

Dear Editor,

First, we would like to thank you for having accepted being co-editor for our paper. Please find below the answers to referee's comments and the new version of the manuscript with corrections highlighted in blue. All comments have carefully been taken into account and corrections have been performed in the manuscript accordingly.

Best Regards.

Bénédicte Picquet-Varrault and co-authors

## **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 and a Figure showing the spectrum of the lamps has been added in SI.

***I. 135 Note that 200 DU is a very low value. This is not important for NO<sub>2</sub>, 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-pentannone, 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(nitrates) from the start?***

The evolution of ln(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  $k_{\text{before}}$ . 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  $k_{\text{before}}$  (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  $k_{\text{before}}$  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.

*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.*

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  $J_{\text{NO}_2}$  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.

## Answer to Anonymous Referee #2

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. Answer has also been provided for the minor comment. Please find below the answers for each comment:

### Minor Comments

**1. The authors have measured the photolytic decay but then assume a quantum yield of unity to allow calculation of photolysis rate coefficients under atmospheric conditions. However, since it appears that the wavelength-dependent light flux in the chamber and the absorption cross-section data are both known, the effective quantum yield can in fact be determined from the ratio  $J(\text{experimental})$  to  $J(\text{maximum})$ , where the latter term is calculated using a quantum yield of unity (Clifford et al., 2011). It is recommended that the authors do this as it will allow for a good estimate of the quantum yield for photolysis of the compounds over the range of their atmospheric absorption.**

In fact, the absorption cross sections of the studied compounds are not known and were not measured in this study. They were estimated by assuming the fact that the enhancement factor  $r_{\text{nk}}$  is the same as the one calculated for 3-nitrooxy-2-propanone. However, this hypothesis could not be confirmed as absorption cross sections are not available. So effective quantum yields cannot be determined from the ratio

$$J_{\text{experimental}}/J_{\text{max}}$$

### Technical Corrections

**1. Lines 20-22: It is probably better to report the measured photolytic rate coefficients as  $j(\text{carbonyl nitrate})/j(\text{NO}_2)$  values, as in Clifford et al (2011). This would allow users of the data to calculate  $j(\text{carbonyl nitrate})$  under a range of sunlight conditions.**

As proposed by the reviewer,  $j(\text{carbonyl nitrate})/j(\text{NO}_2)$  values have been provided.

**2. Lines 22-23. The specific atmospheric conditions that the photolytic lifetimes were calculated for should be stated.**

The irradiation conditions used to estimate the photolysis frequencies are already given in the abstract. It is not clear for us which additional information the reviewer would like us to provide.

**3. Line 35: No need for the abbreviation "ONs" as it does not seem to appear in the rest of the article**

The abbreviation has been removed.

**4. Line 62: Give full name for PANs**

It has been done.

**5. Lines 66 and 68: Replace “works” with investigations or studies.**

It has been done.

**6. Line 83: Replace “photochemical” with atmospheric.**

It has been done.

**7. Line 90: The term “fairly fast” is not specific. This sentence should be improved.**

It has been done.

**8. Page 5 and elsewhere: The rate coefficient terms, *k* and *J*, should be in italics.**

It has been done.

**9. Line 209: The first sentence of this paragraph is not needed here.**

It has been removed.

**10. Line 228: These are not “experimental” photolysis frequencies, but are in fact estimated atmospheric photolysis frequencies under specific light conditions.**

In reply to referee #1 and referee #2 comments, photolysis frequencies estimated for typical tropospheric irradiation conditions have been removed from Table 1 and 2. Only experimental values measured in the simulation chamber are presented and compared.

**11. Line 258: Define PAN**

It has been done.

**12. Line 295: Should be Scheme 2.**

It has been corrected.

**13. Page 15: Captions for the figures, table and schemes should be more detailed to allow the reader to view and understand them without referring to the text too much.**

We did our best to improve the captions of the figures, tables and schemes. We hope they are understandable now.

**14. Page 17, Scheme 2: Why is decomposition of the nitrooxy radical not considered here, but it is in Scheme 1?**

This is an omission and the oxidation scheme has been completed accordingly. However, from the state of the art on the alkoxy chemistry, we expect the decomposition channel to be negligible in comparison to the reaction with O<sub>2</sub>.

**15. Page 19, Figure 2: What do the different data points represent? More detail should be provided in the caption and/or the figure itself.**

The different symbols represent different experiments. This has been added in the figure caption.

**16. Page 20, Table 1: The inclusion of the calculated atmospheric photolysis rate coefficient in this table is a bit confusing. It should be removed.**

We fully agree with this comment. Photolysis frequencies estimated for typical tropospheric irradiation conditions have therefore been removed from Table 1 and 2.

**17. Page 21, Table 2: As explained in point 10 above, the use of the term  $J(\text{experimental})$  here is wrong.**

See answer to comment 10.

**18. Page 23, Table 4: Use the times symbol instead of "x".**

It has been done.

## Photolysis and oxidation by OH radicals of two carbonyl

### 2 nitrates: 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone

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#### 12 **Abstract**

Multifunctional organic nitrates, including carbonyl nitrates, are important species formed in NO<sub>x</sub> rich atmospheres by the degradation of VOCs. These compounds have been shown to play a key role in the transport of reactive nitrogen and consequently in the ozone budget, but also to be important components of the total organic aerosol. However, very little is known about their reactivity in both gas and condensed phases. Following a previous study we published on the gas-phase reactivity of  $\alpha$ -nitrooxy ketones, the photolysis and the reaction with OH radicals of 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone, respectively a  $\beta$ -nitrooxy ketone and a  $\gamma$ -nitrooxy ketone, were investigated for the first time in simulation chambers. The photolysis rates were directly measured in CESAM chamber which is equipped with a very realistic irradiation system. The ratios  $J_{\text{nitrate}}/J_{\text{NO}_2}$  were found to be  $(5.9 \pm 0.9) \times 10^{-3}$  for 4-nitrooxy-2-butanone and  $(3.2 \pm 0.9) \times 10^{-3}$  for 5-nitrooxy-2-pentanone under our experimental conditions. From these results, it was estimated that ambient photolysis frequencies calculated for 40° latitude North (1<sup>st</sup> July, noon) are  $(6.1 \pm 0.9) \times 10^{-5} \text{ s}^{-1}$  and  $(3.3 \pm 0.9) \times 10^{-5} \text{ s}^{-1}$  for 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone, respectively. These results demonstrate that photolysis is a very efficient sink for these compounds with atmospheric lifetimes of few hours. They also suggest that, similarly to  $\alpha$ -nitrooxy ketones,  $\beta$ -nitrooxy ketones have enhanced UV absorption cross sections and quantum yields equal or close to unity and that  $\gamma$ -nitrooxy ketones have lower enhancement of cross sections which can easily be explained by the larger distance between the two chromophore groups. Thanks to a product study, branching ratio between the two possible photodissociation pathways are also proposed. Rate constants for the reaction with OH radicals were found to be  $(2.9 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $(3.3 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. These experimental data are in good agreement with rate constants estimated by the SAR of Kwok and Atkinson (1995) when using the parametrization proposed by Suarez-Bertoa et al.

(2012) for carbonyl nitrates. Comparison with photolysis rates suggests that OH-initiated oxidation of carbonyl nitrates is a less efficient sink than photodissociation but is not negligible in polluted area.

## 1 Introduction

Organic nitrates play an important role as sinks or temporary reservoirs of NO<sub>x</sub>, as well as on ozone production in the atmosphere (Perring et al., 2013; Perring et al., 2010; Ito et al., 2007). They are formed by the degradation of VOCs in presence of NO<sub>x</sub> through two main processes: i) the reaction of peroxy radical, produced by the oxidation of VOCs, with NO. The major pathway is generally the reaction (1a) that leads to NO<sub>2</sub> formation. The reaction (1b) is a minor channel but it becomes gradually more important with increasing peroxy radical carbon chain length (Atkinson and Arey, 2003; Finlayson-Pitts and Pitts, 2000).



ii) The reaction of unsaturated VOCs with NO<sub>3</sub> radical, which proceeds mainly by addition of the nitrate radical on the double bond to produce nitro-alkyl radicals that can evolve into organic nitrates.

