OH and HO\textsubscript{2} chemistry in the North Atlantic free troposphere

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Abstract. Interactions between atmospheric hydrogen oxides and aircraft nitrogen oxides determine the impact of aircraft exhaust on atmospheric chemistry. To study these interactions, the Subsonic Assessment: Ozone and Nitrogen Oxide Experiment (SONEX) assembled the most complete measurement complement to date for studying HO\textsubscript{x} (OH and HO\textsubscript{2}) chemistry in the free troposphere. Observed and modeled HO\textsubscript{x} agree on average to within experimental uncertainties (\pm 40\%). However, significant discrepancies occur as a function of NO and at solar zenith angles >70\°. Some discrepancies appear to be removed by model adjustments to HO\textsubscript{x}-NO\textsubscript{x} chemistry, particularly by reducing HO\textsubscript{2}NO\textsubscript{2} (PNA) and by including heterogeneous reactions on aerosols and cirrus clouds.

Introduction

The hydrogen oxides (HO\textsubscript{x}=OH+HO\textsubscript{2}) play critical roles in atmospheric photochemistry. Produced by sunlight, ozone, and gases from Earth’s surface, OH reacts with other gases emitted from Earth’s surface, starting reaction sequences that convert these gases into water-soluble forms. In addition, HO\textsubscript{2}, a by-product of the OH reactions, combines with NO to form NO\textsubscript{2}, which is destroyed by sunlight, producing O\textsubscript{3}. Whereas HO\textsubscript{x} production is controlled by sunlight and the abundance of source gases, the course of HO\textsubscript{x} reaction sequences and eventual HO\textsubscript{x} loss in the upper troposphere are dictated primarily by the abundance of nitrogen oxides (NO\textsubscript{x}). Aircraft exhaust contains copious amounts of NO\textsubscript{x}. Thus, understanding the atmospheric effects of aircraft, particularly O\textsubscript{3} production [Jaeglé et al., 1999b], requires a firm grasp of the interactions of atmospheric hydrogen oxides with the nitrogen oxides from the aircraft exhaust.

A goal of the Subsonic Assessment: Ozone and Nitrogen Oxide Experiment (SONEX) was to test the understanding of HO\textsubscript{x} sources and chemistry from SONEX.

Measurements, models, and uncertainties

The SONEX measurements most relevant to HO\textsubscript{x} photochemistry are OH, HO\textsubscript{2}, HO\textsubscript{x} sources and sinks, exchange reactants, particularly NO, CO, and O\textsubscript{3}, and environmental conditions. Measurements were made of all known HO\textsubscript{x} sources and most HO\textsubscript{x} sinks (O\textsubscript{3}, H\textsubscript{2}O, CH\textsubscript{4}, HO\textsubscript{2}, CH\textsubscript{3}OOH, acetone (CH\textsubscript{3}O(C)CH\textsubscript{3}), formaldehyde (CH\textsubscript{2}O), HNO\textsubscript{3}), the HO\textsubscript{x} exchange reactants (NO, CO, and many hydrocarbons), and environmental parameters (pressure, temperature, photolysis frequencies, and particle properties) [Singh et al., this issue]. The measurements have the following absolute uncertainties: HO\textsubscript{x} (\pm 40\%), photolysis frequencies by spectroradiometry (\pm 5-14\%), NO (\pm 13\%), H\textsubscript{2}O (\pm 10\%), CO and CH\textsubscript{4} (\pm 2\%), O\textsubscript{3} (\pm 5\%), peroxides (\pm 25\%), formaldehyde (\pm 40-50\%), and other HO\textsubscript{x} source and sink gases (\pm 10-35\%).

The OH and HO\textsubscript{2} measurements are compared to the results of photochemical models, which typically have kinetic uncertainties of (35-50\%). For this letter, we use the Harvard University 0-D diurnal steady-state photochemical model, which forces calculated species mixing ratios to repeat each 24 hours [Jaeglé et al., 1999a]. The model is constrained to all meteorological parameters and observed species, including NO, HNO\textsubscript{3}, HO\textsubscript{2}, CH\textsubscript{3}OOH, and acetone, but not CH\textsubscript{2}O. These constrained steady-state models provide good comparisons with observations because the daytime HO\textsubscript{x} time constants are 10-15 minutes and all significant known HO\textsubscript{x} source, sink, and exchange reactants are used to constrain the model. Thus, we do not need to know the origin of the sampled air as long as we measure all the reactants that influence HO\textsubscript{x}. Other models and other constraints on the Harvard model give similar results [Faloona et al., 1999]. A complementary approach is examining the fundamental dependencies of HO\textsubscript{x} on its primary controlling variables. In this letter, we do both.

Example of results: The flight of 28 October 1997

A flight that illustrates typical HO\textsubscript{x} behavior seen during SONEX was on 28 October 1997 from Ireland (53\°N) to the...
As the sun set and the solar zenith angle exceeded 90°, OH decreased to \((0.010 \pm 0.004)\) pptv and HO2 decreased to \((1.00 \pm 0.05)\) pptv; the Harvard model calculates higher values for HO2 and similar ones for OH. On this day, sunset occurred while the temperature was between 250 and 270 K.

