



Laboratory studies of the atmospheric oxidation of isoprene in clean-air

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Field measurements in regions heavily influenced by biogenic emissions indicate that hitherto unknown radical-recycling mechanisms govern the oxidation of the key biogenic NMHC isoprene (2-methyl butadiene, C₅H₈) in clean air. Accordingly, a series of laboratory studies were conducted to investigate both the rate of atmospheric isoprene removal and one potential radical recycling pathway.

Spectroscopic methods were used to determine UV absorption cross-sections (184.9 nm and 193 – 233 nm) which were subsequently used in kinetic experiments to monitor isoprene concentrations. The pulsed laser photolysis (PLP) method of radical generation coupled to direct laser induced fluorescence (LIF) detection of the hydroxyl radical, OH, was used to determine rate coefficients, $k_1(M,T)$, for the primary addition step $\text{OH} + \text{C}_5\text{H}_8 = \text{HOC}_5\text{H}_8$ (R1). In line with previous studies, no dependence on bath-gas pressure (5 – 200 mbar) or composition (M = N₂ or air) was found and k_1 exhibited a non-Arrhenius temperature dependence (240 – 355 K). Careful consideration of all available spectroscopic and kinetic data allowed small but significant literature anomalies in k_1 (298 K) to be resolved.

PLP of multiple precursors in air was used to generate (R1)-derived peroxy radicals (HOC₅H₈O₂) in the presence of excess hydroperoxyl radicals, HO₂. Calibrated LIF detection of OH, together with analysis by numerical simulation, was used to demonstrate that, in contrast to other biogenic systems (eg. acetaldehyde) no significant quantities of OH are recycled via $\text{HO}_2 + \text{HOC}_5\text{H}_8\text{O}_2$. These results, whilst reducing uncertainties in two key atmospheric reactions, leave unresolved the question of how radicals are recycled during the atmospheric oxidation of isoprene in clean-air.