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Supplement to “Fast photolysis of carbonyl nitrates from isoprene”

J.-F. Müller¹, J. Peeters², and T. Stavrakou²

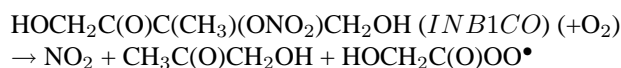
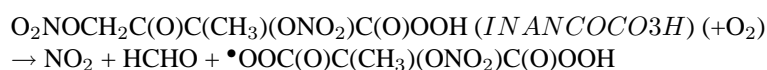
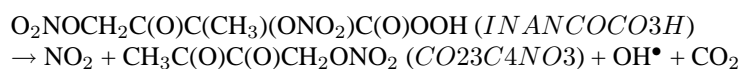
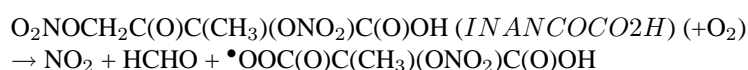
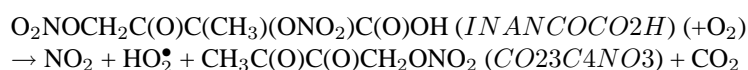
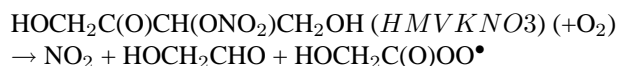
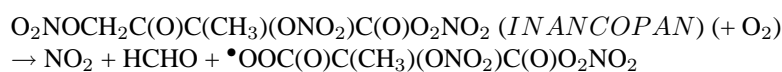
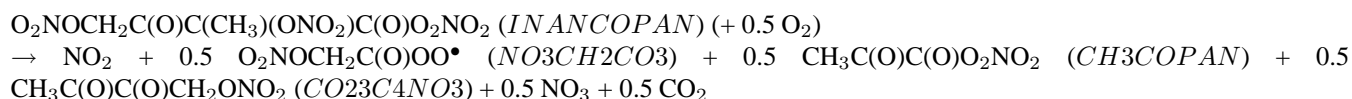
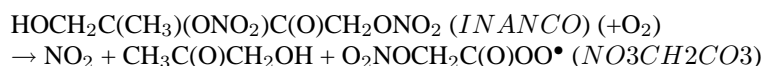
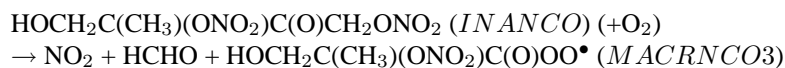
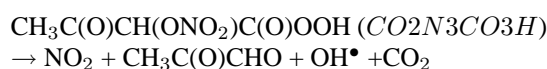
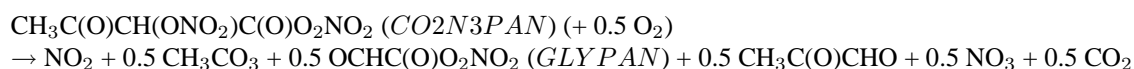
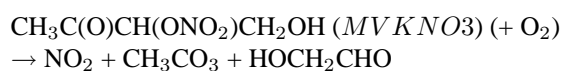
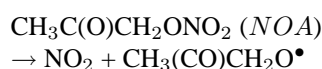
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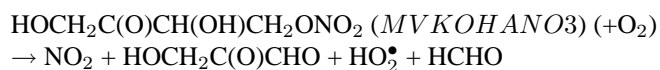
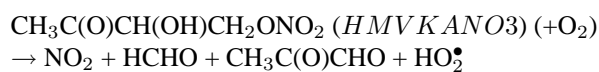
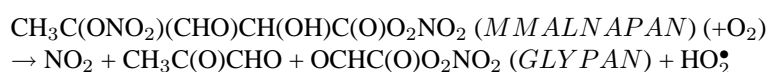
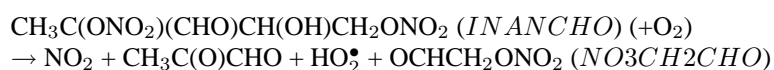
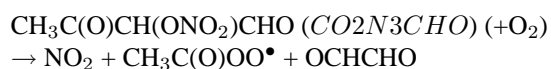
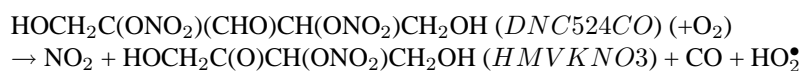
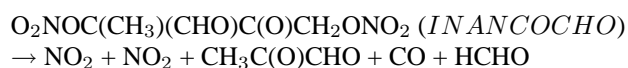
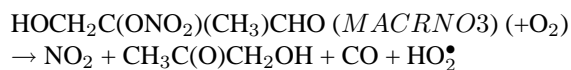
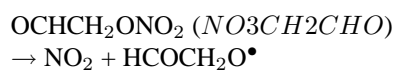
²Department of Chemistry, University of Leuven, B-3001, Heverlee, Belgium

