OH and HO 2 chemistry in the North Atlantic free troposphere

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
doi:10.1029/1999GL900549

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:14117803

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
OH and HO\(_2\) chemistry in the North Atlantic free troposphere

W. H. Brune\(^1\), D. Tan\(^1\), I. F. Falona\(^1\), L. Jaeglé\(^2\), D.J. Jacob\(^2\), B. G. Heikes\(^3\), J. Snow\(^3\), Y. Kondo\(^4\), R. Shetter\(^5\), G.W. Sachse\(^6\), B. Anderson\(^6\), G.L. Gregory\(^6\), S. Vay\(^6\), H. B. Singh\(^7\), D. D. Davis\(^8\), J. H. Crawford\(^6\), and D.R. Blake\(^9\)

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\(_x\) (OH and HO\(_2\)) chemistry in the free troposphere. Observed and modeled HO\(_x\) agree on average to within experimental uncertainties (±40%). However, significant discrepancies occur as a function of NO and at solar zenith angles >70ø. Some discrepancies appear to be removed by model adjustments to HO\(_x\)-NO\(_x\) chemistry, particularly by reducing HO\(_2\)NO\(_x\)(PNA) and by including heterogeneous reactions on aerosols and cirrus clouds.

Introduction

The hydrogen oxides (HO\(_x\)=OH+HO\(_2\)) 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\(_2\), a by-product of the OH reactions, combines with NO to form NO\(_2\), which is destroyed by sunlight, producing O\(_3\). Whereas HO\(_x\) production is controlled by sunlight and the abundance of source gases, the course of HO\(_x\) reaction sequences and eventual HO\(_x\) loss in the upper troposphere are dictated primarily by the abundance of nitrogen oxides (NO\(_x\)). Aircraft exhaust contains copious amounts of NO\(_x\). Thus, understanding the atmospheric effects of aircraft, particularly O\(_3\) 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\(_x\) sources and chemistry in the upper troposphere and to ascertain the influence of aircraft exhaust, particularly NO\(_x\), on it [Singh et al., 1999]. This test needs measurements of: HO\(_x\) sources, including water vapor, acetone [Singh et al., 1995], HOOH, and convectively-lifted CH\(_3\)OOH [Prather and Jacob, 1997; Jaeglé et al., 1997; Crawford et al., 1999]; reactants causing the fast exchange chemistry between OH and HO\(_2\), including NO, CO, and O\(_3\); and HO\(_x\) sinks, whose relative importance depends on NO\(_x\). 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\(_x\) sources and chemistry from SONEX.

Measurements, models, and uncertainties

The SONEX measurements most relevant to HO\(_x\) photochemistry are OH, HO\(_2\), HO\(_x\) sources and sinks, exchange reactants, particularly NO, CO, and O\(_3\), and environmental conditions. Measurements were made of all known HO\(_x\) sources and most HO\(_x\) sinks (O\(_3\), H\(_2\)O, CH\(_4\), HOOH, CH\(_3\)OOH, acetone (CH\(_3\)O(O)CH\(_3\)), formaldehyde (CH\(_2\)O), HNO\(_3\)), the HO\(_x\) 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\(_x\) (±40%), photolysis frequencies by spectroradiometry (±5-14%), NO (±13%), H\(_2\)O (±10%), CO and CH\(_4\) (±2%), O\(_3\) (±5%), peroxides (±25%), formaldehyde (±40-50%) and other HO\(_x\) source and sink gases (±10-35%).

The OH and HO\(_2\) 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\(_3\), HOOH, CH\(_3\)OOH, and acetone, but not CH\(_2\)O. These constrained steady-state models provide good comparisons with observations because the daytime HO\(_x\) time constants are 10-15 minutes and all significant known HO\(_x\) 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\(_x\). Other models and other constraints on the Harvard model give similar results [Falloon et al., 1999a]. A complementary approach is examining the fundamental dependencies of HO\(_x\) 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\(_x\) behavior seen during SONEX was on 28 October 1997 from Ireland (53ø N) to the
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 (circles, pptv), \( \text{O}_3 \) (dashed line, pptv) and CO (line, ppbv). Panels (c), (d), and (e) are HO\(_2\) (pptv), OH (pptv), and HO\(_2\)/OH respectively. Observations (○) 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\(_x\) variations with NO because other main controlling variables, CO and \( \text{O}_3 \), temperature, and photolysis frequencies, were constant to within 20% (Figure 1). Water vapor was 100-800 ppmv, and HOOH and CH\(_3\)OOH were 0-400 pptv and 0-100 pptv respectively. However, the calculated HO\(_x\) production rate, which is the sum of production by water vapor and ozone, formaldehyde, acetone, peroxydes, 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\(_2\) was 2-5 pptv. HO\(_x\) and HOOH calculated by the Harvard model show the same variations as the observations, but the values are larger by as much as a factor of two when HO\(_2\) is high and low (Figure 1). The observed HO\(_2\)/OH ratio is generally well represented by the model.

