 The fast photolysis rate and high reactivity toward OH lead to a lifetime of less than one hour for
21 the ~~carbonyl nitrate~~isoprene nitrooxy enal, with photolysis being a dominant daytime sink. The
22 nitrate products derived from the OH oxidation and the photolysis of the ~~isoprene-nitrooxy~~
23 ~~enal~~carbonyl nitrate were identified with an iodide-based chemical ionization mass spectrometer
24 (CIMS). For the OH oxidation reaction, we quantified the yields of two nitrate products, methyl
25 vinyl ketone (MVK) nitrate and ethanal nitrate, which together contributed to 3736(±5)% of the
26 first-generation products.

27 1 Introduction

28 Over the past century, tropospheric background ozone concentrations have increased from around
29 20 ppb to ~40 ppb, with urban-impacted concentrations often rising to 60-100 ppb (Parrish et al.,
30 2014; Vingarzan, 2004), posing harmful effects on human health and crop yields (Lefohn and
31 Foley, 1993; Lippmann, 1989). Tropospheric ozone is catalytically produced in the chemical
32 reactions of nitrogen oxides ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) and volatile organic compounds (VOCs) (Haagen-
33 Smit, 1952). NO_2 photolysis forms ozone (Blacet, 1952), and the ozone production rate is
34 enhanced when the $\text{NO-NO}_2\text{-O}_3$ cycle is coupled with the oxidation of VOCs (Chameides et al.,
35 1988; Chameides and Walker, 1973; Chameides et al., 1992). When NO_x is incorporated into
36 organic molecules and forms organic nitrates (RONO_2), however, ozone formation is suppressed
37 (Roberts, 1990). Organic nitrates are a temporary NO_x reservoir. Degradation of organic nitrates
38 can release NO_2 back into the atmosphere (Aschmann et al., 2011), and thus facilitate ozone
39 production. Organic nitrates in the gas phase can also adsorb onto atmospheric aerosols, followed
40 by condensed-phase hydrolysis (Rindelaub et al., 2015). This process removes the reactive
41 nitrogen from the atmosphere permanently, as the nitrooxy group is turned-converted into the non-
42 volatile NO_3^- ion (Darer et al., 2011; Hu et al., 2011). The relative importance of these parallel
43 nitrate sinks affects the availability of NO_x and the ozone production rate in the troposphere.
44 Therefore, detailed understanding of the loss mechanisms of organic nitrates is crucial to
45 understanding the dynamics of ground-level ozone formation.

46 Modeling studies suggest that isoprene-derived organic nitrates have substantial influence on the
47 NO_x cycle and tropospheric O_3 production (Horowitz et al., 2007; Mao et al., 2013; Paulot et al.,
48 2012; Wu et al., 2007). During the daytime, isoprene is lost rapidly to OH oxidation, forming
49 organic nitrates through the $\text{RO}_2 + \text{NO}$ reaction, with a yield of 7-14% (Lockwood et al., 2010;
50 Patchen et al., 2007; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990;
51 Xiong et al., 2015). At night, reaction with NO_3 is a significant removal pathway for isoprene
52 (Brown et al., 2009; Starn et al., 1998), and organic nitrates constitute 65-70% of the oxidation
53 products (Perring et al., 2009; Rollins et al., 2009). While NO_3 -initiated isoprene oxidation
54 contributes to a small fraction of isoprene loss, this reaction pathway could generate approximately
55 half of the isoprene-derived organic nitrates on a regional scale, due to its large nitrate yield
56 (Horowitz et al., 2007; Xie et al., 2013).

57 Fig.1 shows the formation pathways of organic nitrate products from NO₃-initiated oxidation of
58 isoprene, including hydroperoxy nitrate, carbonyl nitrate and hydroxy nitrate. Reactions for only
59 one of the nitrooxy peroxy radicals are shown for brevity. The hydroxy nitrates can be also formed
60 in the OH-initiated isoprene oxidation reactions, and their production and degradation have been
61 studied extensively in both laboratory and field studies (Chen et al., 1998; Giacomelli et al., 2005;
62 Grossenbacher et al., 2004; Jacobs et al., 2014; Lee et al., 2014b; Lockwood et al., 2010; Patchen
63 et al., 2007; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990; Xiong et
64 al., 2015). For the hydroperoxy nitrates, Schwantes et al. (2015) investigated their production from
65 the RO₂ + HO₂ reaction and identified the nitrooxy hydroxyepoxide product from the OH oxidation
66 of the isoprene hydroperoxy nitrate. For the isoprene carbonyl nitrates, their formation has been
67 quantified in an experimental study (Kwan et al., 2012), but their sinks and fate can only be inferred
68 from analog molecules, such as nitrooxy ketones, due to lack of direct studies on these specific
69 compounds. Suarez-Bertoa et al. (2012) conducted kinetics experiments on three synthesized
70 saturated nitrooxy ketones, and their results indicate that photolysis is the dominant sink for these
71 nitrate compounds. By comparing the published UV absorption spectra of α -nitrooxy ketones with
72 the UV spectra of the mono-functional nitrates and ketones, Müller et al. (2014) suggested that the
73 nitrooxy ketones have enhanced absorption cross sections, due to the interaction between the –
74 C=O and the –ONO₂ chromophores. In addition, near-unit photolysis quantum yields for α -
75 nitrooxy acetone and 3-nitrooxy-2-butanone were inferred by Müller et al. (2014), based on the
76 photolysis frequencies determined by Suarez-Bertoa et al. (2012) and known absorption cross
77 sections (Barnes et al.). The enhanced absorption cross sections and quantum yields of carbonyl
78 nitrates resulting from chromophore interactions lead to fast photolysis rates that are more
79 consistent with the loss rates constrained by the measured temporal profiles of carbonyl nitrates in
80 an isoprene oxidation experiment performed by Paulot et al. (2009) (Müller et al., 2014), ~~which~~
81 can facilitate the dissociation of the O–NO₂ bond. Like the ~~nitrooxy ketones~~ carbonyl nitrates
82 discussed by Suarez-Bertoa et al. (2012) and Müller et al. (2014), some of the carbonyl nitrate
83 isomers derived from NO₃ + isoprene oxidation ~~has~~ have a conjugated chromophore, –C=C–C=O
84 (enal), at the β position of the nitrate group, which may enhance the UV absorption cross section
85 of the molecule and facilitate its photolytic dissociation. However, since the five-carbon isoprene
86 carbonyl nitrate (nitrooxy enal) (Fig. 1) is unsaturated, it is also expected to be lost rapidly to OH
87 oxidation. To date, the relative importance of the individual photochemical sinks for the

88 unsaturated carbonyl nitrates is still unclear. To answer this question, we synthesized a model
89 compound for the five-carbon isoprene carbonyl nitrates, and investigated its photochemical
90 reactivities and fate.

91 2 Synthesis and characterization

92 A model compound, ~~4,1 isoprene carbonyl nitrate~~ (*trans*-2-methyl-4-nitrooxy-2-buten-1-al (4,1-
93 isoprene nitrooxy enal) was synthesized following the reaction scheme in Fig. 2. The nitrate was
94 prepared by reacting AgNO₃ with the corresponding bromide (*trans*-4-bromo-2-methyl-2-buten-
95 1-al) (Ferris et al., 1953), which was synthesized following Gray (1981). The ¹H and ¹³C NMR
96 spectra of the synthesized product are shown in Fig. S1 and Fig. S2. Its IR absorption spectrum is
97 shown in Fig. S3.

98 Shown in Fig. 3 are the UV absorption cross sections for the ~~carbonyl nitrate~~nitrooxy enal,
99 methacrolein (MACR) and isopropyl nitrate. Each spectrum was obtained using a solution that
100 contained one single pure analyte in acetonitrile solvent. Only solution-phase spectra were
101 determined, because gas-phase cells may have potential wall loss problems and thus the
102 quantitative gas-phase cross sections are difficult to measure. We compared isopropyl nitrate and
103 MACR with isoprene nitrooxy enal, because MACR has the enal structure, and isopropyl nitrate
104 has the nitrooxy group, and the combination of these two compounds helps to illustrate the
105 absorption features of the nitrooxy enal studied in this work. The absorption cross section of the
106 carbonyl nitrate is enhanced relative to that of MACR, but the two spectra have similar features
107 from 320 nm to 400 nm with peak absorption at 325 nm. This is probably because they both contain
108 the O=C-C=C chromophore. Below 320 nm the absorption of the ~~carbonyl nitrate~~nitrooxy enal is
109 enhanced significantly in comparison with that of isopropyl nitrate. This observation is consistent
110 with reports from Müller et al. (2014) that molecules containing α,β -nitrooxy ketone functionalities
111 have enhanced UV absorption.

