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## OH and HO<sub>2</sub> 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<sub>x</sub> (OH and HO<sub>2</sub>) chemistry in the free troposphere. Observed and modeled HO<sub>x</sub> agree on average to within experimental uncertainties ( $\pm 40\%$ ). However, significant discrepancies occur as a function of NO and at solar zenith angles  $>70^\circ$ . Some discrepancies appear to be removed by model adjustments to HO<sub>x</sub>-NO<sub>x</sub> chemistry, particularly by reducing HO<sub>2</sub>NO<sub>2</sub> (PNA) and by including heterogeneous reactions on aerosols and cirrus clouds.

### Introduction

The hydrogen oxides (HO<sub>x</sub>=OH+HO<sub>2</sub>) 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<sub>2</sub>, a by-product of the OH reactions, combines with NO to form NO<sub>2</sub>, which is destroyed by sunlight, producing O<sub>3</sub>. Whereas HO<sub>x</sub> production is controlled by sunlight and the abundance of source gases, the course of HO<sub>x</sub> reaction sequences and eventual HO<sub>x</sub> loss in the upper troposphere are dictated primarily by the abundance of nitrogen oxides (NO<sub>x</sub>). Aircraft exhaust contains copious amounts of NO<sub>x</sub>. Thus, understanding the atmospheric effects of aircraft, particularly O<sub>3</sub> 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<sub>x</sub> sources and chemistry in the upper troposphere and to ascertain the influence of aircraft exhaust, particularly NO<sub>x</sub>,

on it [Singh et al., 1999]. This test needs measurements of: HO<sub>x</sub> sources, including water vapor, acetone [Singh et al., 1995], HOOH, and convectively-lifted CH<sub>3</sub>OOH [Prather and Jacob, 1997; Jaeglé et al., 1997; Crawford et al., 1999]; reactants causing the fast exchange chemistry between OH and HO<sub>2</sub>, including NO, CO, and O<sub>3</sub>; and HO<sub>x</sub> sinks, whose relative importance depends on NO<sub>x</sub>. Measurements were made by instruments on the NASA DC-8 aircraft in and out of the North Atlantic aircraft corridor in fall, 1997. In this letter, we discuss what has been learned about HO<sub>x</sub> sources and chemistry from SONEX.

### Measurements, models, and uncertainties

The SONEX measurements most relevant to HO<sub>x</sub> photochemistry are OH, HO<sub>2</sub>, HO<sub>x</sub> sources and sinks, exchange reactants, particularly NO, CO, and O<sub>3</sub>, and environmental conditions. Measurements were made of all known HO<sub>x</sub> sources and most HO<sub>x</sub> sinks (O<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, HOOH, CH<sub>3</sub>OOH, acetone (CH<sub>3</sub>O(C)CH<sub>3</sub>), formaldehyde (CH<sub>2</sub>O), HNO<sub>3</sub>), the HO<sub>x</sub> 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<sub>x</sub> ( $\pm 40\%$ ), photolysis frequencies by spectroradiometry ( $\pm 5-14\%$ ), NO ( $\pm 13\%$ ), H<sub>2</sub>O ( $\pm 10\%$ ), CO and CH<sub>4</sub> ( $\pm 2\%$ ), O<sub>3</sub> ( $\pm 5\%$ ), peroxides ( $\pm 25\%$ ), formaldehyde ( $\pm 40-50\%$ ) and other HO<sub>x</sub> source and sink gases ( $\pm 10-35\%$ ).

The OH and HO<sub>2</sub> 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<sub>3</sub>, HOOH, CH<sub>3</sub>OOH, and acetone, but not CH<sub>2</sub>O. These constrained steady-state models provide good comparisons with observations because the daytime HO<sub>x</sub> time constants are 10-15 minutes and all significant known HO<sub>x</sub> 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<sub>x</sub>. 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<sub>x</sub> 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<sub>x</sub> behavior seen during SONEX was on 28 October 1997 from Ireland (53° N) to the

