Title
OH and HO2 chemistry in the North Atlantic free troposphere

Permalink
https://escholarship.org/uc/item/5wm1c5s2

Journal
Geophysical Research Letters, 26(20)

ISSN
0094-8276

Authors
Brune, WH
Tan, D
Faloona, IF
et al.

Publication Date
1999-10-15

DOI
10.1029/1999gl900549

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
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 HOx (OH and HO2) chemistry in the free troposphere. Observed and modeled HOx agree on average to within experimental uncertainties (+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 HOx-NOx chemistry, particularly by reducing HO2NO (PNA) and by including heterogeneous reactions on aerosols and cirrus clouds.

Introduction

The hydrogen oxides (HOx=OH+HO2) 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, HO2, a by-product of the OH reactions, combines with NO to form NO2, which is destroyed by sunlight, producing O3. Whereas HOx production is controlled by sunlight and the abundance of source gases, the course of HOx reaction sequences and eventual HOx loss in the upper troposphere are dictated primarily by the abundance of nitrogen oxides (NOx). Aircraft exhaust contains copious amounts of NOx. Thus, understanding the atmospheric effects of aircraft, particularly O3 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 HOx sources and chemistry from SONEX. The SONEX measurements most relevant to HOx photochemistry are OH, HOx, HOx sinks and sinks, exchange reactants, particularly NOx, CO, and O3, and environmental conditions. Measurements were made of all known HOx sources and most HOx sinks (O3, H2O, CH4, HOOH, CH3OOH, acetone (CH3OH), formaldehyde (CH2O), HNO3), the HOx exchange reactants (NOx, 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: HOx (+40%), photolysis frequencies by spectroradiometry (+5-14%), NO (+13%), H2O (+10%), CO and CH4 (+2%), O3 (+5%), peroxides (+25%), formaldehyde (+40-50%) and other HOx source and sink gases (+10-35%).

The OH and HO2 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 NOx, HNO3, HOOH, CH3OOH, and acetone, but not CH2O. These constrained steady-state models provide good comparisons with observations because the daytime HOx time constants are 10-15 minutes and all significant known HOx 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 HOx. Other models and other constraints on the Harvard model give similar results [Falloon et al., 1999]. A complementary approach is examining the fundamental dependencies of HOx 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 HOx behavior seen during SONEX was on 28 October 1997 from Ireland (53° N) to the

Copyright 1999 by the American Geophysical Union.

Paper number 1999GL900549.
0094-8276/99/1999GL900549$05.00
of NO. Observations are compared to an instantaneous steady-state model that uses the average observed values of all reactants except NO. Observations were selected to be in clear air and to have a HO$_x$ production rate, $P($HO$_x$), to within a factor of 2 of the model value, because the HO$_x$ mixing ratio depends on $P($HO$_x$)$^5$ to $P($HO$_x$)$^5$. Tighter constraints on $P($HO$_x$) give the same results. Both OH and HO$_2$ vary roughly as expected, with OH increasing with NO as HO$_2$+NO shifts HO$_x$ into OH, and with HO$_2$ being independent of NO for low NO, as would be expected if HO$_2$+HO$_2$→HOOH+O$_2$ were the major HO$_x$ loss. For NO between 100 and 300 pptv, HO$_2$ $\propto$ NO$^{0.65\pm0.1}$, 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$\pm$0.004) pptv and HO$_2$ decreased to (1.00$\pm$0.05) pptv; the Harvard model calculates higher values for HO$_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, $R_{HO_2}$, 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),
observations are 2 to 4 times model values, while at higher HOx (> 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 ratio (RHO2): NO, solar zenith angle, and aerosols, and HOx 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 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 HO2 ratio is with NO (normalized covariance = 0.68). This relationship of RHO2 with NO does show 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>75°). At sunrise, the observed-to-modeled ratio, RHO2, is as high as 10 for SZA>90°, and decreases toward 1 as the solar zenith angle approaches 70°. At sunset, RHO2 increases as the solar zenith angle increases to 90°, 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 HOx differences

Could the observed-to-modeled differences be due to HOx measurement errors beyond the estimated ±40% absolute uncertainty (90% confidence limits)? The 1-minute, 1-σ precision of the HOx 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 HOx 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/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 HOx difference appears to be atmospheric.