112 3 Methods

113 3.1 Setup for the kinetics chamber experiments

114 Three sets of reaction chamber experiments were conducted to determine the photolysis frequency,
115 OH oxidation rate constant and the O₃ oxidation rate constant for the ~~carbonyl nitrate~~isoprene

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116 nitrooxy enal. Since this work is focused on the photochemistry of the nitrooxy enal, which
117 describes the loss-dominant processes after sunrise, we did not include experiments concerning
118 the NO₃-initiated oxidation processes for this compound. The experiments were performed in the
119 5500 L Purdue photochemical reaction chamber (Chen et al., 1998). A chemical ionization mass
120 spectrometer (CIMS) with I⁻ as the reagent ion (Xiong et al., 2015) was used to quantify the
121 ~~earbonyl nitrate~~nitrooxy enal (observed at nominal mass m/z 272) and its nitrate degradation
122 products (~~Xiong et al., 2015~~). The CIMS has unit mass resolution. Since pure isoprene nitrooxy
123 enal was introduced into the reaction as the precursor, we do not expect significant interference
124 from the isotope signal of m/z 271. The chamber air was sampled into the CIMS through a 5.2 m
125 long FEP tubing (0.8 cm ID, heated to constant 50 °C). The residence time for the sampling tubing
126 was approximately 5 s, and laminar flow was maintained. To assess the influence of the heated
127 inlet on the stability of the nitrooxy enal, we have sampled the nitrooxy enal using the heated 50 °C
128 inlet and using a 20 cm room temperature inlet, and there was no significant difference in their
129 corresponding CIMS signals. In addition, the *trans*-isoprene nitrooxy enal was synthesized in an
130 oil bath maintained at 70 °C, but the formation of the *cis* isomer was not observed. Therefore, we
131 do not consider that there is significant thermal isomerization inside our sampling line. The
132 photolysis frequency was obtained by measuring the loss of the ~~earbonyl nitrate~~nitrooxy enal
133 inside the reaction chamber in the presence of UV radiation and propene as a radical scavenger.
134 When the UV lamps were turned off, the wall loss rate constant for the ~~earbonyl nitrate~~nitrooxy
135 enal was ~~derived~~derived by observing its slow decay, with propene as an ozone and NO₃
136 scavenger. The OH reaction rate constant and O₃ reaction rate constant were obtained using the
137 relative rate method (Atkinson and Aschmann, 1985). Propene was used as the reference
138 compound, and its changing concentrations were measured using a GC-FID equipped with a 0.32
139 mm Rtx-Q-Bond column. For the OH oxidation experiments, OH was generated through the
140 photolysis of isopropyl nitrite, which was synthesized following Noyes (1933). NO was added
141 to the chamber to suppress the formation of O₃. In addition, two OH oxidation experiments were
142 performed without propene in order to quantify the oxidation products. For the OH-initiated
143 oxidation experiments, NO and NO₂ were measured using the Total REactive Nitrogen Instrument
144 (TRENI) (Lockwood et al., 2010). The ozonolysis experiments were performed in the dark, and
145 cyclohexane was added to the chamber as an OH scavenger. The initial conditions for the
146 experiments are listed in Table S1.

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147 3.2 Computational methods

148 The theoretical UV absorption spectra of the ~~carbonyl nitrate~~isoprene nitrooxy enal, MACR,
149 isopropyl nitrate and *n*-butyl nitrate in the gas phase were calculated separately and analyzed, in
150 four stages, using time-dependent density functional theory (TDDFT; (Hohenberg and Kohn, 1964;
151 Kohn and Sham, 1965; Runge and Gross, 1984)). All calculations were carried out using the
152 computational chemistry package Q-Chem 4.3 (Shao et al., 2015). First, the structure of each
153 molecule was optimized employing the long-range corrected hybrid density functional ω B97X-D
154 (Chai and Head-Gordon, 2008) with the 6-31+G* basis set (Frisch et al., 1984). A high accuracy
155 grid was employed. Second, frequency ies calculations were executed on the optimized structures
156 to verify their accuracy. These were run using the same setup described above. Third, after assuring
157 the structures represented adequate minima, the first ten singlet excited states of each molecule
158 were computed with TDDFT, using the same functional and basis set. Finally, a visual analysis of
159 the molecular orbitals (MOs) was carried out with the visualization software IQmol 2.7 (Gilbert,
160 2012).

161 4 Results

162 4.1 Absorption spectra and density functional calculations

163 Fig. 4 shows the TDDFT UV absorption spectra of the ~~carbonyl nitrate~~nitrooxy enal, MACR,
164 isopropyl nitrate and *n*-butyl nitrate. There are three groups of transitions in the simulated spectra.
165 Unlike the absorption bands depicted in Fig 3, the theoretical gas-phase spectra in Fig. 4 are
166 showing only the electronic transition lines. To accurately capture the broadening of these lines in
167 TDDFT so as to simulate absorption bands, we have to consider the effect of the chromophore's
168 vibrational degrees of freedom and/or to include a condensed phase environment that surrounds
169 the chromophore. However, explicit modeling of broadening either due to vibronic interactions or
170 solvent effects is computationally challenging and beyond the scope of this work.

171
172 Both MACR and the ~~carbonyl nitrate~~nitrooxy enal show a relatively weak transition in the region
173 around 330 nm, which corresponds to the first electronic transition, from the highest occupied
174 molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), in both molecules.

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175 Fig. 5a provides comparative information between the first electronic transition of the ~~carbonyl~~
176 ~~nitrate~~nitrooxy enal and the homologous excitation of MACR. As shown in Fig. 5a the character
177 of the molecular orbitals involved in this transition is similar in both cases, indicating that the
178 aldehyde group is involved in the first electronic excitation of the ~~carbonyl nitrate~~nitrooxy enal.

179 Fig. 5b shows the information corresponding to the second electronic transition of the ~~carbonyl~~
180 ~~nitrate~~nitrooxy enal and ~~its~~the homologous excitation ~~in~~of isopropyl nitrate and *n*-butyl nitrate.
181 ~~Both~~ These three transitions are found in the region around 255 nm. The second electronic
182 transition of the nitrooxy enal is 3 orders of magnitude weaker than its first excitation, located at
183 330 nm, and they are 3 orders of magnitude darker than those at 330 nm. Inspection of the
184 character of the MOs involved in these processes reveals a correspondence between the second
185 electronic excitation of the ~~carbonyl nitrate~~nitrooxy enal, HOMO-2 → LUMO+1, and the HOMO
186 → LUMO transitions in both isopropyl nitrate and *n*-butyl nitrate. As with the previous case,
187 that observation confirms that the nitrate group is involved in the second electronic excitation of
188 the ~~carbonyl nitrate~~nitrooxy enal, ~~but at wavelengths shorter than present at the Earth's surface.~~

189 Fig. 5b also shows that in this case, the local character of the MOs involved in the transition is
190 even more pronounced, with bulky lobes placed mainly over the nitrate group.

191 Even though the second electronic transition of carbonyl nitrate is not displayed in the
192 experimental spectra of Fig. 3, because its range covers from 280 nm to 410 nm, it is reasonable
193 to assume that it is caused by the local excitation of the nitrate group, based on the computational
194 results. Thus, it can be suggested that the experimental UV absorption spectrum~~um~~a of isopropyl
195 nitrate is comparable to ~~those~~that of isopropyl nitrate and *n*-butyl nitrate simulated computationally.
196 Thus it is possible that the feature in the region around 280 nm of the ~~carbonyl nitrate~~nitrooxy enal
197 experimental spectrum ~~in~~ef Fig. 3 could be caused by a broadening of the transition located around
198 255 nm.

199 Another plausible explanation of the feature around 280 nm for the nitrooxy enal would be a
200 broadening of its brightest transition in the modeled spectrum. It is located around 210 nm, and it
201 is 3 orders of magnitude brighter than the one at 330 nm. In that region,

202 The brightest transition in the modeled spectra of the carbonyl nitrate, 3 orders of magnitude
203 brighter than the ones at 330 nm, is located around 210 nm. There are two transitions in this region

204 and each one has a homologous excitation: the HOMO-1 → LUMO in carbonyl nitrate nitrooxy
205 enal is similar to HOMO-1 → LUMO in MACR, and the HOMO-5 → LUMO+1 in carbonyl
206 nitrate nitrooxy enal is related to the (mainly) HOMO-1 → LUMO transitions of isopropyl nitrate
207 and n-butyl nitrate. These transitions are beyond the range of the experimental spectra on Fig. 3
208 and beyond the atmospherically relevant absorption wavelengths. The theoretical calculations
209 suggest that the nitrooxy group has electronic transitions at 210 nm and 255 nm, but both
210 wavelengths are outside the solar radiation spectrum near ground. Therefore, we speculate that the
211 isoprene nitrooxy enal absorbs photons primarily through the first electronic transition concerning
212 the enal chromophore, instead of the nitrooxy functionality, and the dissociation of the O-NO₂
213 bond (Sect. 4.3.2) likely results from intramolecular energy redistribution.

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214 4.2 Photochemical sinks of 4,1-carbonyl nitrate the 4,1-isoprene nitrooxy enal

215 Fig. 6 shows the first-order wall loss and photolysis loss of the carbonyl nitrate nitrooxy enal inside
216 the reaction chamber. The wall loss rate constant was $1.3(\pm 0.42) \times 10^{-5} \text{ s}^{-1}$ (95% confidence
217 interval), and the photolysis rate constant was $3.0(\pm 0.42) \times 10^{-5} \text{ s}^{-1}$ (95%), after subtracting the wall
218 loss rate constant from the first-order decay rate constant measured for the photolysis experiments.

219 The radiation intensity inside the chamber is approximately 10% of solar radiation. Therefore, our
220 photolysis rate constant is small, making the wall loss rate constant significant, compared with the
221 photolysis frequency. It is worth mentioning that our reactant carbonyl nitrate nitrooxy enal has a

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222 *trans* configuration, and it may photo-isomerize into the *cis* configuration, which would be
223 detected at the same *m/z* by the CIMS. The *cis*-carbonyl nitrate nitrooxy enal can either photo-

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224 dissociate or isomerize to re-form the *trans* isomer. Our previous work suggests that the CIMS is
225 4 times more sensitive to the *cis* configuration than the *trans* configuration (Xiong et al., 2015). If
226 a significant amount of the *cis* isomer was present, the CIMS signal should resemble a double
227 exponential curve. If the lifetime for the *trans* → *cis* reaction is comparable to the duration of the
228 experiments (approximately 3 hours), we would expect the CIMS signal to resemble a double
229 exponential curve, because the *cis* isomer was being produced and consumed simultaneously. This

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230 double exponential curve is not observed for the photolysis data (Fig. 6). If a *cis-trans* equilibrium
231 is established instantaneously, the CIMS signal would still be a single exponential curve, which
232 represent the loss of both isomers. However, given the similar nitrooxy enal structures for the *cis*
233 and *trans* isomers, we do not expect their photolysis frequencies to differ significantly, so the total

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234 ~~photolysis rate constant obtained from the CIMS measurement can be used as the photolysis~~
235 ~~frequency for the individual *cis* or *trans* isomer. In an extreme scenario with rapid *trans* → *cis*~~
236 ~~isomerization, the CIMS signal should increase under radiation, due to the higher sensitivity of the~~
237 ~~*cis* isomer. For our carbonyl nitrate photolysis experiments, a single exponential decay in the~~
238 ~~CIMS signal was observed, indicating insignificant contribution from the *cis* isomer. Hence,~~
239 ~~Therefore, regardless of the *trans* → *cis* isomerization rate, our measured photolysis frequency~~
240 should well characterize the loss rate of the ~~carbonyl nitrate precursor *trans*-nitrooxy enal~~ inside
241 the reaction chamber.

