

Interactive comment on “Photochemical Degradation of Isoprene-derived 4,1-Carbonyl Nitrate” by F. Xiong et al.

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Received and published: 18 February 2016

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 NO_3 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 O_3 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 non-conjugated 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.

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

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.

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?

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

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

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

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 MV-KNO₃+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 MV-KNO₃ 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.

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.

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..."

References

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Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-74, 2016.

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