Among the organic nitrates, a variety of multifunctional species such as hydroxy-nitrates, carbonyl-nitrates and dinitrates are formed. The formed species have been shown to significantly contribute to the nitrogen budget in both rural and urban areas (Perring et al. 2013). Beaver et al. (2012) have observed that carbonyl nitrates, formed as second generation nitrates from isoprene, are an important fraction of the total organic nitrates observed over Sierra Nevada in summer. These observations are supported by several studies that investigated the photooxidation of isoprene in simulation chambers (Paulot et al., 2009, Müller et al., 2014). These multifunctional organic nitrates are also semi-/non-volatile and highly soluble species and are thus capable of partitioning into the atmospheric condensed phases (droplets, aerosols). Numerous field observations of the chemical composition of atmospheric particles have shown that organic nitrates represent a significant fraction (up to 75% in mass) of the total organic aerosol (OA) demonstrating that these species are important components of total OA (Ng et al., 2017).

Several modeling studies have also confirmed that multifunctional organic nitrates, in particular isoprene nitrates, play a key role in the transport of reactive nitrogen and consequently in the formation of ozone and other secondary pollutants at the regional and global scales (Horowitz et al., 2007; Mao et al., 2013; Squire et al., 2015). In particular, Mao et al. (2013) have performed simulations based on data from the ICARTT aircraft campaign across the eastern U.S. in 2004. They have shown that organic nitrates, which are mainly composed of secondary organic nitrates, including a large fraction of carbonyl nitrates, provide an important pathway for exporting NO<sub>x</sub> from the U.S.'s boundary layer, even exceeding the export of peroxy acyl nitrates (PANs). However, these modeling studies also point out the need for additional experimental data to better describe the sinks in both gas and condensed phases of multifunctional organic nitrates in models.

Recent experimental studies have revealed that hydrolysis in aerosol phase may be a very efficient sink of organic nitrates in the atmosphere (Bean and Hildebrand Ruiz, 2015; Rindelaub et al., 2015). These studies also suggest that the rate of these reactions strongly depends on the organic nitrate chemical structure and that

72 additional work is needed to better understand these processes. In the gas-phase, photolysis and reaction with  
OH radical are expected to dominate the fate of organic nitrates (Roberts et al., 1990; Turberg et al., 1990). In a  
74 previous study, we have measured the photolysis frequencies and the rate constants for the OH-oxidation of 3  
carbonyl nitrates ( $\alpha$ -nitrooxyacetone, 3-nitrooxy-2-butanone, and 3-methyl-3-nitrooxy-2-butanone) and we have  
76 shown that photolysis is the dominant sink for these compounds (Suarez-Bertoa et al., 2012). By comparison  
with absorption cross sections provided by Barnes et al. (1993), Müller et al. (2014) suggested i) that the  $\alpha$ -  
78 nitrooxy ketones have enhanced absorption cross sections, due to the interaction between the  $\text{C}=\text{O}$  and  
the  $\text{-ONO}_2$  chromophore groups and ii) that the photolysis quantum yield is close to unity and  $\text{O}-\text{NO}_2$   
80 dissociation is the likely major channel. They also showed that this enhancement was larger at the higher  
wavelengths, where the absorption by the nitrate chromophore is very small. Therefore, they concluded that the  
absorption by the carbonyl chromophore was the one enhanced due to the neighbouring nitrate group.

82 These results are significant as they demonstrate that photolysis rates of these multifunctional species cannot be  
calculated as the sum of the monofunctional species (ketone + alkyl nitrate) ones. However, only  $\alpha$ -nitrooxy  
84 ketones were studied which leaves open the question of the persistence of the enhancement effect when the  
distance between the two functional groups increases. More recently, Xiong et al. (2016) have studied the  
86 [atmospheric](#) degradation (photolysis, OH-oxidation and ozonolysis) of *trans*-2-methyl-4-nitrooxy-2-buten-1-al  
(also called 4,1-isoprene nitrooxy enal) in order to better assess – as a model compound - the reactivity of  
88 carbonyl nitrates formed by the  $\text{NO}_3$ -initiated oxidation of isoprene. This compound has a conjugated  
chromophore  $\text{-C}=\text{C}-\text{C}=\text{O}$  in  $\beta$  position of the nitrate group. The authors measured the absorption cross sections  
90 of the nitroxy enal and compared them to those for the monofunctional species, i.e. methacrolein and isopropyl  
nitrate. They concluded that molecules containing  $\beta$ -nitrooxy ketones functionalities have also enhanced UV  
92 absorption cross sections. [They also studied the kinetic and mechanisms for the oxidation of the nitroxy enal by  
OH and  \$\text{O}\_3\$ . They conclude that photolysis and reaction with OH are thus the two main loss processes of \*trans\*-2-  
94 methyl-4-nitrooxy-2-buten-1-al, leading to a tropospheric lifetime of less than 1 h.](#)

Given the large contribution of the carbonyl nitrates to the organic nitrate pool and the importance of their  
96 photochemistry for the  $\text{NO}_x$  budget, we present a study that aims at providing new experimental data on the gas-  
phase reactivity of these compounds. The study also seeks to disclose how photolysis and reaction with OH  
98 radical of carbonyl nitrates are affected by modifying their carbon chain length and the position of the two  
functional groups present in their molecular structure. Here, we provide the first photolysis frequencies and also  
100 the first rate constants for the OH-oxidation of two carbonyl nitrates: 4-nitrooxy-2-butanone and 5-nitrooxy-2-  
pentanone.

## 102 **2 Experimental section**

### **2.1 Reactants syntheses**

104 As a usual OH precursor in simulation chamber experiments, isopropyl nitrite was synthesized by dropwise  
addition of a dilute solution of  $\text{H}_2\text{SO}_4$  into a mixture of  $\text{NaNO}_2$  and isopropanol following the classical protocol  
106 proposed by Taylor et al. (1980).

On the contrary, 4-nitroxy-2-butanone and 5-nitroxy-2-pentanone were synthesized for the first time. A great care was taken to the development of a robust process: 4-nitroxy-2-butanone and 5-nitroxy-2-pentanone syntheses are based on Kames' method (Kames et al., 1993). This method consists in a liquid/gas phase reaction where the corresponding hydroxy-ketone reacts with NO<sub>3</sub> radicals released from the dissociation of N<sub>2</sub>O<sub>5</sub>. N<sub>2</sub>O<sub>5</sub> was preliminarily synthesized in a vacuum line by reaction of NO<sub>2</sub> with ozone, as described by Scarfoglio et al. (2006). The synthesis of the carbonyl nitrate is performed in a dedicated vacuum line connected to two bulbs, one containing the hydroxy-ketone, the other one containing N<sub>2</sub>O<sub>5</sub>. The two bulbs are also connected to each other. In a first step, the bulbs are placed in a liquid N<sub>2</sub> cryogenic trap and pumped in order to remove air and impurities. In a second step, the cryogenic trap is removed from the bulb containing N<sub>2</sub>O<sub>5</sub> in order to let it warm and transfer into the bulb containing the hydroxy-ketone. Then, the bulb containing both reactants is stirred and kept at ice temperature for approximately 1h. Finally, the resulting carbonyl nitrate and nitric acid, its co-product, were separated by liquid-liquid extraction using dichloromethane and water. The carbonyl nitrate structure and purity were verified by FT-IR and GC-MS. Traces of impurities (HCOOH and CH<sub>3</sub>COOH) have been detected. The carbonyl nitrates were stored at -18° C and under nitrogen atmosphere to prevent them from decomposition. Infrared spectra of 4-nitroxy-2-butanone and 5-nitroxy-2-pentanone are available on EUROCHAMP Data Centre (<https://data.eurochamp.org>).