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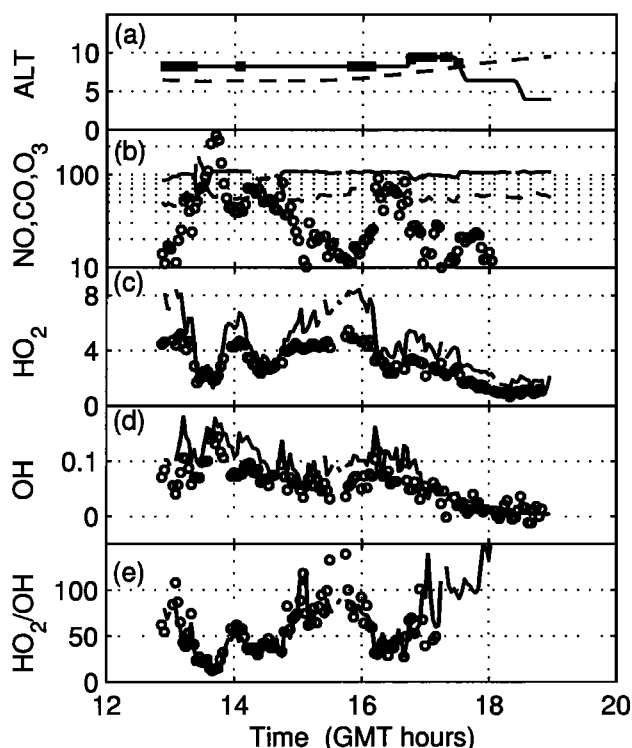
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**Figure 1.** Observations and model calculations for 28 October 1997, a flight between Ireland and the Azores. Panel (a) is altitude (solid line), and solar zenith angle/10 (dashed line). Squares indicate observations in cirrus clouds, as determined by a relative humidity over ice > 100% and the presence of particles with radii > 15  $\mu\text{m}$ . Panel (b) is NO (o's, pptv), O<sub>3</sub> (dashed line, ppbv) and CO (line, ppbv). Panels (c), (d), and (e) are HO<sub>2</sub> (pptv), OH (pptv), and HO<sub>2</sub>/OH respectively. Observations (o) and the Harvard model results (line) are shown.

Azores (39° N), as shown in Figure 1. On the first half of the flight, the DC-8 was held at a constant altitude of 8 km by air traffic control, but then flew at other altitudes as the sun set.

The long, constant altitude leg (13.0-16.5 GMT) was a good test of HO<sub>x</sub> variations with NO because other main controlling variables, CO and O<sub>3</sub>, temperature, and photolysis frequencies, were constant to within 20% (Figure 1). Water vapor was 100-800 ppmv, and HOOH and CH<sub>3</sub>OOH were 0-400 pptv and 0-100 pptv respectively. However, the calculated HO<sub>x</sub> production rate, which is the sum of production by water vapor and ozone, formaldehyde, acetone, peroxides, and pernitric acid, varied by less than a factor of 3. In contrast, NO varied by two orders of magnitude between a few and 300 pptv. Such a good kinetics experiment, in which only one controlling factor changes significantly, rarely occurs in the atmosphere.

During this long, constant altitude leg, OH was 0.05-0.15 pptv; HO<sub>2</sub> was 2-5 pptv. HO<sub>x</sub> and HOOH calculated by the Harvard model show the same variations as do the observations, but the values are larger by as much as a factor of two when HO<sub>2</sub> is high and low (Figure 1). The observed HO<sub>2</sub>/OH ratio is generally well represented by the model.

The dependence of HO<sub>2</sub> and OH on NO [Logan et al., 1981] is tested on the constant altitude leg (Figure 2), the first such test of this important relationship over such a large range

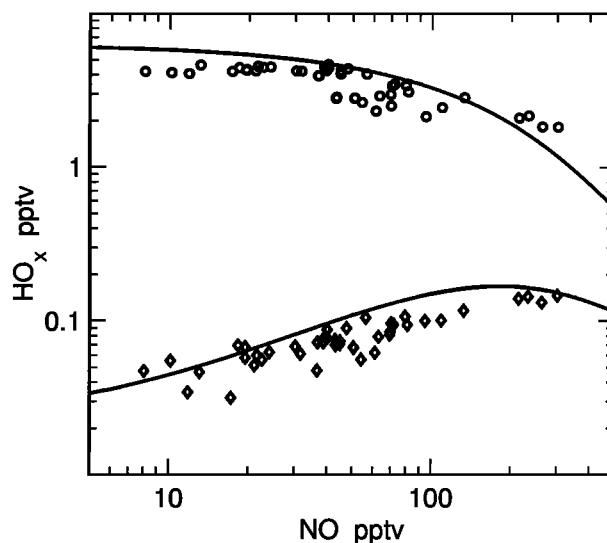
of NO. Observations are compared to an instantaneous steady-state model that uses the average observed values of all reactants except NO. Observations were selected to be in clear air and to have a HO<sub>x</sub> production rate, P(HO<sub>2</sub>), to within a factor of 2 of the model value, because the HO<sub>x</sub> mixing ratio depends on P(HO<sub>x</sub>)<sup>0.5</sup> to P(HO<sub>x</sub>)<sup>1.0</sup>. Tighter constraints on P(HO<sub>x</sub>) give the same results. Both OH and HO<sub>2</sub> vary roughly as expected, with OH increasing with NO as HO<sub>2</sub>+NO shifts HO<sub>x</sub> into OH, and with HO<sub>2</sub> being independent of NO for low NO, as would be expected if HO<sub>2</sub>+HO<sub>2</sub>→HOOH+O<sub>2</sub> were the major HO<sub>x</sub> loss. For NO between 100 and 300 pptv, HO<sub>2</sub> ∝ NO<sup>(-0.5±0.1)</sup>, as would be expected if OH+HO<sub>2</sub>→H<sub>2</sub>O+O<sub>2</sub> were the major loss. Observed HO<sub>2</sub> may be slightly lower than modeled HO<sub>2</sub> at low NO and higher at higher NO, but the overall agreement is within uncertainties.

