

# Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide HO<sub>x</sub> radicals in the tropical upper troposphere

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## Abstract

Concurrent measurements of OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>OOH concentrations were made during an aircraft flight over the tropical South Pacific that followed a back-and-forth pattern at constant 10 km altitude for 4 hours. One end of the pattern sampled an aged convective outflow while the other end sampled the background atmosphere. Concentrations of HO<sub>2</sub> and CH<sub>3</sub>OOH in the convective outflow were elevated by 50% and 350% relative to background, respectively, while concentrations of OH and H<sub>2</sub>O<sub>2</sub> were not elevated. The high CH<sub>3</sub>OOH concentrations in the outflow were due to convective pumping from the marine boundary layer. In contrast to CH<sub>3</sub>OOH, H<sub>2</sub>O<sub>2</sub> was not enhanced in the outflow because its high water solubility allows efficient scavenging in the convective updraft. A photochemical model calculation constrained with the ensemble of aircraft observations reproduces the HO<sub>2</sub> enhancement in the outflow and attributes it to the enhanced CH<sub>3</sub>OOH; the calculation also reproduces the lack of OH enhancement in the outflow and attributes it to OH loss from reaction with CH<sub>3</sub>OOH. Further analysis of model results shows substantial evidence that the rate constant used in standard mechanisms for the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction is about a factor of 3 too low at the low temperatures of the upper troposphere. A sensitivity simulation using a value of  $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 233 K for this rate constant yields better agreement with observed HO<sub>2</sub> concentrations, and better closure of the chemical budgets for both CH<sub>3</sub>OOH and H<sub>2</sub>O<sub>2</sub>. The CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction then becomes the single most important loss pathway for HO<sub>x</sub> radicals (HO<sub>x</sub> = OH + peroxy radicals) in the upper troposphere.

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The full text of this paper is available as a [postscript file](#)