Comparisons of model and observations for all SONEX flights

The observations are compared to the Harvard diurnal steady-state model for the 13 SONEX flights that had complete measurement data sets (Figure 3). The average observed-to-modeled ratio, \(R_{\text{HO2}}\) for the Harvard model is 1.02 \((r^2=0.85)\) for HO2, 1.01 \((r^2=0.72)\) for OH, and 1.00 \((r^2=0.93)\) for HO2/OH [Jaegl6 et al., 1999a]. Other steady-state models and different constraints on the Harvard model give similar results [Faloona et al., 1999]. This agreement is encouraging, but it masks some observation-to-model differences.

Systematic differences are evident between observed and modeled HOx (Figures 1 and 3). At low HOx \((< 1\) pptv),
Clouds and aerosols. Cirrus clouds were encountered about 15-20% of the time during SONEX. Some had sufficient surface area to decrease HO2 but not OH. About 27% of daytime measurements with $R_{HO2} < 1.0$ were in cirrus clouds, a higher percentage than that of cloud encounters. However, most measurements with low daytime $R_{HO2}$ values were in clear air.

**HO2 sources.** For daytime in clear air, the primary HO2 source below 8 km was water vapor. Above 8 km, the primary HO2 sources of about equal magnitude were water vapor, formaldehyde, and peroxides, with acetone being a smaller contribution [Jaegle et al., 1999a; Tan et al., 1999].

CH2O is an important atmospheric HO2 source. When CH2O was observed above 50 pptv, the CH2O instrumental limit-of-detection, it ranged from its LOD to 300 pptv, with over 55% of the observations below 50 pptv. Modeled CH2O, a result of methane and acetone oxidation, is generally less than 50 pptv. The high observed CH2O values are difficult to explain because, with a 12-hour CH2O lifetime, convectively lifted CH2O should decay to background values within a few days. As a result, the Harvard model used here assumes only modeled CH2O values; if observed CH2O is used, then the observed-to-modeled HO2 ratio decreases even more at high HO2. This situation introduces significant uncertainty into calculating the HO2 budget.

**Causes for the observed-to-modeled HO2 differences**

Could the observed-to-modeled differences be due to HO2 measurement errors beyond the estimated ±40% absolute uncertainty (90% confidence limits)? The 1-minute, 1-c precision of the HO2 instrument was 0.010-0.015 pptv for OH and 0.03 pptv for HO2, not an important consideration for this issue. One possible explanation is that the HO2 instrument sensitivity calibration was 1.5-2.0 times too large and a small positive HO2 artifact existed. However, the artifact is not required for some flights, such as on 28 October, 1997 (Figure 1). Also, such an artifact was not seen by in-flight and laboratory tests [Faloona et al., 1999]. Finally, the HO2/NO ratio and its variations agree within experimental uncertainty with model calculations for daytime HO2, meaning that OH would need a variable artifact that maintains this ratio. Thus, at least some of the observed-to-modeled HO2 difference appears to be atmospheric.

We must determine why observed-to-modeled HO2, $R_{HO2}$, is less than 1 for low daytime NO and why it is greater than 1 for high NO and for high solar zenith angles, all in the context of experimental and model uncertainty.

**Low daytime NO (SZA<70°).** Including cloud particle surface areas extrapolated from measurements and a reaction coefficient of 0.025 for HO2 on ice, calculated HO2 agrees with observations to within 20%, whereas before, it was as much as twice as large [Jaegle et al., 1999a]. A difficulty is that low observed-to-modeled HO2 ratio, $R_{HO2}$, persists even away from clouds. However, the main HO2 loss reactions at low NO, HO2 $\rightarrow$ HO + O2, OH + HO2 $\rightarrow$ OH + H2O, and HO2 $\rightarrow$ H2O + O2, are well characterized, suggesting that the observed-to-modeled differences may result from heterogeneous processes on cirrus clouds or aerosol.

**High Solar Zenith Angles.** The large observed-to-modeled HO2 ratio at high solar zenith angles has several possible causes. First, heterogeneous chemistry, particularly
Discrepancies appear to be removed by model adjustments to the observed HOx-NOx chemistry, particularly by reducing HO2NO2 formation and by including heterogeneous reactions on aerosols and cirrus clouds. Thus, we must clarify these SONEX results by examining HOx-NOx chemistry before we can completely resolve issues of HOx sources and their role in tropospheric ozone production.

Summary and Conclusions

Because observed tropospheric HOx had been equal to or larger than modeled HOx prior to SONEX [Wennberg et al., 1998; Brune et al., 1998], due presumably to unmeasured HOx sources like acetone, we had expected that, with the more complete SONEX payload, observed HOx would be roughly equal to or greater than modeled HOx. However, the SONEX result that observed HOx was less than modeled HOx for cleaner, low-NO conditions was surprising. That the observed-to-modeled HOx ratio was greater than experimental uncertainty for high solar zenith angles and for high NO is not as surprising, but it still requires explanation. Some discrepancies appear to be removed by model adjustments to

References


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