As the sun set and the solar zenith angle exceeded 90°, OH decreased to (0.010±0.004) pptv and HO<sub>2</sub> decreased to (1.00±0.05) pptv; the Harvard model calculates higher values for HO<sub>2</sub> and similar ones for OH. On this day, sunset occurred while the temperature was between 250 and 270 K.

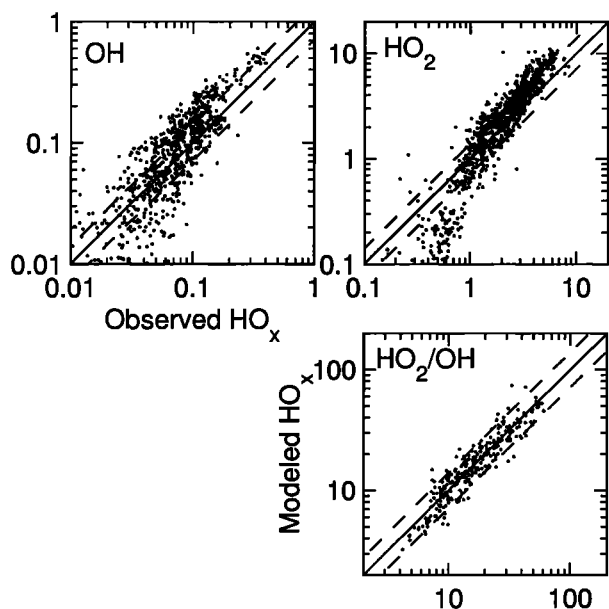
### Comparisons of model and observations for all SONEX flights

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<sub>HO<sub>2</sub></sub>, for the Harvard model is 1.02 (r<sup>2</sup>=0.85) for HO<sub>2</sub>, 1.01 (r<sup>2</sup>=0.72) for OH, and 1.00 (r<sup>2</sup>=0.93) for HO<sub>2</sub>/OH [Jaeglé 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 HO<sub>x</sub> (Figures 1 and 3). At low HO<sub>x</sub> (< 1 pptv),



**Figure 2.** HO<sub>2</sub> and OH as functions of NO for the constant altitude leg of 28 October 1997. Observed HO<sub>2</sub> (circles) and OH (diamonds) are compared to a steady-state model (line) with a fixed HO<sub>x</sub> production rate. Observations are filtered for O<sub>3</sub>, clear air, and HO<sub>x</sub> production within a factor of 2 the model value.



**Figure 3.** Comparison of observed and modeled HO<sub>2</sub>, OH, and HO<sub>2</sub>/OH. The model is the Harvard diurnal steady-state model. The solid line is 1:1; the dashed lines on either side are factors of 1.4, the HO<sub>x</sub> instrument uncertainty. The data for the HO<sub>2</sub>/OH ratio are filtered for OH > 0.1 pptv and HO<sub>x</sub> exchange > HO<sub>x</sub> production, and SZA < 75°.

observations are 2 to 4 times model values, while at higher HO<sub>x</sub> (> 3 pptv), observations are generally lower than model values by a factor of 1.4–2.0, just above experimental uncertainty and increasing with increasing HO<sub>2</sub>. OH shows similar but much weaker trends. On the other hand, observations and models agree for the daytime HO<sub>2</sub>/OH ratio to within experimental and model uncertainties, as seen before [Wennberg et al., 1998; Brune et al., 1998].