## 2.2 Determination of photolysis frequencies

The photolysis frequencies of the two carbonyl nitrates were determined by carrying out experiments in the CESAM simulation chamber which is only briefly described here as detailed information can be found in Wang et al. (2011). The chamber consists of a 4.2 m<sup>3</sup> stainless steel vessel equipped with a multiple reflection optical system interfaced to a FTIR spectrometer (Bruker Tensor 37) and also with NO, NO<sub>2</sub> and O<sub>3</sub> analyzers (Horiba) to monitor the composition of the gas phase. The chamber is also equipped with three high pressure xenon arc lamps (MH-Diffusion, MacBeam 4000) which are combined with 7 mm Pyrex filters. This irradiation device provides a very realistic actinic flux (see comparison with the solar actinic flux in Figure S1) which allows measuring photolysis frequencies under realistic conditions (Wang et al., 2011; Suarez-Bertoa et al., 2012). However, since the intensity of the irradiation in CESAM chamber is lower than the one in ambient environment,  $J_{\text{nitrate}}/J_{\text{NO}_2}$  were provided in order to allow calculating  $J_{\text{nitrate}}$  under various sunlight conditions. Hence, the intensity of the actinic flux was determined by measuring the photolysis rate of NO<sub>2</sub> ( $J_{\text{NO}_2}$ ) during dedicated experiments. 400 ppbv of NO<sub>2</sub> in 1000 mbar of N<sub>2</sub> were injected into CESAM chamber and kept in the dark for 20 min. The lights were then turned on during 20 min, and finally the mixture was left in the dark for an additional 20 min period. The photolysis frequency was subsequently determined using a kinetic numeric model developed for previous NO<sub>x</sub> photo-oxidation experiments in CESAM (Wang et al., 2011). The fitting of modeled values from the measured data provided a NO<sub>2</sub> photolysis frequency equal to  $2.2 \times 10^{-3} \text{ s}^{-1}$  ( $\pm 0.01, 2\sigma$  error).

During a typical experiment, carbonyl nitrates were introduced into the chamber which was preliminarily filled at atmospheric pressure with N<sub>2</sub>/O<sub>2</sub> (80/20). For the injection, the bulb containing the carbonyl nitrate was connected to the chamber and slightly heated while it was flushed with N<sub>2</sub>. Mixing ratios of carbonyl nitrates ranged from hundreds ppb to ppm. Because carbonyl nitrates may decompose during the injection, large amounts of NO<sub>2</sub> (hundreds ppb) were present in the mixture. Cyclohexane was also added to the mixture as an OH-

146 scavenger with mixing ratios of approx. 4 ppm. Considering the fact that cyclohexane is approximately twice  
 148 more reactive with OH radicals than the carbonyl nitrates (see Results section), it was estimated that between 80  
 150 and 98% of the OH radicals were scavenged (depending on the experiment considered). The mixture was kept  
 152 under dark conditions during two hours to be able to assess the impact of the reactor's walls and to minimize  
 their effects by passivation. Then, the mixture was irradiated during 3 hours. For most experiments, the mixture  
 was finally left in the dark for approximately 1 hour after the irradiation period to allow for verifying if wall  
 losses were constant during the entire duration of the experiment.

During the experiment, the carbonyl nitrate loss processes can be described as:



156  $-\frac{d[\text{nitrate}]}{dt} = (J_{\text{nitrate}} + k) \times [\text{nitrate}]$  (Eq. 1)

$\ln[\text{nitrate}]_t = \ln[\text{nitrate}]_0 - (k + J_{\text{nitrate}}) \times t$  (Eq. 2)

158 The reaction (2a) had to be added to the system to take into account the interaction or adsorption of the carbonyl  
 nitrates on the stainless steel walls of CESAM during the experiments. By plotting  $\ln[\text{nitrate}]_t$  vs. time, where  
 160  $[\text{nitrate}]_t$  is the concentration of the carbonyl nitrate at time t, a straight line is obtained with a slope of  $(k +$   
 $J_{\text{nitrate}})$ . The same approach was applied to each of the 'dark' periods, before and after irradiation, to determine  
 162 their respective dark decay rates, namely  $k_{\text{before}}$  and  $k_{\text{after}}$  and  $k$  was calculated as the average of  $k_{\text{before}}$  and  $k_{\text{after}}$  for  
 each experiment. Finally,  $J_{\text{nitrate}}$  was calculated as the difference between the loss rate during the irradiation  
 164 period  $(k + J_{\text{nitrate}})$  and the averaged loss rate during the dark periods  $(k)$ .

The uncertainties were calculated by adding the respective statistical errors ( $2\sigma$ ) associated to the dark and light  
 166 periods, the former set as the average of the uncertainties determined for both dark periods (i.e., before and after  
 irradiation). However, for some experiments, it was observed that the dark decay rate before irradiation was  
 168 significantly higher than the one after, suggesting that wall loss process is more complex than a "simple" first  
 order process and may decrease with time due to a passivation of the walls. More generally, interactions of gases  
 170 with walls remain poorly understood and are currently subject to intensive investigations by the scientific  
 community. Here, in order to determine wall loss decays which are as representative as possible of the one  
 172 during the irradiation period, the first experimental points (after the injection of the carbonyl nitrate) were not  
 taken into account for the linear fit leading to the determination of  $k_{\text{before}}$ . In addition, the uncertainty was not  
 174 calculated using the approach detailed above, the statistical error being too low compared to the difference  
 between  $k_{\text{before}}$  and  $k_{\text{after}}$ . The uncertainty was thus estimated in order to include the lowest and the highest  $J_{\text{nitrate}}$   
 176 values calculated with the highest and the lowest  $k$  value, respectively. Finally, the overall uncertainty associated  
 with the photolysis rate of each of the carbonyl nitrates was calculated as the average of the uncertainties  
 178 obtained for each experiment, divided by the square root of the number of experiments (2 or 3).

### 2.3 Determination of the OH-oxidation rate constants

180 The kinetic experiments for the OH-oxidation of the carbonyl nitrates were performed in the CSA chamber at  
room temperature and atmospheric pressure, in a mixture of N<sub>2</sub>/O<sub>2</sub> (80/20). The chamber consists of a 977 L  
182 Pyrex<sup>TM</sup> vessel irradiated by two sets of 40 fluorescent tubes (Philips TL05 and TL03) that surround the  
chamber. The emissions of these black lamps are centered on 360 and 420 nm, respectively. The chamber is  
184 equipped with a multiple reflection optical system with a path length of 180 m interfaced to a FTIR spectrometer  
(Vertex 80 from Bruker). Additional details about this smog chamber are given elsewhere (Doussin et al., 1997;  
186 Duncianu et al., 2017).

The relative rate technique was used to determine the rate constant for the OH-oxidation of the carbonyl nitrates  
188 with methanol as reference compound. We used the IUPAC recommended value  $k_{(\text{methanol}+\text{OH})} = (9.0 \pm 1.8) \times$   
 $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (<http://www.iupac-kinetic.ch.cam.ac.uk/>). Hydroxyl radicals were generated by  
190 photolyzing isopropyl nitrite. Initial mixing ratios of reactants (carbonyl nitrate, isopropyl nitrite, methanol and  
NO) were in the ppm range. As previously described, the carbonyl nitrate was introduced into the chamber by  
192 connecting the bulb to the chamber and by slightly heating and flushing it with N<sub>2</sub>. NO was added to the mixture  
in order to enhance the formation of OH radicals by reaction with HO<sub>2</sub> radicals which are formed by isopropyl  
194 nitrite photolysis. All experiments were conducted during a 1 h period of continuous irradiation.