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242 Since the UV radiation inside the reaction chamber is different from the UV radiation in the
243 ambient environment (Fig. 7), Cl₂ was used as a reference compound to ~~extrapolate-translate~~
244 the nitrate photolysis rate from chamber radiation to solar radiation. The photolysis decay of Cl₂ in the
245 reaction chamber was measured with the CIMS (Neuman et al., 2010). Cyclohexane was added to
246 the chamber to scavenge the Cl atoms so that Cl₂ was not re-formed from Cl + Cl recombination.
247 The first-order photolysis rate constant for Cl₂ was 2.50(±0.0408)×10⁻⁴ s⁻¹ (Fig. S4).

248 The photolysis frequency (J) is the integrated product of quantum yield (Φ), absorption cross
249 section (σ, cm²) and actinic flux (F, cm⁻² s⁻¹) across all wavelengths (Eq. 1). Therefore, the
250 photolysis frequencies for the ~~carbonyl nitrate nitrooxy enal~~ and Cl₂ in the reaction chamber can
251 be compared as in Eq. 2.

$$252 \quad J = \int \Phi_{\lambda} \sigma_{\lambda} F_{\lambda} d\lambda \quad (\text{Eq. 1})$$

$$253 \quad \frac{J_{\text{Cl}_2}^{\text{chamber}}}{J_{\text{nitrate}}^{\text{chamber}}} = \frac{\sum \Phi_{\text{Cl}_2} \sigma_{\text{Cl}_2} F_{\text{chamber}}}{\sum \Phi_{\text{nitrate}} \sigma_{\text{nitrate}} F_{\text{chamber}}} \quad (\text{Eq. 2})$$

254 $J_{\text{Cl}_2}^{\text{chamber}}$ and $J_{\text{nitrate}}^{\text{chamber}}$ are the photolysis frequencies of Cl₂ and the ~~carbonyl nitrate nitrooxy enal~~
255 inside the chamber. σ_{Cl_2} and σ_{nitrate} are the cross sections for Cl₂ and the ~~carbonyl nitrate nitrooxy~~
256 ~~enal~~ at each wavelength. σ_{nitrate} was determined by this work (Fig. 3). σ_{Cl_2} has been measured
257 previously and the IUPAC recommended values were used (Atkinson et al., 2007). F_{chamber} is the
258 wavelength-dependent flux of photons inside the chamber. The radiation spectrum (Fig. 7) of the
259 chamber UV lamps (UVA 340) was obtained from the manufacturer (Q-lab), but the actual
260 absolute radiation intensity in the chamber is expected to differ from the manufacturer's radiation

261 spectrum by a scaling factor, because of the inverse-square dependence on distance, and our
262 specific multi-lamp geometry. When Cl₂ was used as a reference compound for the nitrate
263 photolysis rate, the scaling factors in Eq. 2 will cancel.

264 The Cl-Cl bond dissociation energy is 243 kJ/mol (Luo, 2007b), equivalent to a photon at 492 nm.
265 Since Cl₂ has only one bond, it has unity quantum yield below 492 nm and zero quantum yield
266 above 492 nm. The emission spectrum of the UV lamps for the reaction chamber is centered from
267 300 nm to 400 nm (Fig. 7). Hence, $\varphi_{Cl_2} = 1$ in Eq. 2, at all wavelengths. For the ~~carbonyl~~
268 ~~nitrate~~~~nitrooxy enal~~, however, its quantum yield is affected by the bond dissociation energy,
269 intramolecular vibrational energy redistribution and relaxation of the excited molecule from
270 collisions, so an average effective quantum yield ($\varphi_{nitrate}^{eff}$) is assumed, and Eq. 2 becomes Eq. 3.
271 Since the photolysis rates, absorption cross sections and chamber radiation spectrum ~~were~~~~are~~
272 known, we calculated that $\varphi_{nitrate}^{eff}$ was 0.48.

$$273 \frac{j_{Cl_2}^{chamber}}{j_{nitrate}^{chamber}} = \frac{\sum \sigma_{Cl_2} F_{chamber}}{\varphi_{nitrate}^{eff} \sum \sigma_{nitrate} F_{chamber}} \quad (\text{Eq. 3})$$

274 The effective quantum yield of 0.48 indicates that when the ~~carbonyl-nitrate~~~~nitrooxy enals~~ absorbs
275 a photon inside the reaction chamber, the probability (averaged across the absorption wavelengths)
276 for it to dissociate is 48%. However, the probability for nitrate photolysis is not equal at all
277 wavelengths, the low energy photons (long wavelength) being less likely to induce photo-
278 dissociation. Hence, we introduced a threshold wavelength λ_0 , for which the ~~carbonyl~~
279 ~~nitrate~~~~nitrooxy enal~~ has unity quantum yield below λ_0 and zero quantum yield above λ_0 . Although
280 this approach accounts for the energy difference of photons with different wavelengths, it is still a
281 very rough estimation. Using the threshold wavelength, the effective quantum yield can be
282 expressed by Eq. 4 and Eq. 5, where $\varphi(\lambda)$ is the quantum yield of the ~~carbonyl-nitrate~~~~nitrooxy enal~~,
283 and $F(\lambda)$ is the chamber photon flux (Fig. 7), as a function of the wavelength λ . Solving for the
284 unknown λ_0 in Eq. 5, we calculated that λ_0 ~~was~~~~should be~~ 347 nm.

$$285 \varphi(\lambda) = \begin{cases} 1 & (\lambda \leq \lambda_0) \\ 0 & (\lambda > \lambda_0) \end{cases} \quad (\text{Eq. 4})$$

$$286 \frac{\sum_{\lambda} F(\lambda) \cdot \varphi(\lambda)}{\sum_{\lambda} F(\lambda)} = 0.48 \quad (\text{Eq. 5})$$

287 The solar radiation spectrum was calculated with the TUV model (Madronich and Flocke, 1998).
288 By assuming that the carbonyl nitrate nitrooxy enal has zero quantum yield above 347 nm and unity
289 quantum yield below 347 nm, its photolysis frequency is $2.6 \times 10^{-4} \text{ s}^{-1}$ for a solar zenith angle
290 (SZA) of 45° , and $3.7 \times 10^{-4} \text{ s}^{-1}$ for SZA of 0° . It is worth mentioning that the condensed-phase and
291 gas-phase absorption spectra should be different, because the solvent molecules affect the
292 polarization and dipole moment of the solute (Bayliss and McRae, 1954; Braun et al., 1991; Linder
293 and Abdalnur, 1971). Although we were unable to measure the gas-phase cross section of the
294 carbonyl nitrate nitrooxy enal, we could assess the uncertainty caused by using the condensed-
295 phase spectrum in our calculation, by comparing the gas-phase and condensed-phase spectra of
296 MACR and isopropyl nitrate (Fig. S5a). On average, the gas-phase absorption cross sections of
297 MACR and isopropyl nitrate are 1.7 times those in the solution phase (Fig. S5b), calculated as the
298 ratio of the gas-phase cross sections divided by the condensed-phase cross sections at each
299 wavelength. For the carbonyl nitrate nitrooxy enal, if the gas-phase cross section is assumed to be
300 1.7 times that of the solution-phase cross section, the calculated effective quantum yield becomes
301 0.28, leading to a threshold wavelength (λ_0) of 336 nm. Using this set of cross section and quantum
302 yields, we calculated that the nitrate photolysis frequency was $3.1 \times 10^{-4} \text{ s}^{-1}$ for SZA of 45° , and
303 $4.6 \times 10^{-4} \text{ s}^{-1}$ for SZA of 0° , which are 19% and 24% larger than results obtained using the
304 condensed-phase cross section. The calculated ambient photolysis frequency is not affected as
305 significantly by the change in the absorption cross section, because it is constrained by the
306 measured photolysis frequency in the reaction chamber. When a larger cross section is applied, a
307 smaller quantum yield is derived, and the calculated ambient photolysis frequency, being the
308 integrated product of the cross section, quantum yield and radiation, will not increase as much as
309 the cross section. In addition to the cross section, our treatment of the wavelength-dependent
310 quantum yield can also introduce uncertainty to the calculated results. If a constant effective
311 quantum yield is used in the calculation, the ambient photolysis frequency is $2.0 \times 10^{-4} \text{ s}^{-1}$ for SZA
312 of 45° , and $2.8 \times 10^{-4} \text{ s}^{-1}$ for SZA of 0° , which are 23% and 24% lower than assuming a threshold
313 wavelength. Therefore, our calculated ambient photolysis frequency, based on condensed-phase
314 absorption cross section and a threshold energy for unity quantum yield, has an uncertainty of
315 25%. Since we believe that the cross sections are indeed larger in the gas phase, our best estimate
316 is $3.1(\pm 0.8) \times 10^{-4} \text{ s}^{-1}$ for SZA= 45° .

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317 Fig. 8 shows the results for the relative rate experiments for the OH-initiated and O₃-initiated
318 oxidation of the ~~carbonyl nitrate nitrooxy enal~~, with propene as the reference compound. The loss
319 of the ~~carbonyl nitrate nitrooxy enal~~ to wall uptake and photolysis is corrected when comparing the
320 oxidative loss of the nitrate to that of propene, using the same method as Hallquist et al. (1997).
321 The OH and O₃ oxidation rate constants for propene are $3.0(\pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Klein
322 et al., 1984; Zellner and Lorenz, 1984) and $1.00(\pm 0.06) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Herron and
323 Huie, 1974; Treacy et al., 1992). These are the IUPAC preferred rate constants for T=298K
324 (<http://iupac.pole-ether.fr/>). Hence, the OH and O₃ oxidation rate constants for the isoprene
325 ~~carbonyl nitrate nitrooxy enal~~ are, based on the results from the relative rate experiments,
326 $4.1(\pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $4.4(\pm 0.3) \times 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ respectively, at 295
327 K.