Studies of the SONEX data indicate that four factors appear to be mainly responsible for the observed-to-modeled HO<sub>x</sub> differences, typified by the observed-to-modeled ratio ( $R_{HO_2}$ ): NO, solar zenith angle, clouds and aerosols, and HO<sub>x</sub> sources. Other factors appear to have influence: altitude, water vapor, and daytime solar zenith angle. However,  $R_{HO_2}$  varies even for constant altitude and solar zenith angle (Figure 1). In addition, the  $R_{HO_2}$  for water vapor less than 50 ppmv is the same as in the entire data set shown in Figure 3.

**NO.** The strongest and most consistent covariance for the daytime observed-to-modeled HO<sub>2</sub> ratio is with NO (normalized covariance = 0.68). This relationship of  $R_{HO_2}$  with NO does show model-to-model variations in slope and intercept, but the change in  $R_{HO_2}$  with NO is on average 0.25–0.40 per 100 pptv [Faloona et al., 1999]. This dependence of  $R_{HO_2}$  on NO appears to be independent of the NO source, be it convection, lightning, aircraft, or the stratosphere.

**Solar zenith angle.** 75% of the large observed-to-modeled HO<sub>2</sub> ratios occur for high solar zenith angles (SZA > 75°). At sunrise, the observed-to-modeled ratio,  $R_{HO_2}$ , is as high as 10 for SZA > 90°, and decreases toward 1 as the solar zenith angle approaches 70°. At sunset,  $R_{HO_2}$  increases as the solar zenith angle increases to 90°, but only when NO is greater than 100 pptv does  $R_{HO_2}$  become larger than 2. This difference in  $R_{HO_2}$  behavior at sunrise and sunset may be significant.

**Clouds and aerosols.** Cirrus clouds were encountered about 15–20% of the time during SONEX. Some had sufficient surface area to decrease HO<sub>2</sub> but not OH. About 27% of daytime measurements with ( $R_{HO_2}$ ) < 1.0 were in cirrus clouds, a higher percentage than that of cloud encounters. However, most measurements with low daytime  $R_{HO_2}$  values were in clear air.

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

CH<sub>2</sub>O is an important atmospheric HO<sub>x</sub> source. When CH<sub>2</sub>O was observed above 50 pptv, the CH<sub>2</sub>O instrumental limit-of-detection, it ranged from its LOD to 300 pptv, with over 55% of the observations below 50 pptv. Modeled CH<sub>2</sub>O, a result of methane and acetone oxidation, is generally less than 50 pptv. The high observed CH<sub>2</sub>O values are difficult to explain because, with a 12-hour CH<sub>2</sub>O lifetime, convectively lifted CH<sub>2</sub>O should decay to background values within a few days. As a result, the Harvard model used here assumes only modeled CH<sub>2</sub>O values; if observed CH<sub>2</sub>O is used, then the observed-to-modeled HO<sub>2</sub> ratio decreases even more at high HO<sub>x</sub>. This situation introduces significant uncertainty into calculating the HO<sub>x</sub> budget.

### Causes for the observed-to-modeled HO<sub>x</sub> differences

Could the observed-to-modeled differences be due to HO<sub>x</sub> measurement errors beyond the estimated ±40% absolute uncertainty (90% confidence limits)? The 1-minute, 1-σ precision of the HO<sub>x</sub> instrument was 0.010–0.015 pptv for OH and 0.03 pptv for HO<sub>2</sub>, not an important consideration for this issue. One possible explanation is that the HO<sub>x</sub> instrument sensitivity calibration was 1.5–2.0 times too large and a small positive HO<sub>2</sub> 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 HO<sub>2</sub>/OH ratio and its variations agree within experimental uncertainty with model calculations for daytime HO<sub>2</sub>, meaning that OH would need a variable artifact that maintains this ratio. Thus, at least some of the observed-to-modeled HO<sub>x</sub> difference appears to be atmospheric.

We must determine why observed-to-modeled HO<sub>2</sub>,  $R_{HO_2}$ , 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 HO<sub>2</sub> on ice, calculated HO<sub>2</sub> agrees with observations to within 20%, whereas before, it was as much as twice as large [Jaeglé et al., 1999a]. A difficulty is that low observed-to-modeled HO<sub>2</sub> ratio,  $R_{HO_2}$ , persists even away from clouds. However, the main HO<sub>x</sub> loss reactions at low NO, HO<sub>2</sub>+HO<sub>2</sub>→HOOH+O<sub>2</sub>, OH+HOOH→H<sub>2</sub>O+HO<sub>2</sub>, and HO<sub>2</sub>+OH→H<sub>2</sub>O+O<sub>2</sub>, 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 HO<sub>x</sub> ratio at high solar zenith angles has several possible causes. First, heterogeneous chemistry, particularly