Prior to the experiments, it was verified that photolysis and wall losses of the studied compounds were negligible  
196 under our experimental conditions. This can be explained by the facts that i) the irradiation system of CSA  
chamber emits photons at significantly higher wavelengths than the one of CESAM chamber, and ii) the walls of  
198 the chamber are made of Pyrex which is more chemically inert than stainless steel. It was therefore assumed that  
reaction with OH is the only fate of both, the studied compound (carbonyl nitrate) and the reference compound  
200 (methanol) and that neither of these compounds is reformed at any stage during the experiment. Based on these  
hypotheses, it can be shown that (Atkinson, 1986):

$$202 \ln \frac{[\text{nitrate}]_0}{[\text{nitrate}]_t} = \frac{k_{\text{nitrate}}}{k_{\text{methanol}}} \times \frac{[\text{methanol}]_0}{[\text{methanol}]_t} \quad (\text{Eq. 3})$$

where [nitrate]<sub>0</sub> and [methanol]<sub>0</sub>, and [nitrate]<sub>t</sub> and [methanol]<sub>t</sub> stand for the concentration of the carbonyl nitrate  
204 and the reference compound at times 0 and t, respectively. The plot  $\ln([\text{nitrate}]_0/[\text{nitrate}]_t)$  vs.  
 $\ln([\text{methanol}]_0/[\text{methanol}]_t)$  is linear with a slope equal to  $k_{\text{nitrate}}/k_{\text{methanol}}$  and an intercept of zero. The uncertainty  
206 on  $k_{\text{nitrate}}$  was calculated by adding the relative uncertainty corresponding to the statistical error on the linear  
regression ( $2\sigma$ ) and the error on the reference rate constant (here 20 % for methanol).

## 208 2.4 Chemicals and gases

Dry synthetic air was generated using N<sub>2</sub> (from liquid nitrogen evaporation, >99.995% pure, <5 ppm H<sub>2</sub>O, Linde  
210 Gas) and O<sub>2</sub> (quality N45, >99.995% pure, <5 ppm H<sub>2</sub>O, Air Liquide). Chemicals obtained from commercial  
sources are: NO (quality N20, >99% Air Liquide), NO<sub>2</sub> (quality N20, >99% Air Liquide), 4-hydroxy-2-butanone  
212 (95% Aldich), 5-hydroxy-2-pentanone (95% Aldich), cyclohexane (VWR), methanol (J.T. Baker), H<sub>2</sub>SO<sub>4</sub> (95%  
VWR), NaNO<sub>2</sub> (≥99 Prolabo), isopropanol (VWR).

## 214 3 Results and discussion

### 3.1 Photolysis of carbonyl nitrates

216 Figure 1 presents the kinetic plots obtained for the two compounds, where  $\ln[\text{nitrate}]$  was plotted as a function of  
218 time. A significant decrease was observed for both compounds during the dark period, before and after  
220 irradiation, suggesting that they adsorb or decompose on the walls. Photolysis frequencies were thus calculated  
222 as the difference between the decay rates in the dark and the one under irradiation (see section 2.2). Results  
224 obtained for both compounds and for all experiments are given in Table 1. For 4-nitrooxy-2-butanone, photolysis  
226 frequencies are in good agreement despite the fact that decay rates in the dark differ from an experiment to  
another. For 5-nitrooxy-2-butanone, it can be seen that the decay rate in the dark before irradiation is  
significantly higher than the one after (in particular for experiments 3 and 4), suggesting that wall losses may  
decrease with time due to a passivation of the walls. Despite this, comparison of the three experiments showed  
good agreement. For CESAM irradiation conditions, the photolysis rates are  $(1.3 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$  for 4-nitrooxy-  
2-butanone and  $(0.7 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$  for 5-nitrooxy-2-pentanone. Hence,  $J_{\text{nitrate}}/J_{\text{NO}_2}$  were found to be  $(5.9 \pm 0.9)$   
 $\times 10^{-3}$  for 4-nitrooxy-2-butanone and  $(3.2 \pm 0.9) \times 10^{-3}$  for 5-nitrooxy-2-pentanone.

228 These photolysis rates have been compared in Table 2 to those we obtained in a previous study (Suarez-Bertoa et  
230 al., 2012) for 3-nitrooxy-2-propanone, 3-nitrooxy-2-butanone and 3-methyl-3-nitrooxy-2-butanone using the  
same experimental conditions and methodology. Experimental photolysis frequencies have also been compared  
232 to those calculated using cross sections published in the literature and by assuming a quantum yield equal to  
unity. The intensity of the actinic flux in CESAM chamber was determined by combining measurement of the  
234 spectrum of the lamps with a spectroradiometer and determination of  $J_{\text{NO}_2}$  by chemical actinometry (see section  
2.2). For 3-nitrooxy-2-propanone and 3-nitrooxy-2-butanone, cross sections were taken from Barnes et al.  
(1993). For 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone, for which no data have been provided in the  
236 literature, cross sections were estimated using those for corresponding monofunctional species and by applying  
the enhancement factor ( $r_{nk}$ ) obtained for 3-nitrooxy-2-propanone (Müller et al., 2014):

$$238 \quad r_{nk} = \frac{s_{nk}}{s_n + s_k} \quad (\text{Eq.4})$$

Where  $s_{nk}$ ,  $s_n$  and  $s_k$  are the absorption cross sections of the keto nitrate, the alkyl nitrate and the ketone,  
240 respectively. For 4-nitrooxy-2-butanone, cross sections of 2-butanone and 1-butyl nitrate were taken from  
IUPAC, 2006. For 5-nitrooxy-2-pentanone, cross sections of 2-pentanone ([http://satellite.mpic.de/spectral\\_atlas](http://satellite.mpic.de/spectral_atlas))  
242 and 1-pentyl nitrate (Clemitshaw et al., 1997) were used. From these results, it can be observed that the  
experimental photolysis frequencies ( $J_{\text{exp}}$ ) obtained for 3-nitrooxy-2-propanone and 4-nitrooxy-2-butanone are  
244 very close and can be considered as equal within uncertainties. This suggests that the strong enhancement in the  
cross sections induced by the interaction between the two functional groups, which has been observed for  $\alpha$ -  
246 nitrooxy ketones, also exists with the same amplitude for  $\beta$ -nitrooxy ketones. This is confirmed by the fact the  
experimental value for 4-nitrooxy-2-butanone is in very good agreement with the calculated value, obtained by  
248 assuming that the enhancement factor is the same as the one for 3-nitrooxy-2-propanone. This effect,  
nonetheless, seems to fade away when the two functions are one carbon further away: The experimental  
250 photolysis frequency obtained for 5-nitrooxy-2-pentanone is indeed significantly lower than those for 3-  
nitrooxy-2-propanone and 4-nitrooxy-2-butanone. It is also much lower than the J value calculated by assuming  
252 the same enhancement factor as for 3-nitrooxy-2-propanone. This result suggests that the enhancement is

254 significantly reduced for  $\gamma$ -nitrooxy ketones even if it is probably not totally absent. This can easily be explained  
256 by the fact that the inductive effect of the nitrate group is expected to decrease when the distance between the  
258 functional groups increases. Another explanation would be that the quantum yield is significantly lower than  
260 unity. Finally, by comparing results for 3-nitrooxy-2-propanone, 3-nitrooxy-2-butanone and 3-methyl-3-  
nitrooxy-2-butanone, it can be observed that photolysis frequencies increase with the substitution of the alkyl  
chain. From these kinetic data, it can be concluded that photolysis frequencies of  $\alpha$ - and  $\beta$ -nitrooxy ketones are  
much higher than those obtained when considering the sum of the photolysis frequencies for monofunctional  
species.