328 The OH oxidation rate constant for the ~~carbonyl nitrate nitrooxy enal~~ can be estimated through the
329 structure-activity-relationship (SAR) approach proposed by Kwok and Atkinson (1995). The rate
330 constant for OH addition to the double bond can be calculated as $k(-\text{CH}=\text{CH})$, which is 8.69×10^{-11}
331 $\text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, multiplied by the two correction factors C(-CHO) and C(-CH₂ONO₂), which
332 are 0.34 and 0.47 respectively. The resulting OH addition rate constant is $1.39 \times 10^{-11} \text{ cm}^3$
333 $\text{ molecules}^{-1} \text{ s}^{-1}$. The rate constant for H abstraction from the -CHO group is $1.61 \times 10^{-11} \text{ cm}^3$
334 $\text{ molecules}^{-1} \text{ s}^{-1}$, after multiplying by a correction factor of 1 for having a double bond at its α
335 position. The rate constant for H abstraction from the methylene group is $3.7 \times 10^{-14} \text{ cm}^3$
336 $\text{ molecules}^{-1} \text{ s}^{-1}$, calculated by multiplying the base rate constant for methylene groups, which is
337 $9.34 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, by the correction factors of the nitrate group and the double bond,
338 which are 0.04 and 1, respectively. OH addition to the nitrate group has a rate constant of 4.4×10^{-13}
339 $\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, after taking account of the enhancement factor of 1.23 for the methylene group.
340 H abstraction from the methyl group has a rate constant of $1.36 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. By
341 summing up the rate constants for all these reaction pathways, the SAR-derived OH oxidation rate
342 constant for the ~~4,1-carbonyl nitrate rate constant isoprene nitrooxy enal~~ is $3.1 \times 10^{-11} \text{ cm}^3$
343 $\text{ molecules}^{-1} \text{ s}^{-1}$, approximately 30% lower than the experimental measurement. The dominant
344 reaction channels are OH addition to the double bond and H abstraction from the aldehyde group.
345 Contributions from the other reaction pathways are small (<3%).

346 The relative importance of the three photochemical sinks, photolysis, OH oxidation and O₃
347 oxidation, depends on the solar radiation and the concentrations of OH and O₃. To better illustrate
348 their relative contributions, observations of OH and O₃ from previous field campaigns were used
349 to calculate the loss rates of the ~~carbonyl nitrate~~nitrooxy enal. The local solar radiation was
350 calculated with the TUV model (Madronich and Flocke, 1998), which was then used to derive the
351 photolysis frequency. The calculated results (Fig. 9) suggest that photolysis is a significant
352 degradation pathway for the ~~carbonyl nitrate~~nitrooxy enal, which can dominate over OH oxidation
353 toward mid-day. When the solar radiation intensity is small (such as 6:00 AM for the 1999 SOS
354 campaign), OH oxidation is likely the dominant sink. Due to the fast photolysis and high reactivity
355 toward OH, the photochemical lifetime of the ~~carbonyl nitrate~~nitrooxy enal can be as short as less
356 than one hour.

357 **4.3 Degradation products of the ~~4,1-carbonyl nitrate~~4,1-isoprene nitrooxy enal**

358 **4.3.1 OH oxidation**

359 The products from the OH-initiated oxidation of the ~~4,1-carbonyl nitrate~~isoprene nitrooxy enal
360 were observed by the CIMS. The change in the CIMS signals before and after the reaction are
361 illustrated in Fig. 10, along with assignment of some of the molecular structures based on the
362 molecular weight and likely chemistry. The OH-initiated oxidation reaction can proceed through
363 two channels: H abstraction from the aldehyde group and OH addition to the double bond.

364 For the H abstraction pathway, a peroxyacyl nitrate (PAN) product was observed at m/z 349 (Fig.
365 10), which can be formed as shown in Fig. 11. The first-order dissociation rate constant for the
366 PAN compound was determined at room temperature (295 K) using the following method. A 100
367 L Teflon bag containing the air mixture of approximately 1 ppm isopropyl nitrite and 30 ppb
368 ~~isoprene nitrooxy enal~~4,1-carbonyl nitrate was irradiated, and the PAN compound was formed
369 ~~from when the nitrooxy enal reacted with~~ OH and NO₂ (produced through the photolysis of
370 isopropyl nitrite) ~~reaction with the 4,1-carbonyl nitrate~~. After 5 min reaction time, the bag was
371 removed from the UV radiation, and NO was injected into the bag to around 4 ppm in concentration.
372 The bag was then sampled simultaneously by the CIMS, which monitored the decrease in the
373 signal of the PAN compound, and by the TRENI, which monitored the concentrations of NO and
374 NO₂. The PAN dissociation reaction is a reversible process, where the dissociation products,

375 peroxyacyl (PA) radical and NO₂, can re-combine to form PAN. With the addition of the large
 376 amount of NO, PA radicals are predominantly consumed by the irreversible PA + NO reaction,
 377 leading to the decay of the PAN compound. The apparent PAN dissociation rate constant can be
 378 described by Eq. 6 (Shepson et al., 1992), where k is the first-order loss rate constant measured by
 379 the CIMS (Fig. S6), k_{PAN} is the real PAN dissociation rate constant, [NO] and [NO₂] are the
 380 concentrations for NO and NO₂, and k_{NO} and k_{NO₂} are the rate constants for PA + NO and PA +
 381 NO₂ reactions. Since the rate constants k_{NO} and k_{NO₂} for the ~~nitrooxy enal~~~~carbonyl nitrate~~-derived
 382 PA radical are unknown, the IUPAC recommended rate constants for the peroxyacetyl radicals
 383 (CH₃C(O)O₂) are used, with k_{NO} = 2.0×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ and k_{NO₂} = 8.9×10⁻¹² cm³
 384 molecule⁻¹ s⁻¹. The PAN dissociation rate constant, after correcting for the competing PA + NO
 385 and PA + NO₂ reactions using Eq. 6, is 5.7(±0.8)×10⁻⁴ s⁻¹, based on three experimental trials. In
 386 addition to dissociation, the PAN compound in the 100 L bag could also undergo wall loss. This
 387 loss rate was estimated by multiplying the wall loss rate of the ~~carbonyl nitrate~~~~nitrooxy enal~~ in the
 388 5500 L chamber by a factor of 16, which is the square diffusion distance of the chamber relative
 389 to that of the 100 L bag, assuming the PAN compound and the isoprene carbonyl nitrate have
 390 similar diffusion and adsorption coefficients. Considering the uncertainty in wall loss rate, the
 391 PAN dissociation rate constant is 5.7(+0.8/-2.8)×10⁻⁴ s⁻¹. Previous studies of the dissociation rate
 392 constants for peroxyacyl nitrates have reported results ranging from 1.6×10⁻⁴ s⁻¹ to 6.0×10⁻⁴ s⁻¹ at
 393 298 K (Bridier et al., 1991; Grosjean et al., 1994; Kabir et al., 2014; Roberts and Bertman, 1992).
 394 Our result is consistent with previous work.

$$395 \quad k = k_{PAN} \left(1 - \frac{1}{1 + \frac{k_{NO}[NO]}{k_{NO_2}[NO_2]}} \right) \quad (\text{Eq. 6})$$

396 Since our OH oxidation experiments were conducted in the presence of high NO concentration, a
 397 significant fraction of the PA radicals from the H abstraction reaction channel were expected to
 398 react with NO to form alkoxy radicals. Based on the product observed at m/z 321, a reaction
 399 scheme (Fig. 11) is proposed, where the alkoxy radical dissociates into CO₂ and an ~~alkyl~~~~alkenyl~~
 400 radical, which is further oxidized to form a C₄ dinitrate (m/z 321, Fig. 10), along with ethanal
 401 nitrate (m/z 232, Fig. 10).

402 For the OH addition pathway, OH can add to the C₂ and the C₃ position of the ~~4,1-isoprene~~
 403 ~~carbonyl nitrate~~~~isoprene nitrooxy enal~~, but the less substituted C₃ position should be preferential

404 (Peeters et al., 2007). For the C2 addition, the expected nitrate products are C5 dinitrate and ethanal
405 nitrate (Fig. 12a), ~~as~~and their nominal masses were observed at m/z 351 and m/z 232 (Fig. 10).
406 NO₂ could potentially be released with the concurrent formation of a C4 di-aldehyde (Fig. 12a).
407 The CIMS signal for this compound at m/z 229 did not increase (Fig. 10), but the CIMS sensitivity
408 for this compound could be relatively low. For the C3 addition, the expected nitrate products are
409 C5 dinitrate, MVK nitrate and ethanal nitrate (Fig. 12b), observed at m/z 351, m/z 276 and m/z
410 232 (Fig. 10). We assigned m/z 276 to solely MVK nitrate, instead of MACR nitrate, because the
411 precursor nitrooxy enal has a secondary carbon at its C3 position, and the OH oxidation reaction
412 cannot add a functional group at this position while still maintaining it as a secondary carbon as is
413 the case for MACR nitrate. The C2 and C3 OH addition pathway would lead to two C5 dinitrate
414 isomers, but they were detected at the same mass by the CIMS.

