Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide $\text{HO}_x$ radicals in the tropical upper troposphere


**Abstract**

Concurrent measurements of OH, HO$_2$, H$_2$O$_2$, and CH$_3$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$_2$ and CH$_3$OOH in the convective outflow were elevated by 50% and 350% relative to background, respectively, while concentrations of OH and H$_2$O$_2$ were not elevated. The high CH$_3$OOH concentrations in the outflow were due to convective pumping from the marine boundary layer. In contrast to CH$_3$OOH, H$_2$O$_2$ 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$_2$ enhancement in the outflow and attributes it to the enhanced CH$_3$OOH; the calculation also reproduces the lack of OH enhancement in the outflow and attributes it to OH loss from reaction with CH$_3$OOH. Further analysis of model results shows substantial evidence that the rate constant used in standard mechanisms for the CH$_3$O$_2$ + HO$_2$ reaction is about a factor of 3 too low at the low temperatures of the upper troposphere. A sensitivity simulation using a value of $3.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 233 K for this rate constant yields better agreement with observed HO$_2$ concentrations, and better closure of the chemical budgets for both CH$_3$OOH and H$_2$O$_2$. The CH$_3$O$_2$ + HO$_2$ reaction then becomes the single most important loss pathway for HO$_x$ radicals (HO$_x$ = OH + peroxy radicals) in the upper troposphere.

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