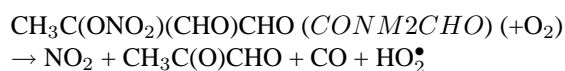
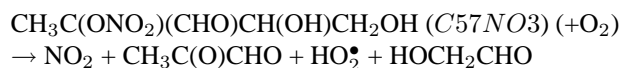
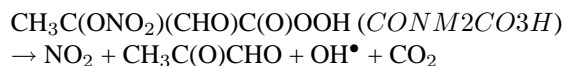
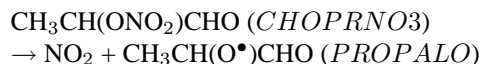
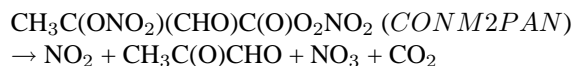
The photolysis reactions of carbonyl nitrates formed in the oxidation of isoprene according to MCMv3.2 are listed below. Photolysis proceeds by NO₂ elimination. Decomposition barriers of the oxy co-product are determined from Vereecken and Peeters (2009). Subsequent reaction steps involving O₂ are indicated by (+O₂) on the reactant side. MCMv3.2 notation is indicated in italics and between parentheses.

Cross sections and quantum yields are estimated as discussed in the main article. For α -dicarbonyl nitrates, we use the cross sections of the closest α -dicarbonyl (e.g. methylglyoxal), with quantum yields assumed equal to unity. For the α -nitrooxy enal, we use the cross sections of methacrolein, also with unit quantum yield.

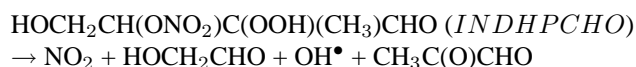
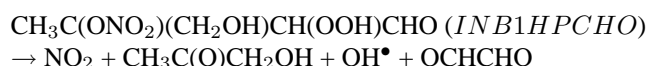
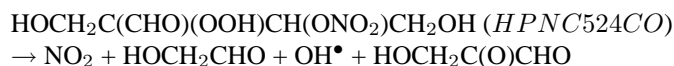
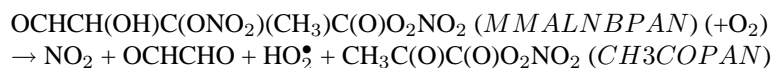
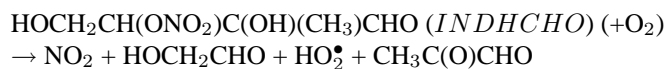
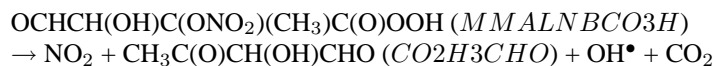
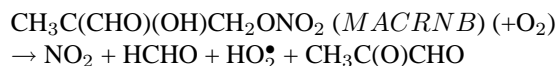
1 α -nitrooxy ketones



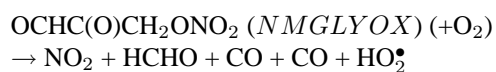
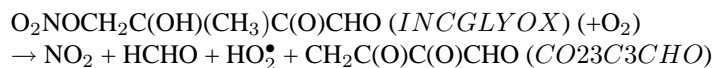
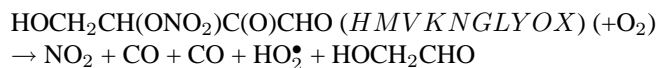
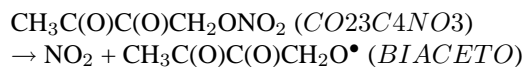
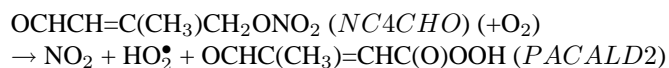
2 β -nitrooxy ketones**3 α -nitrooxy aldehydes**



4 β -nitrooxy aldehydes



Note that RO–OH dissociation is another possible significant photolysis pathway for the nitrooxy hydroperoxy carbonyls (*HPNC524CO*, *INB1HPCHO*, *INDHPCHO*). The photolysis of hydroperoxy carbonyls will be investigated in a forthcoming study.

5 α -dicarbonyl nitrates**6 α -nitrooxy enal**

The peracid aldehyde *PACALD2* is formed in the photolysis of a hydroperoxy enal (HPALD) from isoprene (Peeters and Müller, 2010).

References

- Peeters, J., and J.-F. Müller: HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: Experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 12(42), 14227–14235, doi:10.1039/C0CP00811G, 2010.
- Vereecken, L., and J. Peeters: Decomposition of substituted alkoxy radicals - part I: a generalized structure-activity relationship for reaction barrier heights, *Phys. Chem. Chem. Phys.*, 11, 9062–9074, 2009.