415 Using a GC-ECD/CIMS method similar to the one described by Xiong et al. (2015), the CIMS
416 sensitivities of the nitrate products were determined relative to the CIMS sensitivity of the ~~4,1-~~
417 ~~carbonyl nitrate~~isoprene nitrooxy enal. The setup was modified to operate the GC separation under
418 pressure lower than 1 atm (Fig. S7), which helped to lower the elution temperature. A Teflon bag
419 filled with the ~~4,1-carbonyl nitrate~~nitrooxy enal, isopropyl nitrite, and NO was irradiated to
420 generate the OH oxidation products. The mixture of the ~~4,1-carbonyl nitrate~~nitrooxy enal and its
421 products ~~was~~ere then cryo-focused and separated on the GC column, and the eluent species were
422 detected by the ECD and the CIMS simultaneously. We were able to quantify the MVK nitrate
423 and the ethanal nitrate using this method, assuming identical ECD sensitivities for nitrates. The
424 other products shown in Fig. 10, however, were not detected with simultaneous good signal-to-
425 noise ratio on the ECD and the CIMS. The ECD/CIMS chromatograms are shown in Fig. 13. We
426 determined that the reaction of the ~~4,1-carbonyl nitrate~~isoprene nitrooxy enal ~~and with~~
427 ion I⁻ could form NO₃⁻, but the same reaction did not occur for the MVK nitrate and the ethanal
428 nitrate (Fig. 13). Formation of NO₃⁻ from I⁻ reaction with organic nitrates has not been reported
429 previously. Since I⁻ is a poor nucleophile, it is unclear if this reaction proceeds by S_N2 substitution.
430 Using the same I⁻ ionization method, Wang et al. (2014) observed NO₃⁻ signal equivalent to a NO₃
431 + N₂O₅ concentration of 200-1000 ppt during a field study in Hong Kong. Through interference
432 tests, the authors attributed 30-50% of the observed NO₃⁻ signal to the interference from
433 peroxyacetyl nitrate and NO₂. Since I⁻ reaction with the ~~carbonyl nitrate~~nitrooxy enal can also
434 generate NO₃⁻, organic nitrates (RONO₂) could be a potential source of interference for NO₃⁻.

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435 N₂O₅ measurement with the I⁻ ionization method. For field measurement of isoprene nitrooxy enal,
436 this compound could be mistakenly measured as NO₃⁻ when iodide-based CIMS was used without
437 tuning the instrument specifically to favor iodide-nitrate clustering. While no field observations of
438 this type of compound have been reported to date, they can still potentially be an important NO_y
439 reservoir. For instance, Brown et al. (2009) estimated that in the 2004 NEAQS study the total
440 concentration of nitrates derived from NO₃ + isoprene chemistry could reach 500 ppt. The carbonyl
441 nitrates (nitrooxy enone and nitrooxy enal) can contribute to a significant fraction of the total.

442 For the GC-ECD/CIMS calibration, 9 trials were conducted at three different pressures. The results
443 are summarized in Table S2. The relative CIMS sensitivities for the nitrooxy enal~~4,1-carbonyl~~
444 ~~nitrate~~, ethanal nitrate and MVK nitrate are 1:15(±3):34(±3) respectively. The absolute CIMS
445 sensitivity of the ~~4,1-carbonyl nitrate~~isoprene nitrooxy enal was determined with standard gas
446 samples prepared following Xiong et al. (2015), and the result was used to calculate the absolute
447 sensitivities for the ethanal nitrate and the MVK nitrate. The ethanal nitrate and the MVK nitrate
448 both have the -ONO₂ group at the β position of the acidic H, so their CIMS sensitivities are
449 comparable. For the MVK nitrate, the electron-withdrawing ketone group can further enhance its
450 gas-phase acidity and its affinity to bind with I⁻. Hence, the CIMS sensitivity for the MVK nitrate
451 is greater than for the ethanal nitrate. For the ~~4,1-carbonyl nitrate~~nitrooxy enal, its low CIMS
452 sensitivity can be caused by the *trans*-δ configuration of the -ONO₂ group and the -CHO group.
453 Our previous studies on isoprene-derived hydroxynitrates suggested that the CIMS sensitivity for
454 the β isomer is 8 times greater than for the *trans*-δ isomer (Xiong et al., 2015). Lee et al. (2014a)
455 also reported the β isomer sensitivity being over 16 times greater than the *trans*-δ isomer
456 sensitivity, using iodide as the reagent ion. Hence, our calibration results, with the sensitivity for
457 the ethanal nitrate 15 times greater than the sensitivity for the ~~4,1-carbonyl nitrate~~nitrooxy enal, is
458 consistent with previous work.

459 With the CIMS sensitivities determined, the yield of the MVK nitrate and the ethanal nitrate from
460 the OH-initiated oxidation of ~~4,1-carbonyl nitrate~~the isoprene nitrooxy enal was obtained by
461 comparing the formation of the products relative to the loss of the reactant (Fig. 14). The yield of
462 the ethanal nitrate was corrected for loss to OH oxidation and photolysis, using the method
463 described by Tuazon et al. (1984). The applied ethanal nitrate + OH rate constant was 3.4×10⁻¹²
464 cm³ molecules⁻¹ s⁻¹, calculated using the structure-reactivity relationship (SAR) proposed by

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465 Kwok and Atkinson (1995). The applied photolysis frequency for ethanal nitrate was 1.69×10^{-5}
466 s^{-1} , calculated with the cross section recommended by Muller et al. (2014) and a unity quantum
467 yield. The photolysis frequency of the isoprene carbonyl nitrate was applied to account for the
468 photolytic loss of ethanal nitrate inside the chamber, because the β ketone group is known to
469 enhance the absorption cross section of the nitrate (Müller et al., 2014). The yield of the MVK
470 nitrate was corrected for loss to photolysis, wall uptake and OH oxidation using the same method
471 as that for the ethanal nitrate yield. For the MVK nitrate, no OH loss correction was applied,
472 because MVK nitrate is saturated and is not expected to undergo significant loss to OH. The applied
473 photolysis frequency for the MVK nitrate was $4.5 \times 10^{-6} s^{-1}$, calculated using the absorption cross
474 section of 3-nitrooxy-2-butanone (Barnes et al., 1993) as a surrogate and unity quantum yield
475 across all wavelengths (Müller et al., 2014). However, its loss to wall uptake and photolysis loss
476 was corrected, following the same method as used for the ethanal nitrate. The MVK nitrate loss
477 rates wall loss rate for wall uptake and photolysis inside the chamber were set the same as
478 those that for the 4,1-carbonyl nitrate nitrooxy enal, because MVK nitrate is also a ketone nitrate,
479 which is prone to photolysis loss, and it has a molecular weight close to that of the nitrooxy enal 4,1-
480 carbonyl nitrate. Based on the Kwok and Atkinson (1995) SAR method, we calculated that the rate
481 constant for MVK nitrate reaction with OH should be $1.78 \times 10^{-12} cm^3 molecules^{-1} s^{-1}$. After the
482 correction for secondary loss, the apparent yield is 24.523.3% for MVK nitrate and 8.088.0% for
483 ethanal nitrate. Considering the uncertainties in the sensitivities of MVK nitrate and ethanal nitrate
484 (Table S2), the MVK nitrate yield is 24.23(±3)%, and the ethanal nitrate yield is 8(±2)%. The
485 fractional inlet sampling loss for the three nitrates was determined by comparing the CIMS signals
486 of sampling through the 5.2 m long 50°C tubing and through a 20 cm room temperature tubing.
487 By correcting for the inlet sampling loss, the MVK nitrate yield is 24.23(±5)%, and the ethanal
488 nitrate yield is 8(±3)%. For the two OH oxidation experiments, the first-order loss rate of the 4,1-
489 carbonyl nitrate nitrooxy enal was $3 \times 10^{-4} s^{-1}$ (Fig. S8). Since the total wall uptake and photolysis
490 loss rate for 4,1-isoprene carbonyl nitrate nitrooxy enal was $4.3 \times 10^{-5} s^{-1}$, approximately 85% of
491 the 4,1-carbonyl nitrate nitrooxy enal was lost to OH oxidation. After correcting for this factor, the
492 MVK nitrate yield is 28.27(±5)%, and the ethanal nitrate yield is 9(±3)%. While we were able to
493 determine the yields of MVK nitrate and ethanal nitrate from the OH oxidation reaction, the exact
494 branching ratios for reactions described in Fig. 11 and 12 cannot be derived. This is because ethanal
495 nitrate can be produced in both H abstraction and OH addition pathways (including both the (a)

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496 and (b) pathways). For MVK nitrate, even though it is produced in pathway (b) only, it has ethanal
497 nitrate as a byproduct, making it impossible for us to determine the branching ratio for pathway
498 (b).

499 4.3.2 Photolysis

500 Previous work on acetaldehyde suggests that at 313 nm the dominant photolysis reaction is
501 dissociation of the C-CHO bond, forming a formyl radical ($\bullet\text{CHO}$) (Blacet and Loeffler, 1942).
502 At shorter wavelength (265 nm), the reaction can proceed by intramolecular rearrangement
503 forming CH_4 and CO (Blacet and Loeffler, 1942). For compounds with longer carbon chain length,
504 such as propyl- and butyl- aldehydes, the photo-dissociation reaction can produce alkenes and
505 smaller aldehydes at 238 nm and 187 nm (Blacet and Crane, 1954). Since the UV radiation that
506 reaches the earth's surface is mostly above 300 nm, the formyl radical pathway is expected to be
507 the most important photolysis reaction for alkyl aldehydes (Shepson and Heicklen, 1982). For the
508 isoprene ~~carbonyl nitrate~~nitrooxy enal, the C-CHO bond is strengthened by the delocalized
509 electrons from the vinyl and the carbonyl groups, leading to a bond dissociation energy of 413
510 kJ/mol, as measured for acrolein, which is larger than the C-CHO bond dissociation energy of
511 acetaldehyde (355 kJ/mol) (Wiberg et al., 1992). In comparison, the O-NO₂ bond dissociation
512 energy is 175 kJ/mol (Luo, 2007a), much lower than the dissociation energy of the C-CHO bond.
513 Hence, dissociation of the weak O-NO₂ bond may be an important reaction pathway for the
514 ~~carbonyl nitrate~~nitrooxy enal. This process likely involves the absorption of a photon by the
515 C=C-C=O chromophore, followed by intramolecular energy redistribution to deposit energy into
516 the O-NO₂ bond prior to dissociation. This reaction step would generate NO₂ and an alkoxy radical,
517 which upon reaction with O₂ forms a conjugated dialdehyde.

518 Fig. 15 shows the CIMS spectra before and after the photolysis of the isoprene ~~carbonyl~~
519 ~~nitrate~~nitrooxy enal. Cyclohexane was used as the OH scavenger for this experiment. The CIMS
520 signal for the dialdehyde, which is the O-NO₂ bond dissociation product (reaction mechanism
521 shown in Fig. 16), did not increase significantly. This may be because the CIMS was not sensitive
522 to the dialdehyde, and/or the dialdehyde underwent rapid secondary reactions, rendering its steady-
523 state concentration below the CIMS detection limit. Alternatively, it is possible that the alkoxy
524 radical derived from O-NO₂ bond dissociation undergoes a 1,5-H shift reaction (Fig. 16),
525 rendering the formation of the dialdehyde an insignificant pathway. The resulting alkyl radical can

526 immediately form a peroxy radical, which may follow the H shift mechanism proposed by Peeters
527 et al. (2009) and form a hydroperoxy aldehyde (HPALD) compound, as observed at m/z 257 by
528 the CIMS (Fig. 15). When the peroxy radical reacts with NO or RO₂, the resulting alkoxy radical
529 will form a hydroxy dialdehyde (Fig. 16) with m/z ratio at 241, which was also observed by the
530 CIMS (Fig. 14). It is worth noting that we also observed CIMS signals for the deprotonated ions
531 derived from the HPALD compound (m/z 129 and m/z 147) and the hydroxy dialdehyde (m/z 113
532 and m/z 131). The proton transfer reaction between the iodide ion and alcohols/peroxides have not
533 been observed previously, but it is possible that the conjugated structures help stabilize the charge
534 and hence make the proton transfer reaction a viable reaction channel.

535 The product at m/z 276 has the molecular weight of MVK nitrate. In the presence of OH scavenger,
536 however, the reaction is unlikely to proceed by the OH-initiated oxidation pathway to form MVK
537 nitrate. Instead, we hypothesize that the isoprene ~~carbonyl nitrate~~ nitrooxy enal could dissociate via
538 the C-CHO bond, which, following reaction with O₂ and HO₂, would form a vinyl hydroperoxide
539 with the same molecular weight as MVK nitrate. Vinyl hydroperoxides are known to be a reactive
540 intermediate from the intramolecular H shift of Criegee biradical, which can decompose into OH
541 and alkoxy radicals (Kroll et al., 2002). However, the un-energized vinyl hydroperoxides should
542 have a lifetime long enough to be detected by mass spectrometers (Liu et al., 2015). In fact,
543 theoretical calculations suggest that at 25 °C vinyl hydroperoxide has a lifetime of 58 hours
544 (Richardson, 1995). Therefore, the product at m/z 276 is likely the vinyl hydroperoxide. For the
545 OH oxidation product experiments, however, we attributed m/z 276 to MVK nitrate only, because
546 RO₂ + NO reaction (forming MVK nitrate) should dominate over RO₂ + HO₂ reaction (forming
547 vinyl hydroperoxide), in the presence of high NO concentration.

548 Based on the CIMS spectra of the photolysis products, we conclude that the photolysis of the
549 isoprene ~~carbonyl nitrate~~ nitrooxy enal leads to the dissociation of both the O-NO₂ and the C-CHO
550 bonds. A reaction scheme is proposed in Fig. 16. While we were able to identify some of the
551 photolysis products based on the nominal masses observed with the CIMS, the branching ratio for
552 the two reaction pathways was not determined, due to lack of quantitative measurements during
553 the photolysis experiment. Future studies are needed to evaluate the relative importance of these
554 two processes.

555 5 Conclusions and future work

556 An isoprene-derived ~~carbonyl-nitrate~~nitrooxy enal model compound was synthesized to study its
557 photochemical degradation chemistry in the atmosphere. The UV absorption spectrum of this
558 compound has contributions from both the C=C-C=O and the -ONO₂ chromophores, as is
559 confirmed by theoretical calculations, but absorption in the actinic region involves a transition
560 involving the ~~enale~~carbonyl group. The combination of the C=C-C=O and the -ONO₂
561 chromophores enhances the UV cross section of this molecule relative to alkyl nitrates, making
562 photolysis its dominant daytime sink. The photochemical lifetime of the ~~carbonyl-nitrate~~nitrooxy
563 enal can be less than one hour, due to its rapid photolysis loss, together with high reactivity toward
564 OH and O₃. The OH and O₃ oxidation rate constants for the 4,1-isoprene ~~carbonyl-nitrate~~nitrooxy
565 enal obtained in this study were both smaller than the reported rate constants for the δ-isoprene
566 hydroxy nitrates (Jacobs et al., 2014; Lee et al., 2014b). This could be because the oxidation by
567 either OH or O₃ would break the resonance structure of the C=C-C=O moiety, thus increasing the
568 activation energy.

569 Using the iodide-based CIMS, we identified the first-generation nitrate products from the OH-
570 initiated oxidation of the synthesized ~~carbonyl-nitrate~~nitrooxy enal, including mononitrate,
571 dinitrate and nitrooxy peroxyacyl nitrate. Two of the products, the MVK nitrate and the ethanal
572 nitrate, were quantified, which together contributed to 37.36(±5)% of the total products. The CIMS
573 spectra of the nitrate photolysis products suggest that both the C-CHO bond and the O-NO₂ bond
574 dissociate in the reaction. Since photolysis is a significant sink for the ~~carbonyl-nitrate~~nitrooxy
575 enal, it is important for future studies to investigate the relative importance of the two reaction
576 pathways, in order to fully understand the fate of NO_x in isoprene-rich atmospheres. Dissociation
577 of the O-NO₂ bond may afford highly oxidized alcohol and hydroperoxide, which can potentially
578 undergo uptake into the particle phase and facilitate the formation of secondary organic aerosols.
579 The C-CHO dissociation pathway may form a vinyl hydroperoxide product.

580 The NO₃-initiated isoprene oxidation can produce a series of isomeric carbonyl nitrates. The 1,4-
581 ~~carbonyl-nitrooxy enal~~nitrate, which is the dominant isomer, is expected to have similar photolysis
582 reactivity as the 4,1-~~carbonyl-nitrate~~nitrooxy enal studied in this work, because they both have the
583 O=C-C=C-C chromophore and the -ONO₂ chromophore, which would enhance the molecular

584 absorption cross section. For the unsaturated ketones (enones) derived from isoprene oxidation,
585 the ketone functionality may reduce their reactivity toward OH, in comparison with aldehydes, but
586 we expect them to have similar photochemical properties as the nitrooxy enals, since isomers such
587 as methyl vinyl ketone (MVK) and methacrolein (MACR) have similar absorption cross sections
588 and quantum yields (Gierczak et al., 1997).

589 ~~The influence of the unsaturated ketone functionality on nitrate photolysis is still unclear, and~~
590 ~~future studies are needed to understand how the different conjugated structures can affect the~~
591 ~~photochemical processes.~~

592 The experiments in this work were conducted in the presence of relatively high NO concentration.
593 In the ambient environment, organic nitrates produced in the high NO_x regime can undergo
594 photochemical degradation in the low NO regime, due to the wide span of ambient NO_x
595 concentrations (Su et al., 2015; Xiong et al., 2015). Crouse et al. (2012) proposed that under low
596 NO conditions, the oxidation of methacrolein (MACR) can regenerate OH radicals and form a
597 lactone that is prone to reactive uptake onto the aerosol phase. Since the ~~4,1-carbonyl~~
598 ~~nitrate~~ isoprene nitrooxy enal has a structure similar to that of MACR, it might also undergo similar
599 reaction in the clean environment. Further experimental work is needed to investigate how the
600 photochemical oxidation process of the ~~carbonyl-nitrate~~ nitrooxy enal can influence the formation
601 of OH radicals and growth of secondary organic aerosols.

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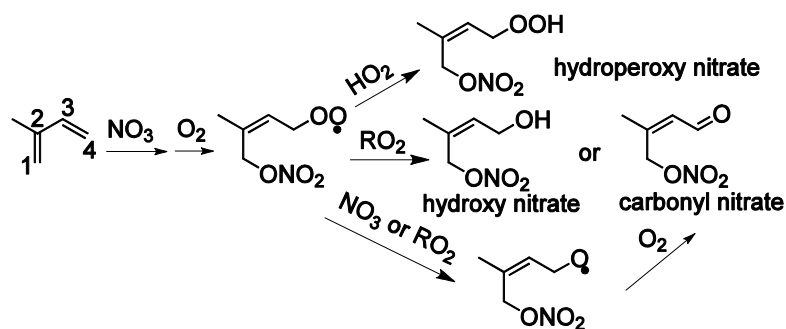
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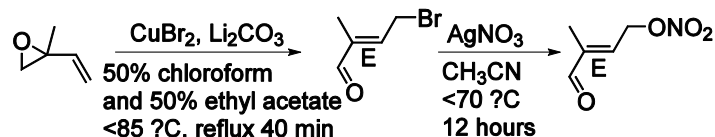


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909 Figure 1. Organic nitrates produced from NO_3 -initiated isoprene oxidation.