NO<sub>2</sub>+aerosols→1/2 HNO<sub>3</sub> + 1/2 HONO, followed by HONO photolysis into OH, could explain observations at sunrise [Jaeglé et al., 1999a]. However, it does not explain observations at sunset, since at sunset, sufficient HONO would not have had time to build up. The HO<sub>2</sub> persistence at sunset was also observed by Wennberg et al. [1999], who attribute it to additional red photolysis of HO<sub>2</sub>NO<sub>2</sub>. Our observations cannot result only from photolysis because HO<sub>2</sub> persists even when SZA>100° on 2 flights.

Yet another possibility is that HO<sub>2</sub> persists during the night and that HO<sub>2</sub>NO<sub>2</sub> is not forming. HO<sub>2</sub>NO<sub>2</sub> was the dominant nighttime HO<sub>x</sub> reservoir during SONE X. If HO<sub>x</sub> is not going into HO<sub>2</sub>NO<sub>2</sub>, the dominant nighttime HO<sub>x</sub> loss would be HO<sub>2</sub>+HO<sub>2</sub>→HOOH+O<sub>2</sub>. When HO<sub>2</sub> is less than 1 pptv, the HO<sub>x</sub> lifetime becomes several hours and at sunrise sub-pptv levels of HO<sub>x</sub> would still be present from the day before. For this to occur, the equilibrium constant for HO<sub>2</sub>NO<sub>2</sub> would need to be significantly less than currently believed, but the uncertainty in the equilibrium constant is at least a factor of 5 [DeMore et al., 1997]. Additional qualitative evidence for lower-than-expected HO<sub>2</sub>NO<sub>2</sub> comes from three SONE X flights with nighttime observations (SZA>95°). For two cases, the temperature was less than 240 K and R<sub>HO2</sub> > 1. For one case, 28 October, the temperature was 250-270 K and R<sub>HO2</sub> < 1. In the model, HO<sub>2</sub>NO<sub>2</sub> is a nighttime reservoir only when the temperature is low.

**High NO.** The large observed-to-modeled ratio at high NO could result if additional, unmeasured HO<sub>x</sub> sources were injected simultaneously with NO into the upper troposphere. The fact that the NO-dependence of R<sub>HO2</sub> persists despite the origin of the sampled air indicates that such additional sources are unlikely, but the issue is far from closed. The NO dependence could also occur if less HO<sub>2</sub>NO<sub>2</sub> were present. The reactions HO<sub>2</sub>+NO<sub>2</sub>+M→HO<sub>2</sub>NO<sub>2</sub>+M and OH+HO<sub>2</sub>NO<sub>2</sub>→H<sub>2</sub>O+O<sub>2</sub>+NO<sub>2</sub> are about 35% of the daytime HO<sub>x</sub> sink for SONE X conditions [Jaeglé et al., 1999a]. If we assume in a model that no HO<sub>2</sub>NO<sub>2</sub> forms, then NO-dependent difference between the daytime observed and modeled HO<sub>2</sub> is reduced to 1/3. Also, if we assume that the products of the OH+HO<sub>2</sub>NO<sub>2</sub> reaction are HO<sub>2</sub>+HNO<sub>3</sub>, then the observed-to-modeled difference is similarly reduced. While this evidence is only suggestive, it points to the need for much greater scrutiny of HO<sub>x</sub>-NO<sub>x</sub> chemistry.

## Summary and Conclusions

Because observed tropospheric HO<sub>x</sub> had been equal to or larger than modeled HO<sub>x</sub> prior to SONE X [Wennberg et al., 1998; Brune et al., 1998], due presumably to unmeasured HO<sub>x</sub> sources like acetone, we had expected that, with the more complete SONE X payload, observed HO<sub>x</sub> would be roughly equal to or greater than modeled HO<sub>x</sub>. However, the SONE X result that observed HO<sub>x</sub> was less than modeled HO<sub>x</sub> for cleaner, low-NO conditions was surprising. That the observed-to-modeled HO<sub>2</sub> 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

HO<sub>x</sub>-NO<sub>x</sub> chemistry, particularly by reducing HO<sub>2</sub>NO<sub>2</sub> formation and by including heterogeneous reactions on aerosols and cirrus clouds. Thus, we must clarify these SONE X results by examining HO<sub>x</sub>-NO<sub>x</sub> chemistry before we can completely resolve issues of HO<sub>x</sub> sources and their role in tropospheric ozone production.

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