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Atmospheric Chemistry and Physics Discussions

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 #2

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This article presents results from simulation chamber studies of the photolysis and hydroxyl radical initiated oxidation of two carbonyl nitrates, 4-nitrooxy-2-butanone and 5-nitrooxy-2-pentanone. Experimental photolysis frequencies were determined and used to calculate photolysis rates and lifetimes under atmospheric conditions. Rate coefficients for the reaction of these compounds with hydroxyl radicals were also determined using the relative rate method. Some information on the products arising from these atmospheric degradation processes is reported.

Overall, this is a good piece of work, which is both relevant and of interest to the atmo-

spheric science community. The experiments have been carefully performed and the data has been treated and interpreted well. The work is suitable for publication in Atmospheric Chemistry and Physics provided that the one minor comment and technical corrections are addressed appropriately.

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(experimental) to J(maximum), where the latter term is calculated using a quantum yield of unity (Clifford et al., 2011). It is recommend 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.

Technical Corrections

1. Lines 20-22: It is probably better to report the measured photolytic rate coefficients as j(carbonyl nitrate)/j(NO2) values, as in Clifford et al (2011). This would allow users of the data to calculate j(carbonyl nitrate) under a range of sunlight conditions.

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

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

4. Line 62: Give full name for PANs

5. Lines 66 and 68: Replace "works" with investigations or studies.

6. Line 83: Replace "photochemical" with atmospheric.

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

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

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

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

11. Line 258: Define PAN

12. Line 295: Should be Scheme 2.

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.

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

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.

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.

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

18. Page 23, Table 4: Use the times symbol instead of “x”.

References:

Clifford, G. M.; Hadj-Aissa, A.; Healy, R. M.; Mellouki, A.; Muñoz, A.; Wirtz, K.; Martín-Reviejo, M.; Borrás Garcia, E.; Wenger, J. C.: The atmospheric photolysis of o-tolualdehyde, Environmental Science & Technology, 45, 9649-9657 (2011).

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