Observations of HO\textsubscript{x} and its relationship with NO\textsubscript{x} in the upper troposphere during SONEX


Abstract

Simultaneous measurements of the oxides of hydrogen and nitrogen made during the NASA Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX) afforded an opportunity to study the coupling between these two important families throughout the free troposphere and lowermost stratosphere. Moreover, the suite of measurements made during the campaign was unprecedented in its completeness, thus providing a uniquely detailed picture of the radical photochemistry that drives oxidation and ozone production in this part of the atmosphere. On average, observed hydrogen oxides (HO\textsubscript{x} = OH + HO\textsubscript{2}) agree well with both instantaneous and diel steady state models; however, there is a persistent deviation of the observations that correlates with the abundance of nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) in the sampled air mass. Specifically, the observed HO\textsubscript{x} tends to exceed the model predictions in the presence of high NO\textsubscript{x} concentrations, by as much as a factor of 5 (> 500 pptv NO\textsubscript{x}) and is sometimes as little as half that expected by steady state at lower NO\textsubscript{x} levels. While many possibilities for these discrepancies are discussed, it is argued that an instrumental artifact is not probable and that the discrepancy may bespeak a shortcoming of our understanding of HO\textsubscript{x} chemistry. The consistently elevated HO\textsubscript{x} in the presence of elevated NO\textsubscript{x} leads directly to greater ozone production than expected, thereby extending the NO\textsubscript{x}-limited regime of the upper troposphere. These results could thus have bearing on the predicted impacts of increasing NO\textsubscript{x} emissions into this region of the atmosphere from, for example, the growth of global air traffic.