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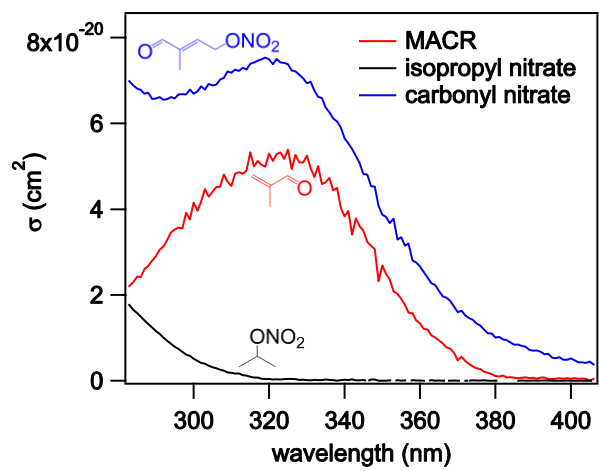
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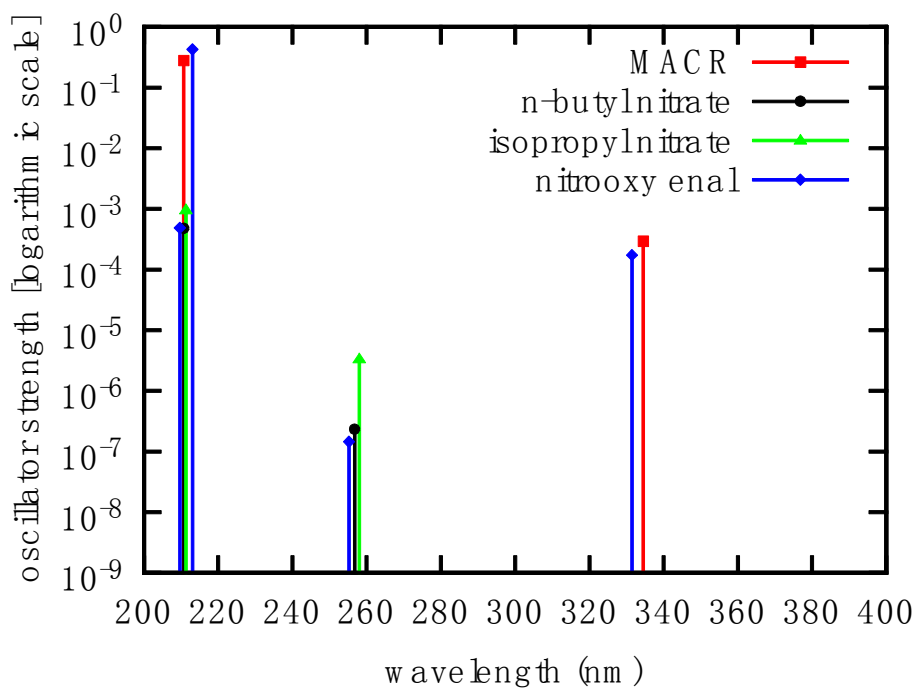
914 Figure 2. The synthesis route for the 4,1-isoprene carbonyl nitrate/nitrooxy enal.

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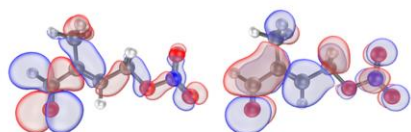
917
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 919 Figure 3. UV absorption cross section of the ~~carbonyl nitrate~~nitrooxy enal, MACR and isopropyl
 920 nitrate. The spectra were all obtained in acetonitrile solvent.
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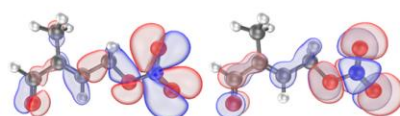
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 925 Figure 4. Theoretical gas-phase absorption spectra of the carbonyl nitrate nitrooxy enal, MACR,
 926 isopropyl nitrate and *n*-butyl nitrate in the gas phase.
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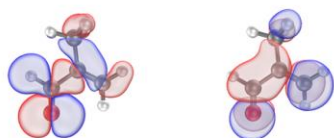
(a) First excitation in nitrooxy enal
331.51 nm \approx 3.7404 eV
HOMO \rightarrow LUMO



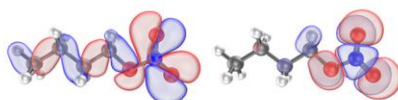
(b) Second excitation in nitrooxy enal
255.27 nm \approx 4.8575 eV
HOMO-2 \rightarrow LUMO+1



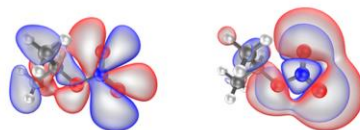
Homologous excitation in MACR
334.54 nm \approx 3.7066 eV
HOMO \rightarrow LUMO



Homologous excitation in *n*-butyl nitrate
256.76 nm \approx 4.8295 eV
HOMO \rightarrow LUMO

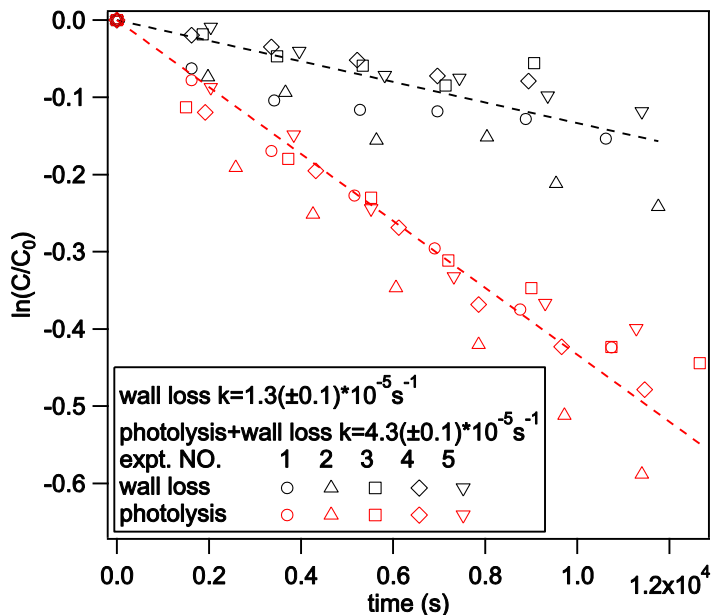


Homologous excitation in isopropyl nitrate
258.02 nm \approx 4.8058 eV
HOMO \rightarrow LUMO



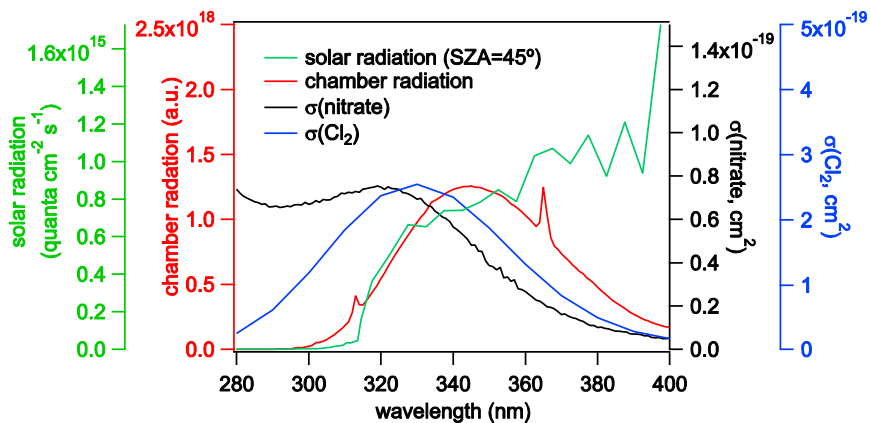
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Figure 5. Molecular orbital analysis of the first (a) and second (b) electronic excitations of the ~~carbonyl nitrate~~ nitrooxy enal, along with analogous excitations of MACR, isopropyl nitrate and *n*-butyl nitrate. The blue and red colors represent the opposite phases of molecular orbitals.



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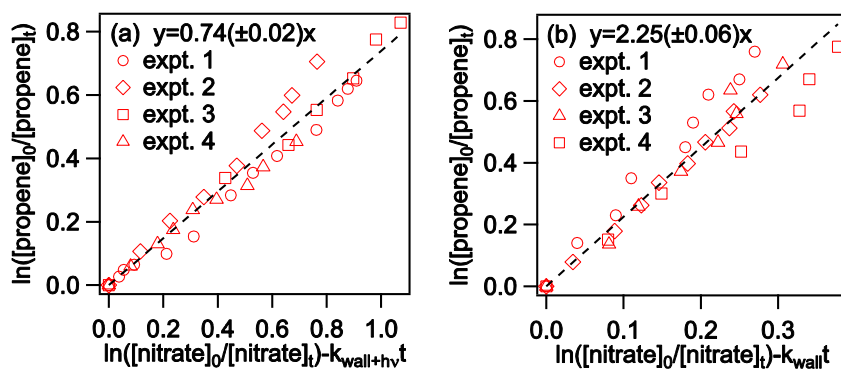
Figure 6. Wall loss and photolysis loss of the carbonyl nitrate nitrooxy enal in the reaction chamber.



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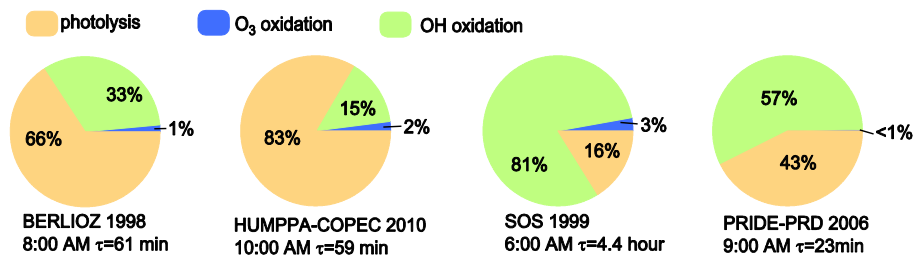
Figure 7. The radiation spectra of the chamber (red) and the sun (green, SZA=45° as an example), and the absorption spectra of the carbonyl nitrate nitrooxy enal (black, obtained in the liquid phase using acetonitrile solvent) and chlorine (blue).

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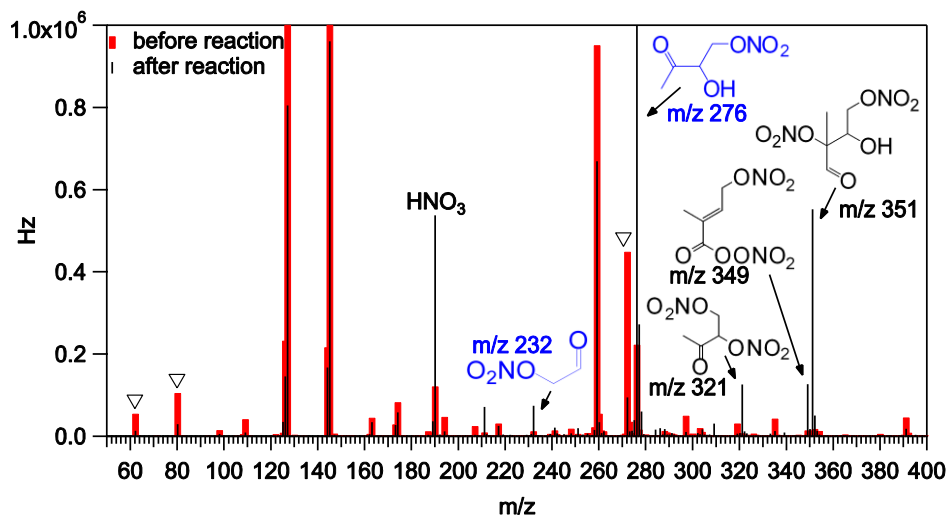
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Figure 8. The first-order loss of propene relative to that of the carbonyl nitrate for OH-initiated (a) and O₃-initiated (b) oxidation reactions.