262 Products formed by the photolysis of the carbonyl nitrates were investigated by FTIR spectrometry. For both  
264 compounds, only peroxy acetyl nitrate (PAN) was detected. To calculate its formation yield, concentration of  
266 PAN was plotted as a function of  $-\Delta[\text{nitrate}]_{\text{photolysis}}$ , i.e., the carbonyl nitrate loss rate due to photolysis. This one  
268 was calculated by subtracting the loss rate measured during the dark period before the photolysis to the one  
270 measured during the photolysis. Because the yield was calculated as the initial slope of the plot, it was  
considered that the dark period before irradiation was more representative than the one after. The uncertainty on  
the yield was calculated by taking into account the uncertainties on the infrared absorption cross sections of PAN  
(10%) and carbonyl nitrates (10%) as well as the uncertainty on  $J$  (see table 1). For 5-nitrooxy-2-pentanone, this  
uncertainty is quite large because the photolysis rate is relatively slow in comparison to loss to the reactor walls.  
PAN formation yields obtained for both compounds are given in Table 1.

272 For 4-nitrooxy-2-butanone, PAN is formed with a yield equal to unity. Its formation can be explained by the  
274 dissociation of the C(O)-C bond as shown in Scheme 1. This pathway also leads to the formation of the alkyl  
276 radical  $\cdot\text{CH}_2\text{-CH}_2\text{ONO}_2$  which reacts with  $\text{O}_2$  to form the corresponding peroxy radical, this latter evolving to the  
278 formation of the alkoxy by reaction with NO. Two pathways have been considered for the evolution of the  
280 alkoxy radical: i) the decomposition which may lead to the formation of  $\text{NO}_2$  and two molecules of HCHO and  
282 ii) the reaction with  $\text{O}_2$  which produces nitrooxy ethanal, also called ethanal nitrate ( $\text{CH}_2(\text{ONO}_2)\text{-CH(O)}$ ). None  
284 of these two products have been detected by FTIR. However, absorption bands of ethanal nitrate are expected to  
286 be very similar to those of the reactant and it may thus be difficult to distinguish them. In addition, ethanal  
nitrate is expected to photodissociate much faster than the keto nitrate. The other photodissociation pathway is  
the cleavage of the O- $\text{NO}_2$  bond. It leads to the formation of the radical  $\text{CH}_3\text{C(O)CH}_2\text{CH}_2\text{O}\cdot$  which is expected  
to react with  $\text{O}_2$  to form a dicarbonyl product. This product was not observed and this is in good agreement with  
the formation of PAN with a yield equal to unity by the other photodissociation pathway. It should be noticed  
that PAN has been detected as a primary product suggesting that its formation via the photolysis of the  
dicarbonyl product is not expected. In our experiments, it was not possible to measure  $\text{NO}_2$  formation yield  
because large amounts of  $\text{NO}_2$  (hundreds ppb) were introduced with the carbonyl nitrate (probably due to its  
decomposition during the injection).

288 As discussed above, since the enhancement in the cross sections is larger at the higher wavelengths, where  
290 absorption by the nitrate chromophore is very small, it was proposed by Müller et al. (2014) that the absorption  
by the carbonyl chromophore is enhanced due to the neighboring nitrate group. The authors also suggest that the  
photodissociation proceeds by a dissociation of the weak O- $\text{NO}_2$  bond, i.e. that a photon absorption by one  
chromophore (carbonyl group) causes dissociation in another part of the molecule (nitro group). This is not in

292 line with what we observed in our study. From our experiments, we conclude that the photolysis of 4-nitrooxy-2-  
butanone proceeds mainly by a dissociation of the C(O)-C bond. In the former study on the photolysis of 3-  
294 nitrooxy-2-propanone, 3-nitrooxy-2-butanone and 3-methyl-3-nitrooxy-2-butanone (Suarez-Bertoa et al., 2012),  
PAN and carbonyl compounds (respectively, formaldehyde, acetaldehyde and acetone) were detected as major  
296 products. However, branching ratio of the two pathways (dissociation of O-NO<sub>2</sub> and C(O)-C bonds) could not be  
determined as the formation of these products, in particular PAN, can be explained by the two pathways.

298 For 5-nitrooxy-2-pentanone, formation yield of PAN has been observed to be much lower:  $0.16 \pm 0.08$ . As for 4-  
nitrooxy-2-butanone, its formation can be explained by the dissociation of the C(O)-C bond (see Scheme 2). This  
300 result suggests that both dissociation pathways may occur and that O-NO<sub>2</sub> dissociation could be the major one.  
However, this was not confirmed by the detection of the dicarbonyl compound (2-oxo-pentanal) which is  
302 expected to be formed by this pathway. Despite the fact that no standard was available for this compound, no  
characteristic band was observed in the residual spectrum (after subtraction of reactants and PAN spectra).  
304 Because the photolysis rate of 5-nitrooxy-2-pentanone is very low, we suspect that the concentration of this  
product is below the detection limit. Nevertheless, the low PAN yield is a strong indication that O-NO<sub>2</sub>  
306 dissociation may be the major pathway, contrary to what has been observed for 4-nitrooxy-2-butanone. This  
should be considered in the light of the low enhancement of absorption cross sections which has been assumed  
308 for this compound. Hence, in the case of  $\gamma$ -nitrooxy ketones, the enhancement of the absorption by the carbonyl  
chromophore seems to significantly decrease, leading to a lower branching ratio of the C(O)-C bond  
310 dissociation.

### 3.2 OH-oxidation of carbonyl nitrates

312 Rate constants of the OH-oxidation have been measured for 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone.  
Prior to the experiments, it was checked that the carbonyl nitrates do not photolyse nor decompose/adsorb on the  
314 walls of the chamber. Figure 2 represents the kinetic plots obtained for the two carbonyl nitrates. For each  
compound, several independent kinetic experiments were performed and data were combined to provide the  
316  $k_{\text{ketonitrate}}/k_{\text{methanol}}$  for each compound (see Figure 3). In order to limit errors in the quantification of reactants due  
to the possible formation of carbonyl nitrates as products, only the very beginning of the experiments was taken  
318 into account for the kinetic plots. This explains the small number of experimental points. The obtained rate  
constants are given in Table 3. These data are, to our knowledge, the first determinations of the rate constants for  
320 the reaction of OH with these two carbonyl nitrates. From these data, it can be concluded that 4-nitrooxy-2-  
butanone and 5-nitrooxy-5-pentanone have similar reactivity towards OH radicals with rate constants equal to  
322  $(2.9 \pm 1.0) \times 10^{-12}$  and  $(3.3 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

Rate constants provided in this study, as well as those previously reported for a series of  $\alpha$ -nitrooxy-ketones  
324 (Suarez-Bertoa et al., 2012) have been compared to those estimated using structure-activity relationships (SARs)  
in Table 4. Different SARs have been evaluated: i) the one developed by Kwok and Atkinson (1995) with  
326 updated factors  $F(-\text{ONO}_2) = 0.14$  and  $F(-\text{C-ONO}_2) = 0.28$  from Bedjanian et al. (2018); ii) the one developed by  
Kwok and Atkinson (1995) with updated factors  $F(-\text{ONO}_2) = 0.8$  and  $F(-\text{C-ONO}_2) = 0.1$  from Suarez-Bertoa et  
328 al. (2012); iii) the one developed by Neeb (2000) which proposes a different type of parametrization and has  
been observed to be particularly accurate for oxygenated species; and iv) the one developed by Jenkin et al.

330 (2018) which proposes a parametrization very similar to the one from Kwok and Atkinson (1995) and Bedjanian  
et al. (2018). The rate constant for 5-nitrooxy-2-pentanone is reasonably well reproduced by all SARs (within a  
332 factor of 2). For 4-nitrooxy-2-butanone, only the parametrization provided by Suarez-Bertoa et al. (2012)  
succeeds in reproducing the experimental value. This can be explained by the fact that this parametrization has  
334 been optimized for carbonyl nitrates while the others have been developed using the entire dataset for  
compounds containing a nitrate group (-ONO<sub>2</sub>) (Jenkin et al., 2018) or using the dataset for alkyl nitrates  
336 (Bedjanian et al., 2018). The main difference between these parametrizations is that in Suarez-Bertoa et al.  
(2012), the factor F(-ONO<sub>2</sub>) is much less deactivating than for the others. This could result from electronic  
338 interactions between the two functional groups. However, Suarez-Bertoa et al. (2012) noticed that their  
parametrization gives poor results for alkyl nitrates, suggesting that a specific parametrization has to be used for  
340 multifunctional species. This also suggests that the principle of SARs based on the group additivity method may  
not be suitable for multifunctional molecules.

