Atmos. Chem. Phys. Discuss., 13, C12028–C12030, 2014
www.atmos-chem-phys-discuss.net/13/C12028/2014/

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Fast photolysis of carbonyl nitrates from isoprene" *by* J.-F. Müller et al.

J.-F. Müller et al.

jean-francois.muller@aeronomie.be

Received and published: 6 February 2014

Reply to Reviewers

We thank the referees for their very positive comments on our manuscript. We answer below the minor points raised by Reviewer 1.

Pg. 31129, line 25 and 31134, line 24 - MACR is an enal not an enone. Maybe the wording could be changed to "enals and enones" in both cases?

Changed as suggested.

Pg. 31133, and Figure 2. It might be worth showing the calculated spectra for the additional species considered here, perhaps in the supplement?

The cross sections of other (non-conjugated) monofunctional aldehydes are all very similar to those of either acetaldehyde or i-butyraldehyde. Therefore, the cross sections of other nitrooxy aldehydes estimated using Eq. (2) will be also very similar to those shown on the figure.

Pg. 31135, end of Section 3. It would be helpful to refer to Table 3 here, to present thephotolysis rates implied by the cross section and quantum yield estimates provided in Sections 2 and 3.

Done as suggested.

Additional changes to the manuscript

We revised two paragraphs in Section 3 discussing the possible photolysis pathways of nitrooxy-ketones. In particular, an additional pathway (releasing NO instead of NO_2) is presented as a possible route. Furthermore, a recent study (Favero et al., 2013) is mentioned, indicating that internal conversion of the excited S1 state to the ground state S0 might compete with intersystem crossing to the triplet state. Since dissociation of S0 has to compete with collisional stabilisation,it follows that the photolysis quantum yield of large carbonyl nitrates might be lower than unity. The updated text now read:

“The near-unity quantum yield of nitrooxy-ketones can be rationalized by mechanisms similar to that proposed for the hydroperoxy enals HPALDs (Peeters and Müller, 2010). Photon absorption by the carbonyl chromophore yielding the excited S1 state and fast intersystem crossing (ISC) to the triplet T1 state may be followed, via spin exchange, by avoided crossing of the T1 surface with the repulsiveT2 surface of the O-NO_2 chromophore, resulting in fast dissociation of the weak (ca. 40 kcal/mol) O-NO_2 bond. Alternatively, a chemical rearrangement of the excited T1 state may lead to either indirect dissociation to the same final products, or to multistep decomposition yielding NO, a carbonyl and an acyloxy radical. Another possible mechanism is internal conversion (IC) of the initially excited singlet state S1 to the ground state S0, followed by prompt dissociation of the weakest bond, i.e. O-NO_2, due to the high vibrational energy. Indeed, in the photodissociation dynamics of ketones, IC of S1 to S0 is expected to compete effectively with ISC of S1 to the triplet T1 state (Favero et al., 2013). Due to the competition with collisional stabilisation, this latter mechanism can only be effective for molecules that are not too large, allowing dissociation on the S0 surface still faster than $10^9 s^{-1}$.

In any case, a quantum yield not much below unity is likely also for other carbonyl nitrates, including the β-nitrooxy ketone and nitrooxy aldehydes of Table 1, in particular the enal NC4CHO structurally very similar to HPALDs (replacing ONO_2 by a hydroperoxy group). For simplicity, we'll assume a value of unity in the calculations presented in the next section, and O–NO_2 breakup will be assumed to be the only photolysis channel considered. Typical photolysis rates of key carbonyl nitrates from isoprene implied by the above recommendations for cross sections and quantum yields are given in Table 3. "

Favero, L., G. Granucci, and M. Persico: Dynamics of acetone photodissociation: a surface hopping study, Phys. Chem. Chem. Phys., 15, 20651–20661, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 31127, 2013.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper