



Fast photolysis of carbonyl nitrates from isoprene

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We show that photolysis is, by far, the major atmospheric sink of isoprene-derived carbonyl nitrates. Empirical evidence from published laboratory studies on the absorption cross sections and photolysis rates of α -nitrooxy ketones suggests that the presence of the nitrate group (i) greatly enhances the absorption cross sections, and (ii) facilitates dissociation to a point that the photolysis quantum yield is close to unity, with O–NO₂ dissociation as the likely major channel. On this basis, we provide new recommendations for estimating the cross sections and photolysis rates of carbonyl nitrates. The newly estimated photorates are validated using a chemical box model against measured temporal profiles of carbonyl nitrates in an isoprene oxidation experiment by Paulot et al. (2009). The comparisons for ethanal nitrate and for the sum of methacrolein- and methylvinylketone nitrates strongly supports our assumptions of large cross section enhancements and a near-unit quantum yield for these compounds. These findings have significant atmospheric implications, as carbonyl nitrates constitute an important component of the total organic nitrate pool over vegetated areas: the photorates of key carbonyl nitrates from isoprene are estimated to be typically between ~ 3 and 20 times higher than their sink due to reaction with OH in relevant atmospheric conditions. Moreover, since the reaction is expected to release NO₂, photolysis is especially effective in depleting the total organic nitrate pool.