342 From these experiments, several oxidation products have been detected: HCHO, PAN and methylglyoxal for 4-  
nitrooxy-2-butanone, and HCHO, PAN and 3-nitrooxy-propanal for 5-nitrooxy-2-pentanone. However, their  
344 quantification was highly uncertain because the infrared spectra were complex due to the presence of methanol,  
isopropyl nitrite, impurities (in particular acetic acid) and their oxidation products. Dedicated mechanistic  
346 experiments should now/in the near future be performed using HONO as OH source in order to simplify the  
chemical mixture.

### 348 3.3 Atmospheric implications

Atmospheric lifetimes of the investigated compounds are presented in Table 5. The photolysis rates were  
350 estimated using  $J_{\text{nitrate}}/J_{\text{NO}_2}$  ratios measured in this study and using  $J_{\text{NO}_2}$  for typical tropospheric irradiation  
conditions corresponding to the 1<sup>st</sup> July at noon and at 40° latitude North with (overhead ozone column 300,  
352 albedo 0.1; TUV NCAR Model, [http://www.cprm.acd.ucar.edu/Models/TUV/Interactive\\_TUV/](http://www.cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/)). For  $J_{\text{NO}_2} = 1.03$   
 $\times 10^{-2} \text{ s}^{-1}$ , photolysis frequencies of carbonyl nitrates are:  $(6.1 \pm 0.9) \times 10^{-5} \text{ s}^{-1}$  for 4-nitrooxy-2-butanone and  $(3.3$   
354  $\pm 0.9) \times 10^{-5} \text{ s}^{-1}$  for 5-nitrooxy-2-pentanone. Under these irradiation conditions, lifetimes ( $\tau_{\text{hv}} = 1/J$ ) were found  
to be 4 and 8 hours, respectively. For OH-oxidation, lifetimes ( $\tau_{\text{OH}} = (1/(k_{\text{OH}}[\text{OH}])))$  were calculated using typical  
356 OH concentrations of  $2 \times 10^6 \text{ molecule cm}^{-3}$  (Atkinson and Arey, 2003). They are both equal to approximately  
two days. Hence, it appears that for 4-nitrooxy-2-butanone and for 5-nitrooxy-2-pentanone, photolysis is a more  
358 efficient sink than oxidation by OH radicals. An identical conclusion was obtained for  $\alpha$ -nitrooxy carbonyls  
(Suarez-Bertoa et al., 2012; Barnes et al., 1993; Zhu et al., 1991). However, OH-initiated oxidation is not  
360 negligible, especially under polluted conditions where OH concentrations can be higher than  $1 \times 10^7 \text{ molecule}$   
 $\text{cm}^{-3}$ .

362 In order to evaluate the impact of these carbonyl nitrates on the nitrogen budget and the transport of NO<sub>x</sub>, it  
is crucial to determine whether their atmospheric sinks, here mainly photolysis, release NO<sub>2</sub> or not. For 4-nitrooxy-  
364 2-butanone, we observed that the photolysis proceeds mainly by a dissociation of the C(O)-C bond which does  
not necessarily lead to the release of NO<sub>2</sub> (see Scheme 2). In our experimental conditions (i.e., with high NO<sub>2</sub>  
366 mixing ratios), this pathway leads to the formation of PAN which was detected with a yield equal to unity.  
Under more realistic NO/NO<sub>2</sub> ratio, this reaction may also produce HCHO and CO<sub>2</sub>. The co-products of PAN,

368 which could not be detected in our study, are expected to be formaldehyde + NO<sub>2</sub> or ethanal nitrate. One NO<sub>2</sub>  
molecule is hence released in the first hypothesis. Ethanal nitrate may react and undergo photolysis even faster  
370 than nitrooxy ketones and may thus lead to NO<sub>2</sub> release quite rapidly. However, as data on the reactivity of  
ethanal nitrate are not available in the literature, one cannot provide a definite conclusion. In the case of 5-  
372 nitrooxy-2-pentanone, the dissociation of the C(O)-C bond has been observed to be a minor pathway suggesting  
that the major one, which was not directly observed here, is the O-NO<sub>2</sub> dissociation. This process certainly leads  
374 to the release of NO<sub>2</sub>.

#### 4 Conclusions

376 This paper presents the first study on the atmospheric reactivity of 4-nitrooxy-2-butanone and 5-nitrooxy-2-  
pentanone. Thanks to experiments in simulation chambers, photolysis frequencies and rate constants of the OH-  
378 oxidation were measured for the first time. From these results, it is concluded that, similarly to  $\alpha$ -nitrooxy  
ketones,  $\beta$ -nitrooxy ketones have enhanced UV absorption cross sections and quantum yields equal or close to  
380 unity, making photolysis a very efficient sink for these compounds. Results obtained for 5-nitrooxy-2-pentanone  
which is a  $\gamma$ -nitrooxy ketone, suggest a lower enhancement of cross sections leading to slightly longer  
382 atmospheric lifetimes. This can easily be explained by the increasing distance between the two chromophore  
groups. Some photolysis products were also detected allowing estimating the branching ratio between the two  
384 possible pathways, i.e., the dissociation of the C(O)-C bond and the one of the O-NO<sub>2</sub> bond. For 4-nitrooxy-2-  
butanone, we conclude that the photolysis proceeds mainly by a dissociation of the C(O)-C bond which does not  
386 necessarily lead to the release of NO<sub>2</sub>. In the case of 5-nitrooxy-2-pentanone, our results suggest that the  
dissociation of the O-NO<sub>2</sub> bond is the major pathway. Reactivity of 4-nitrooxy-2-butanone and 5-nitrooxy-2-  
388 pentanone with OH radicals was also investigated. Both compounds have similar reactivity towards OH radicals  
leading to lifetimes of approximately two days. Experimental rate constants are in good agreement with those  
390 estimated by the SAR proposed by Kwok and Atkinson (1995) when using the parametrization proposed by  
Suarez-Bertoa et al. (2012) for carbonyl nitrates. However, this specific parametrization does not allow  
392 reproducing experimental data for monofunctional alkyl nitrates, suggesting that specific parametrization should  
be used for multifunctional species. Finally, these compounds are expected to be removed from the atmosphere  
394 fairly rapidly and to act as (only) temporary reservoirs of NO<sub>x</sub>. If formed during the night, they could however  
contribute to longer range transport of NO<sub>x</sub>.

#### 396 *Author contributions*

BPV coordinated the research project. BPV, RSB and JFD designed the experiments in simulation chambers.  
398 RSB performed the experiments with the technical support of MC and EP. RSB and MDa performed the organic  
syntheses. BPV, RSB and MDu performed the data treatment and interpretation. BPV and RSB wrote the paper  
400 and BPV was in charge of its final version. All coauthors revised the manuscript content, giving final approval of  
the version to be submitted.

#### 402 *Competing interests*

The authors declare that they have no conflict of interest.

