

Interactive comment on “Photolysis and oxidation by OH radicals of two carbonyl nitrates: 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone” by Bénédicte Picquet-Varrault et al.

Anonymous Referee #1

Received and published: 26 September 2019

This paper addresses the photolysis and reaction with OH of two ketonitrates for which no data were available yet. The two compounds - a β -ketonitrate and a γ -ketonitrate - were chosen primarily because there were reasons to believe that they might behave differently from α -ketonitrates (for which experimental data is available) owing to the larger distance between the ketone and nitrate functional groups in those molecules. Previous work has suggested that the proximity of the two groups in α -ketonitrates causes interactions which greatly enhance the photolysis rates. The present laboratory study shows that the same might apply to β -ketonitrates, but not (or not as much) to

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the γ -ketonitrates. In addition, a product study has been conducted, with interesting, albeit puzzling, results. The OH-reaction rates of the two compounds are determined through a relative rate determination study, which suggests a relatively low reactivity for both compounds with OH.

The experimental methodology appears appropriate, and the analysis is convincing, although some specific points could be improved or clarified (see further below). The conclusions from this work are very relevant for our understanding of the role of VOC emissions on atmospheric chemistry, and more especially regarding their impact on nitrogen oxides. I recommend this work for publication, after the following minor comments below are addressed.

Minor comments

- I. 37 Organic nitrates are also formed in relatively pristine locations, where they play an important role (e.g. over forests)!
- I. 106 'Because of their importance for atmospheric chemistry': This is a bit odd, a robust synthesis process would be needed even if those 2 compounds were unimportant. They are model compounds. Best to drop that part of the sentence.
- I. 128 What filter is being used? Wang et al. refers to different widths.
- I. 135 Note that 200 DU is a very low value. This is not important for NO₂, but it will be for the organic nitrates.
- I. 144-145 Cyclohexane is more reactive than the ketonitrates, yes, but **not** 'very much' as stated here (7E-12 for cyclohexane, 3E-12 for the ketonitrates). The 95% OH scavenging efficiency might be a bit overestimated, at least for the experiments with ~1 ppm ketonitrate.

Section 3.1 first paragraph: I see a lot of repetitions between this part and Section 2.2. It could be shortened.

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Section 3.1 Why not use TUV to calculate the photolysis rates in laboratory conditions, with the known lamp spectrum? The discussion would be more convincing and straightforward. The scaling by a factor 3.2 is an approximation. It is not valid for the monofunctional nitrates of Table 2, and might be on the high side for the ketonitrates, because the lamp irradiates too much below ~ 310 nm. I have the feeling that the 200 Dobson Units assumed here for TUV calculations (a very low ozone column, unrealistic for mid-latitudes) were chosen to mitigate the issue. Note that this remark does not affect the main conclusions of the study.

Figure 1. What is the zero of the x axis? Why not show the evolution of $\ln(\text{nitrates})$ from the start?

Table 1. I'm surprised by the very low uncertainty estimate for k_{before} (0.2) for the second compound. The corresponding dark period on the graph looks very short.

I. 248-249 For 5-nitrooxy-2-pentanone, the discrepancy between the calculated J and the experimental value could be due to the cross sections, or the quantum yields, or both. I would be therefore more cautious when discussing the enhancement of the cross section. I admit that the proposed reasoning seems plausible. We expect less cross section enhancement due to the larger distance, it is therefore likely to explain the lower J.

I. 303 and I. 372 Same thing, the low enhancement of absorption cross sections has not been observed, only assumed.

Technical corrections

- I. 26 Replace 'increasing' by 'larger'
- I. 27 Replace 'products' by 'product'
- I. 33 Replace 'that' by 'than'
- I. 68 Replace 'works are' by 'work is'

- I. 75 Insert 'photolysis' before 'quantum yield', and drop 'photolysis' after 'unity'
- I. 85 Insert 'of' before 'carbonyl nitrates'
- I. 90 Replace 'process' by 'processes of'
- I. 90 Insert a comma before 'leading to'
- I. 107 Delete 'the' before 'Kames'
- I. 138 Replace 'proportional' by 'proportionality'
- I. 145 Insert 'the' before 'ketonitrates'
- I. 145 Replace 'section results' by 'Results section'
- I. 154 and elsewhere in the manuscript: Do not italicize 'ln' as well as 'nitrate' in equations
- I. 191 Delete the ""
- I. 250 Replace 'annihilated' by 'absent'
- I. 263 Insert 'infrared' before 'absorption cross sections'
- I. 268 You mean Scheme 1, not Scheme 2
- I. 281 Delete 'together'
- I. 298 Insert 'the fact that' after 'Despite'
- I. 309 You mean Figure 2, not Figure 3
- I. 328 Replace 'to reproduce' by 'in reproducing'
- I. 330 Insert 'a' before 'nitrate group'
- I. 349 Delete 'the' before 'oxidation'
- I. 350 Replace 'Same conclusion' by 'An identical conclusion'

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I. 378 You may drop 'leading to NO₂ release'

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-801>, 2019.

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