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Figure 9. The relative contributions of photolysis (orange), OH oxidation (green) and O₃ oxidation (blue) to the photochemical decay of the carbonyl nitrate, calculated based on measured OH and O₃ concentrations for the following field studies: BERLIOZ 1998 study at Pabstthum, Germany (Mihelcic et al., 2003; Platt et al., 2002), HUMPPA-COPEC 2010 study at Hyytiälä (Hens et al., 2014), Finland, SOS 1999 study at Nashville, US (Martinez et al., 2003; Roberts et al., 2002) and PRIDE-PRD 2006 study at Guangzhou, China (Lu et al., 2012).



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Figure 10. The CIMS spectra before (red) and after (black) the OH + carbonyl nitrate nitrooxy enal oxidation reaction. The inverted triangles show the decreases in CIMS signals for the carbonyl nitrate nitrooxy enal (m/z 272) and the NO₃⁻ fragments (m/z 62, water cluster at m/z 80) derived from the carbonyl nitrate (Fig. 11). The molecular structures are inferred from the nominal masses observed by CIMS. The compounds that were observed by both CIMS and GC (Fig. 13) are colored in blue.

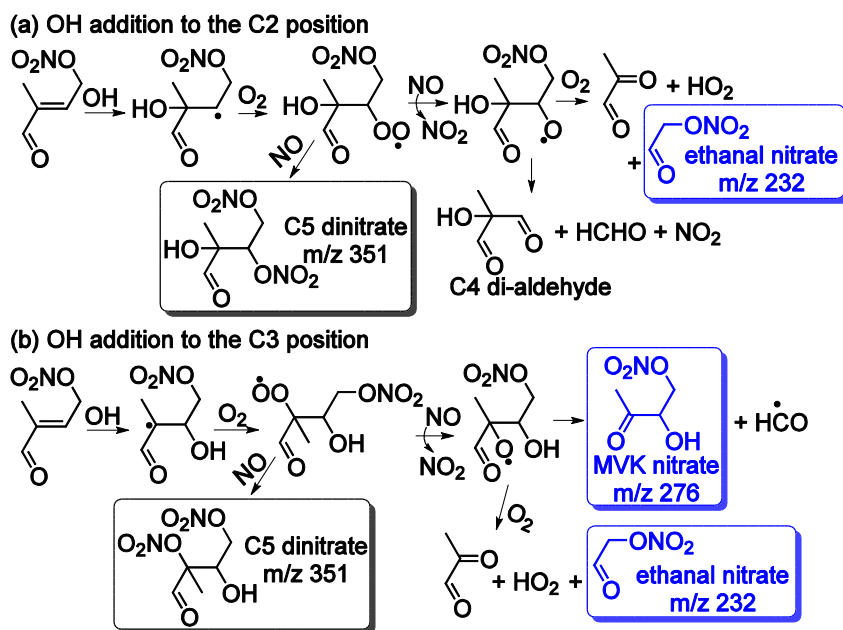
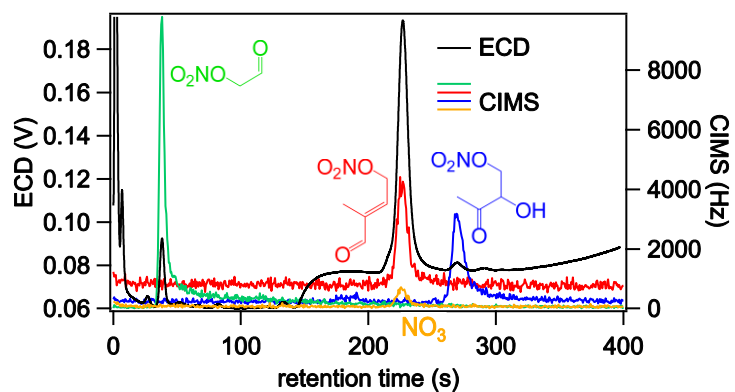
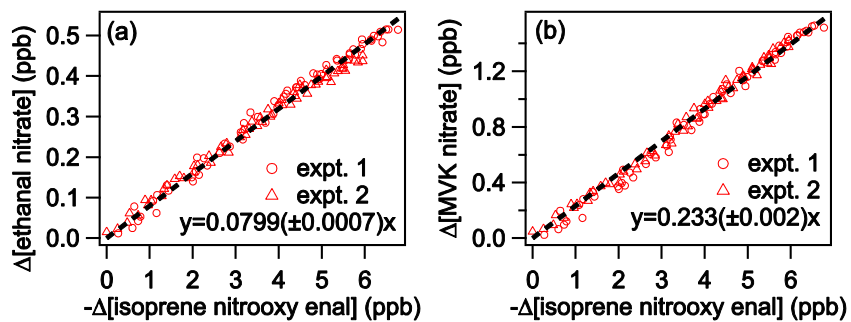


Figure 12. Proposed reaction mechanisms for OH addition to the C2 (a) and C3 (b) position of the carbonyl nitrate/nitrooxy enal. The compounds in boxes are proposed products inferred from the nominal masses observed by the CIMS (Fig. 8). The compounds that were observed by both CIMS and GC (Fig. 13) are colored in blue.

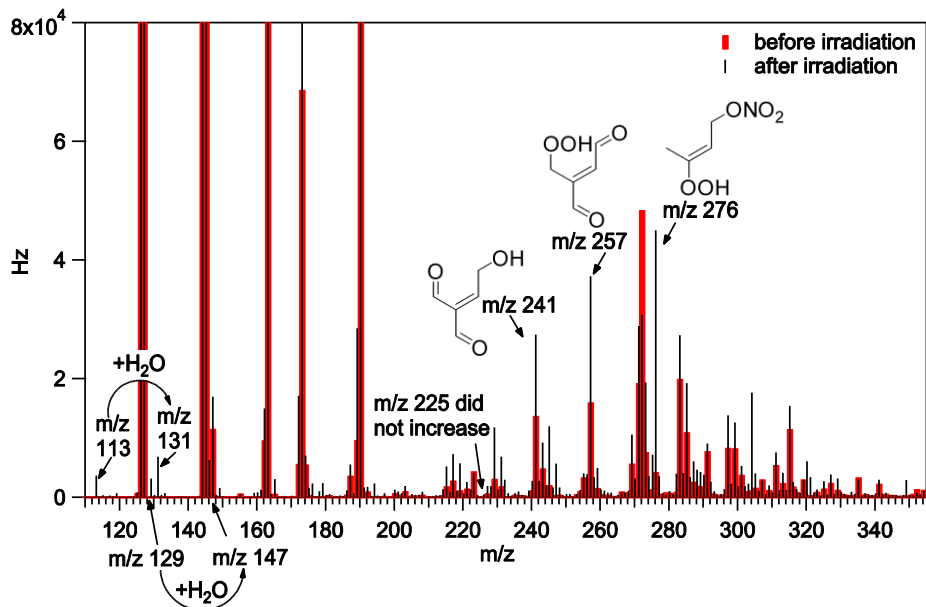
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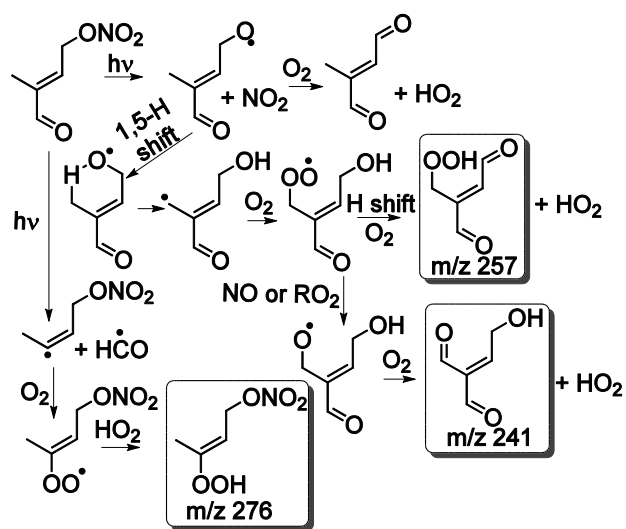
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998 Figure 13. The GC-ECD/CIMS spectra for the ~~carbonyl nitrate~~nitrooxy enal (red), MVK nitrate
999 (blue) and ethanal nitrate (green). The reaction of iodide with the ~~carbonyl nitrate~~nitrooxy enal
1000 generated NO_3^- ion (orange). The ECD chromatogram is shown in black.
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1005 Figure 14. The formation of ethanal nitrate (a) and MVK nitrate (b) relative to the loss of the
1006 isoprene ~~carbonyl nitrate~~nitrooxy enal for the OH + ~~carbonyl nitrate~~nitrooxy enal oxidation
1007 experiments.
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 1011 Figure 15. CIMS spectra before (red) and after (black) the photolysis of the isoprene ~~carbonyl~~
 1012 ~~nitrate~~nitrooxy enal. The molecular structures are inferred from the nominal masses observed by
 1013 CIMS.
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 1018 Figure 16. A proposed reaction mechanisms for the carbonyl-nitrate-nitrooxy enal photolysis
 1019 reaction. The compounds in boxes are proposed products as inferred from nominal masses observed
 1020 by the CIMS (Fig. 13).
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