

Answer to Anonymous Referee #1

First of all, the authors would like to thank the anonymous referee for this interactive discussion and its constructive comments, corrections and suggestions that ensued. We have carefully replied to all its comments and the paper has been improved following its recommendations.

All technical corrections suggested by the referee have been carefully performed. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the minor comments:

I. 37 Organic nitrates are also formed in relatively pristine locations, where they play an important role (e.g. over forests)!

The sentence has been modified in order to be less restrictive.

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.

This part of the sentence has been removed.

I. 128 What filter is being used? Wang et al. refers to different widths.

7 mm Pyrex filters have been used. This information has been added in the manuscript.

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.

This was a typographic error. Determination of photolysis frequencies, in particular those given in Table 2, were performed with 300 DU.

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 1ppm ketonitrate.

We agree that for experiments which were performed with 1-2 ppm of ketonitrate, only approx. 80% of the OH were scavenged. This has been changed in the manuscript.

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

Section 3.1 has been shortened as suggested.

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.

The authors thank the referee for this very good suggestion and fully agree with it. Changes have been made accordingly: photolysis frequencies have been calculated for experimental conditions, i.e. using CESAM actinic flux. These new values are now compared to experimental data in Table 2. As expected, experimental and calculated photolysis frequencies are in good agreement for 4-nitrooxy-butanone when using the enhancement factor (r_{nk}) obtained for 3-nitrooxy-2-propanone. However, for 5-nitrooxy-pentanone, the experimental value is significantly lower than the calculated one confirming that the enhancement effect is reduced.

In the previous version of the manuscript, these data were also compared to the sum of the J for the monofunctional species using TUV model (for typical solar irradiation conditions and using 300 DU for the ozone total column, and not 200 DU as indicated by error in the manuscript). However, as we could not find in the literature the quantum yields of these species, this comparison was not possible for CESAM irradiation conditions and has been removed.

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

The evolution of $\ln(\text{nitrates})$ was not shown from the start (i.e. from the injection) in order to optimize the scale of the y axis. In addition, only experimental points which were taken into account for the linear regression were shown. Indeed, as explained in section 2.2, it was observed that the dark decay rate before irradiation may be significantly higher than the one after, suggesting a passivation effect of the walls. So, in order to determine wall loss decays which are as representative as possible of the one during the irradiation period, the first experimental points (after the injection of the carbonyl nitrate) were not taken into account for the linear regression leading to the determination of k_{before} . It has been explained more explicitly in the manuscript (l.166-171).

Following the referee comment, the figure 1 has been changed in order to show the experimental points from the start. The scale of the y axis is now optimized thanks to a break.

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.

As explained above, the first experimental points were not taken into account for the linear regression leading to the determination of k_{before} because we believe that, due to passivation effect, the period just after the injection of the carbonyl nitrate (and during which the decay rate is slightly faster) may not be representative of the wall loss rate during the irradiation period. The linear regression has hence been performed for a period of 30 min before the irradiation and the value of 0.2 for the uncertainty is calculated as twice the standard deviation on these points.

1. 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.

The sentences have been changed.

Additional correction made by the authors:

In addition to the changes performed to take into account the referee's comments, we noticed that we made an error in the J_{NO_2} value measured in CESAM chamber. The good value which was measured at the period during which these experiments were conducted, is $2.2 \times 10^{-3} \text{ s}^{-1}$ and not $3.0 \times 10^{-3} \text{ s}^{-1}$. This has been corrected in the new version of the manuscript and calculations have been modified accordingly.