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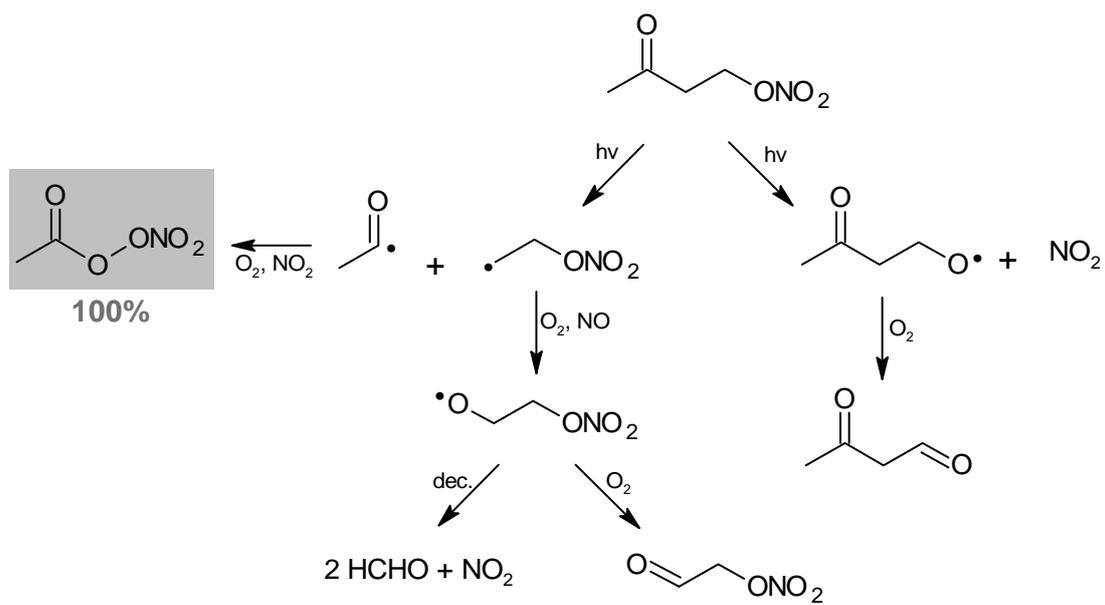
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**Figure, scheme and table captions**

- 514 **Scheme 1.** Photolysis pathways of 4-nitrooxy-2-butanone. Detected products are indicated with a grey background and their formation yield in given (in %).
- 516 **Scheme 2.** Photolysis pathways of 5-nitrooxy-2-pentanone. Detected products are indicated with a grey background and their formation yield in given (in %).
- 518 **Figure 1.** Kinetic plots for (a) the photolysis of 4-nitrooxy-2-butanone (experiment 2) and (b) the photolysis of 5-nitrooxy-2-pentanone (experiment 5). Red lines correspond to linear regressions.
- 520 **Figure 2.** Kinetic plots for the oxidation by OH radicals of 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone. For 5-nitrooxy-2-pentanone, data have been shifted by 0.2 in y axis. Different symbols correspond to different experiments.
- 522
- Table 1.** Photolysis rates and PAN yields for 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone measured in
- 524 CESAM chamber.
- Table 2.** Comparison of experimental photolysis rates of carbonyl nitrates with those calculated for CESAM irradiation conditions and by assuming a quantum yield equal to unity.
- 526
- Table 3.** Rate constants for the OH-oxidation of 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone.
- 528 **Table 4.** Comparison of experimental rate constants for the OH-oxidation of carbonyl nitrates with those estimated by SARs.
- 530 **Table 5.** Atmospheric lifetimes of carbonyl nitrates towards photolysis and reaction with OH radicals.

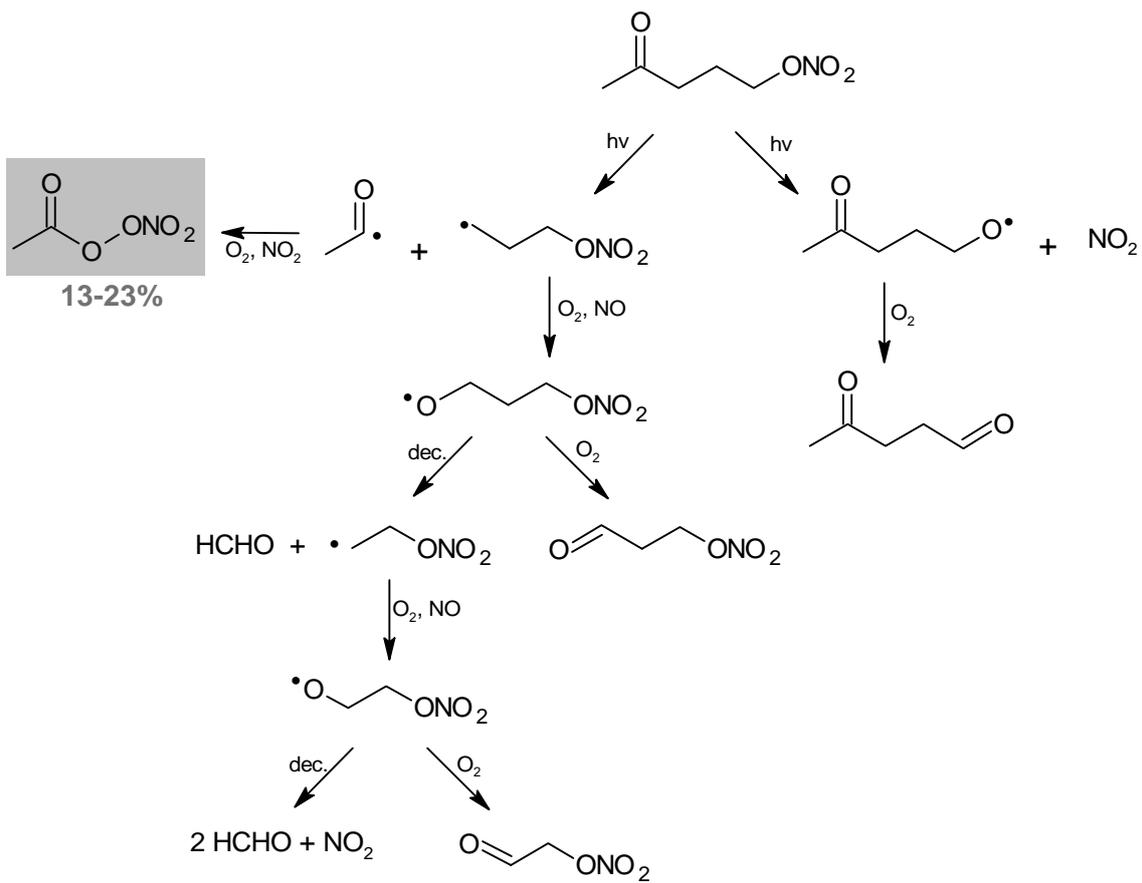
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**Scheme 1.**

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538 **Scheme 2 (corrected).**

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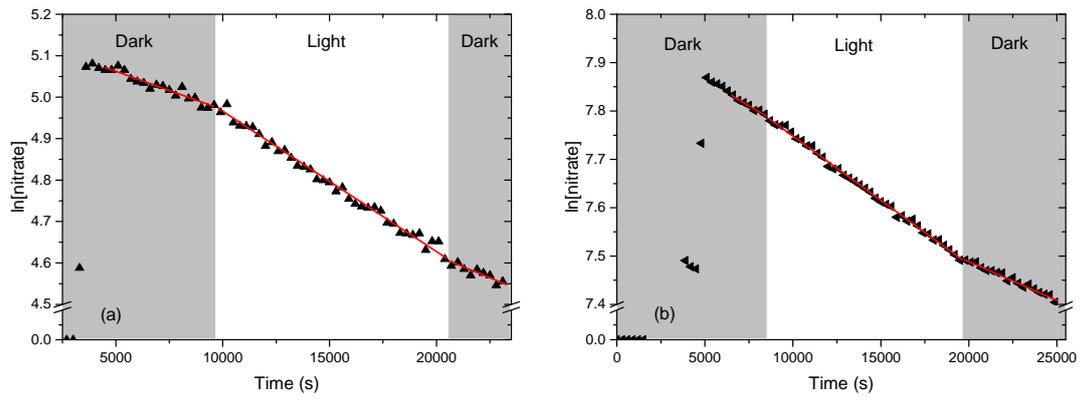


Figure 1 (corrected by showing the experiment from the beginning).

