

Production of OH from Organic Peroxy Radical Photolysis: Absorption Cross-Sections, Quantum Yields, and Atmospheric Implications

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In urban environments, there is reasonable agreement (within a factor of 2) between measured ambient concentrations of OH and those predicted by computer models. However, for environments with high concentrations of biogenic VOCs and low concentrations of NO_x (= NO + NO₂), measured-to-modelled ratios of up to 10 have been reported.¹ Model-measurement discrepancies (approx. a factor of 4) have also been seen in more anthropogenically-influenced areas with low concentrations of NO_x.² One possible source of OH that has not been explored is the photolysis of organic peroxy radicals (RO₂). Production of OH has been observed from the photolysis of methylperoxy radicals,³ and model calculations suggest that RO₂ photolysis could be a significant source of OH.⁴ One difficulty in assessing the impact of RO₂ photolysis as a potential OH source has been a lack of reported measurements of total absorption cross-sections and OH quantum yields for RO₂ photolysis at wavelengths greater than 300 nm, a region where tropospheric solar flux is steadily increasing.

Total absorption cross-sections for RO₂ were measured in the near ultraviolet (λ = 280–400 nm) with a novel multipass UV-visible spectrometer. Absorption cross-sections for OH production were measured with a three-laser flash photolysis apparatus at wavelengths from 310–360 nm. Both measurements were used to calculate OH yields from the photolysis of RO₂. We present total absorption cross-sections, absorption cross-sections for OH production, and OH quantum yields for RO₂ radicals derived from isoprene, ethylene, and tetramethylethylene (2,3-methyl-2-butene). To assess the impact of the photolysis of isoprene-derived RO₂ on ambient OH concentrations in an environment characterized by high concentrations of biogenic VOCs and low concentrations of NO_x, a modeling case study based on the conditions for the 2008 Oxidant and Particle Photochemical Processes above a South-East Asian Tropical Rainforest (OP-3) field campaign was conducted. Model results suggest that the photolysis of RO₂ from isoprene is a minor source of OH at the site of the OP-3 campaign and is insufficient to account for the model-measurement discrepancy seen during this campaign.

References

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