The dependence of HO\(_2\) 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\(_x\) production rate, \( \text{P(HO}_x\) \), to within a factor of 2 of the model value, because the HO\(_x\) mixing ratio depends on \( \text{P(HO}_x\)^5 \) to \( \text{P(HO}_x\)^5 \). Tighter constraints on \( \text{P(HO}_x\) give the same results. Both OH and HO\(_2\) vary roughly as expected, with OH increasing with NO as HO\(_x\)+NO shifts HO\(_x\) into OH, and with HO\(_2\) being independent of NO for low NO, as would be expected if HO\(_x\)+HO\(_2\)→HOOH+O\(_2\) were the major HO\(_x\) loss. For NO between 100 and 300 pptv, HO\(_2\)≈ NO\(^{0.6\pm0.1}\), as would be expected if OH+HO\(_2\)→H\(_2\)O+O\(_2\) were the major loss. Observed HO\(_2\) may be slightly lower than modeled HO\(_2\) 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\(_2\) decreased to (1.00±0.05) pptv; the Harvard model calculates higher values for HO\(_2\) 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, \( \text{R}_{\text{HO}_2}\), for the Harvard model is 1.02 (\( r^2=0.85 \)) for HO\(_2\), 1.01 (\( r^2=0.72 \)) for OH, and 1.00 (\( r^2=0.93 \)) for HO\(_2\)/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\(_x\) (Figures 1 and 3). At low HO\(_x\) (< 1 pptv),
behavior at sunrise and sunset may be significant. PPTV does RHO2 become larger than 2. This difference in RHO2 for high solar zenith angles (SZA>75º) occurs for high solar zenith angles (SZA>75º). At sunset, RHO2 increases as the solar zenith angle approaches 70º. At sunset, RHO2 becomes larger than 2. This difference in RHO2 behavior at sunrise and sunset may be significant.

Figure 3. Comparison of observed and modeled HO2, OH, and HO2/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 HO2 instrument uncertainty. The data for the HO2/OH ratio are filtered for OH>0.1 pptv and HO2 exchange > HO2 production, and SZA<75º.

Observations are 2 to 4 times model values, while at higher HO2 (> 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 HO2. OH shows similar but much weaker trends. On the other hand, observations and models agree for the daytime HO2/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 HOx differences, typified by the observed-to-modeled RHO2 ratio (RHO2O: NO, solar zenith angle, clouds and aerosols, and HO2 sources. Other factors appear to have influence: altitude, water vapor, and daytime solar zenith angle. However, RHO2 varies even for constant altitude and solar zenith angle (Figure 1). In addition, the RHO2 for water vapor less than 50 pptv 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 HO2 ratio is with NO (normalized covariance = 0.68). This relationship of RHO2 with NO shows model-to-model variations in slope and intercept, but the change in RHO2 with NO is on average 0.25-0.40 per 100 pptv [Faloona et al., 1999]. This dependence of RHO2 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 HO2 ratios occur for high solar zenith angles (SZA>75º). At sunrise, the observed-to-modeled ratio, RHO2O, is as high as 10 for SZA>90º, and decreases toward 1 as the solar zenith angle approaches 70º. At sunset, RHO2 increases as the solar zenith angle increases to 90º, but only when NO is greater than 100 pptv does RHO2 become larger than 2. This difference in RHO2 behavior at sunrise and sunset may be significant.

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-σ 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 in in-flight and laboratory tests [Faloona et al., 1999]. Finally, the HO2/OH 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, RHO2O, 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<70º). 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 [Jaeglé et al., 1999a]. A difficulty is that low observed-to-modeled HO2 ratio, RHO2O, persists even away from clouds. However, the main HO2 loss reactions at low NO, HO2+HO2→HOOH+O2, OH+HOOH→H2O+HO2, and HO2+OH→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
NO2+aerosols→1/2 HNO3 + 1/2 HONO, followed by HONO photolysis into OH, could explain observations at sunrise [Jaegelé 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 HO2 persistence at sunset was also observed by Wennberg et al. [1999], who attribute it to additional red photolysis of HO2NO2. Our observations cannot result only from photolysis because HO2 persists even when SZA>100° on 2 flights.

Yet another possibility is that HO2 persists during the night and that HO2NO2 is not forming. HO2NO2 was the dominant nighttime HO2 reservoir during SONEX. If HO2 is not going into HO2NO2, the dominant nighttime HO2 loss would be HO2+HO2→HOOH+O2. When HO2 is less than 1 pptv, the HO2 lifetime becomes several hours and at sunrise sub-pptv levels of HO2 would still be present from the day before. For this to occur, the equilibrium constant for HO2NO2 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 HO2NO2 comes from three SONEX flights with nighttime observations (SZA>95°). For two cases, the temperature was less than 240 K and R_HO2 > 1. For one case, 28 October, the temperature was 250-270 K and R_HO2 < 1. In the model, HO2NO2 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 HOX sources were injected simultaneously with NO into the upper troposphere. The fact that the NO-dependence of R_HO2 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 be less if no HO2NO2 were present. The reactions HO2+NO2+M→HO2NO2+M and OH+HO2NO2→H2O+O2+NO2 are about 35% of the daytime HOX sink for SONEX conditions [Jaegelé et al., 1999a]. If we assume in a model that no HO2NO2 forms, then NO-dependent difference between the daytime observed and modeled HO2 is reduced to 1/3. Also, if we assume that the products of the OH+HO2NO2 reaction are HO2+HNO3, 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 HO2-NOX chemistry.

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 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.

Acknowledgements. The NASA Atmospheric Effects of Aircraft Program supported this work. We thank AEP managers R. Friedl, R. Kawa, and D. Anderson, mission scientists A. Thompson and H. Singh, mission manager J. Eilers, and the DC-8 managers, flight and ground crews for their encouragement and unfailing support. We especially thank R. Lester, C. Frame, and D. Taylor, and the EMS shop, without whose talents and tireless efforts these HOX measurements would not have been possible.

References

Jaegelé, L., et al., Ozone production in the upper troposphere and the influence of aircraft: evidence for NOX-saturated conditions, this issue, 1999b.