We must determine why observed-to-modeled HO2, RH02, 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 HOx 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, RH02, persists even away from clouds. However, the main HOx 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...
Discrepancies appear to be removed by model adjustments to as surprising, but it still requires explanation. Some uncertainty for high solar zenith angles and for high NO is not result that observed HOx was less than modeled HOx for equal to or greater than modeled HOx. However, the SONEX complete SONEX payload, observed HOx would be roughly sources like acetone, we had expected that, with the more larger than modeled HOx prior to SONEX [Wennberg et al., 1998; Brune et al., 1998], due presumably to unmeasured HOx origins, submitted to Geophys. Res. Lett., 1999. Evidence from HONO photolysis into OH, could explain observations at sunrise [Jaegle 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 HOx persistence at sunset was also observed by Wennberg et al. [1999], who attribute it to additional red photolysis of HO2/NOx. 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 HOx reservoir during SONEX. If HO2 is not going into HO2NO2, the dominant nighttime HOx loss would be HO2+HO2→HO2+H2O. When HO2 is less than 1 pptv, the HOx 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 RHO2 > 1. For one case, 28 October, the temperature was 250-270 K and RHO2 < 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 RHO2 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 different if less HO2NO2 were present. The reactions HO2+NO2→HO2NO2 and OH+HO2→HOOH+O2 are about 35% of the daytime HOx sink for SONEX conditions [Jaegle et al., 1999a]. If we assume in a model that no NO2NO2 forms, then NO-dependent difference between the daytime observed and modeled HOx 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 HO2/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 HO2/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. Lesher, C. Frame, and D. Taylor, and the EMS shop, without whose talents and tireless efforts these HOx measurements would not have been possible. References Brune, W. H., D. Tan, L.C. Faloona, A.J. Weinheimer, T.L. Campos, B.A. Ridley, S.A. Vay, J.E. Collins, G.W. Sachse, L. Jaegle, D.J. Jacob, Airborne in situ OH and HO2 observations in the cloud-free troposphere and lower stratosphere during SUCCESS, Geophys. Res. Lett., 25, 1701-1704, 1998. Crawford, J. H., et al., Assessment of upper tropospheric HOx sources over the tropical Pacific on NASA GTE/PEM data: Net effect on HOx and other photochemical parameters, accepted for J. Geophys. Res., 1999. DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, JPL Publ. 97-4, 1997. Faloona, L.C., et al., Observations of HOx and its relationship with NO in the upper troposphere during SONEX, submitted to J. Geophys. Res., 1999. Jaegle, L., et al., Observations of OH and HO2 in the upper troposphere suggest a strong source from convective injection of peroxy radicals, Geophys. Res. Lett., 24, 3181-3184, 1997. Jaegle, L., et al., Photochemistry of HOx and ozone production at northern mid-latitudes, submitted to J. Geophys. Res., 1999a. Jaegle, L., et al., Ozone production in the upper troposphere and the influence of aircraft: evidence for NOx-saturated conditions, this issue, 1999b. Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, J. Geophys. Res., 86, 7210, 1981. Prather, M.J. and D.J. Jacob, A persistent imbalance in HOx and NOx photochemistry of the upper troposphere driven by deep convection, Geophys. Res. Lett., 24, 3189-3192, 1997. Singh, H.B., et al., High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, Nature, 378, 50-54, 1995. Singh, H.B., A. M. Thompson, and H. Schlager, 1997 SONEX airborne mission and coordinated POLINAT-2 activity: Overview and accomplishments, Geophys. Res. Lett., this issue, 1999. Tan, D., et al., Observations of HOx and HO2 production during SONEX, submitted to J. Geophys. Res., 1999. Wennberg, P.O., T.F. Hanisco, L. Jaegle, D.J. Jacob, E.J. Hintsa, E.L. Lanzendorf, J.G. Anderson, et al., Hydrogen radicals, nitrogen radicals, and the production of O3 in the upper troposphere, Science, 279, 49-53, 1998. Wennberg, P.O., et al., Twilight observations of OH and HO2 suggest unknown HOx sources, submitted to Geophys. Res. Lett., 1999. (Received March 10, 1999; revised June 4, 1999; accepted June 14, 1999)