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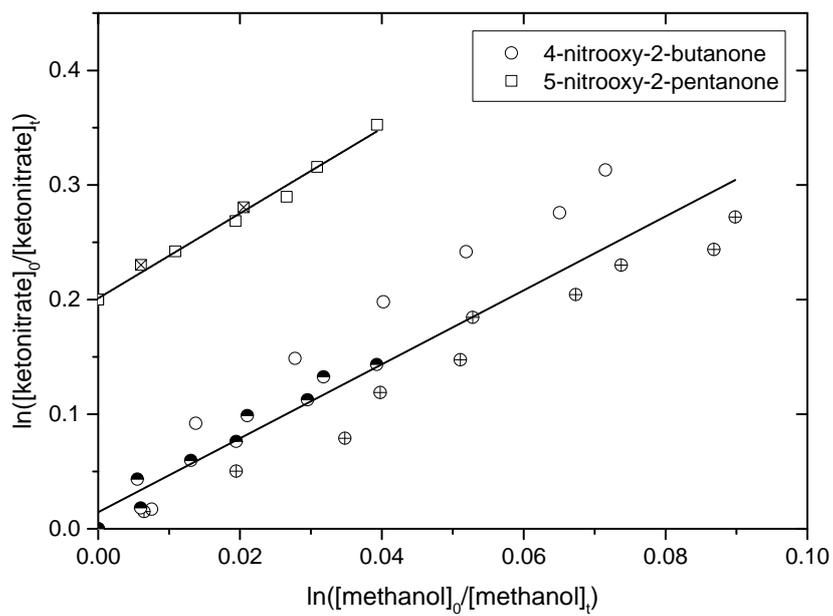


Figure 2.

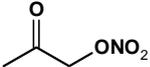
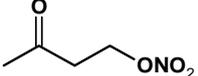
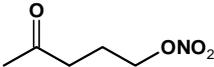
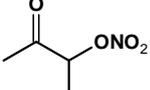
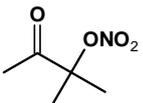
Table 1 (corrected).

Compound	Experim.	$k_{\text{before}}^{\text{a}}$ ( $\times 10^{-5} \text{ s}^{-1}$ )	$k_{\text{after}}^{\text{b}}$ ( $\times 10^{-5} \text{ s}^{-1}$ )	$(k+J_{\text{nitrate}})^{\text{c}}$ ( $\times 10^{-5} \text{ s}^{-1}$ )	$J_{\text{nitrate}}^{\text{d}}$ ( $\times 10^{-5} \text{ s}^{-1}$ )	PAN yield (%)
4-nitrooxy- 2-butanone	1	$0.8 \pm 0.1$	-	$2.1 \pm 0.1$	$1.3 \pm 0.2$	$100 \pm 35$
	2	$1.9 \pm 0.2$	$2.1 \pm 0.1$	$3.3 \pm 0.1$	$1.3 \pm 0.3$	$100 \pm 40$
<b>Average</b>					<b><math>1.3 \pm 0.2</math></b>	<b><math>100 \pm 30</math></b>
5-nitrooxy- 2-pentanone	3	$2.0 \pm 0.2$	$1.1 \pm 0.2$	$2.3 \pm 0.1$	$0.7 \pm 0.4$	$13 \pm 9$
	4	$1.9 \pm 0.2$	$1.1 \pm 0.1$	$2.2 \pm 0.1$	$0.7 \pm 0.4$	$13 \pm 9$
	5	$2.1 \pm 0.2$	$1.6 \pm 0.2$	$2.7 \pm 0.1$	$0.8 \pm 0.3$	$23 \pm 13$
<b>Average</b>					<b><math>0.7 \pm 0.2</math></b>	<b><math>16 \pm 8</math></b>

552 <sup>a, b</sup> dark decay rate due to wall loss, before and after irradiation; <sup>c</sup> decay rate during irradiation  
 554 period; <sup>d</sup> photolysis rate calculated as the difference between the decay rate during irradiation and  
 556 the average dark decay rate.

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Compound	$J_{\text{exp}} (\times 10^{-5} \text{ s}^{-1})$	$J_{\text{calc}} (\times 10^{-5} \text{ s}^{-1})$ ( $\phi=1$ )
<b>3-nitrooxy-2-propanone</b> 	$1.5 \pm 0.1$ (Suarez-Bertoa et al., 2012)	$1.4^{\text{b}}$
<b>4-nitrooxy-2-butanone</b> 	$1.3 \pm 0.2$ (This work)	$1.6^{\text{a}}$
<b>5-nitrooxy-2-pentanone</b> 	$0.7 \pm 0.2$ (This work)	$1.8^{\text{a}}$
<b>3-nitrooxy-2-butanone</b> 	$1.8 \pm 0.1$ (Suarez-Bertoa et al., 2012)	$2.2^{\text{b}}$
<b>3-methyl-3-nitrooxy-2-butanone</b> 	$2.31 \pm 0.05$ (Suarez-Bertoa et al., 2012)	ND

<sup>a</sup> calculated with estimated cross sections (see text); <sup>b</sup> calculated with experimental cross sections from literature;

**Table 3.**

<b>Compound</b>	$k_{\text{nitrate}}/k_{\text{methanol}}$	$k_{\text{nitrate}} \times 10^{-12}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
4-nitrooxy-2-butanone	$3.25 \pm 0.47$	$2.9 \pm 1.0$
5-nitrooxy-2-pentanone	$3.70 \pm 0.28$	$3.3 \pm 0.9$

Compound	$k_{\text{exp}}$ $\times 10^{-13}$	$k_{\text{SAR}}$ Atkinson/Bedjanian <sup>a</sup> $\times 10^{-13}$	$k_{\text{SAR}}$ Atkinson/Suarez <sup>b</sup> $\times 10^{-13}$	$k_{\text{SAR}}$ Neeb <sup>c</sup> $\times 10^{-13}$	$k_{\text{SAR}}$ Jenkin <sup>d</sup> $\times 10^{-13}$
3-nitrooxy-2-propanone	6.7 <sup>e</sup>	2.0	6.6	5.8	2.5
3-nitrooxy-2-butanone	10.1 <sup>e</sup>	4.5	13.2	6.8	3.7
3-methyl-3nitrooxy-2-butanone	2.6 <sup>e</sup>	4.0	2.1	2.4	4.3
4-nitrooxy-2-butanone	29 <sup>f</sup>	8.1	30.9	8.7	8.1
5-nitrooxy-2-pentanone	33 <sup>f</sup>	21.4	22.5	47.6	19.5

566 Rate constants are expressed in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; <sup>a</sup> SAR developed by Kwok and Atkinson (1995) with F(-  
568  $\text{ONO}_2$ ) and F(-C- $\text{ONO}_2$ ) from Bedjanian et al., 2018; <sup>b</sup> SAR developed by Kwok and Atkinson (1995) with F(-  
 $\text{ONO}_2$ ) and F(-C- $\text{ONO}_2$ ) from Suarez-Bertoa et al., (2012) ; <sup>c</sup> SAR developed by Neeb (2000); <sup>d</sup> SAR developed  
by Jenkin et al. (2018) ; <sup>e</sup> experimental data from Suarez-Bertoa et al. (2012); <sup>f</sup> This work.

**Table 5.**

Compound	$J \times 10^{-5}$ <sup>a</sup> (s <sup>-1</sup> )	$\tau_{hv}$ (hours)	$k_{OH} \times 10^{-12}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$\tau_{OH}$ <sup>b</sup> (hours)
4-nitrooxy-2-butanone	6.1 ± 0.9	4	2.9 ± 1.0	48
5-nitrooxy-2-pentanone	3.3 ± 0.9	8	3.3 ± 0.9	42

570 <sup>a</sup> photolysis frequencies estimated for a typical solar actinic flux (40°N, 1<sup>st</sup> July, noon) by applying a factor 4.7  
to those measured in CESAM chamber (see section 2.2); <sup>b</sup> estimated for [OH] = 2 × 10<sup>6</sup> molecule cm<sup>-3</sup>

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