Twilight observations suggest unknown sources of HOx


Abstract. Measurements of the concentrations of OH and HO2 in the high-latitude lower stratosphere imply the existence of unknown photolytic sources of HOx. The strength of the additional HOx source required to match the observations depends only weakly on solar zenith angle (SZA) for 80° < SZA < 93°. The wavelengths responsible for producing this HOx must be longer than 650 nm because the flux at shorter wavelengths is significantly attenuated at high SZA by scattering and absorption. Provided that the sources involve only a single photon, the strength of the bonds being broken must be < 45 kcal mol⁻¹. We speculate that peroxynitric acid (HNO₄) dissociates after excitation to an unknown excited state with an integrated band cross section of 2-3 x 10⁻²⁶ cm² molecule⁻¹ nm (650 < λ < 1250 nm).

Introduction

Measurement of the SZA dependence of short-lived radical species such as OH and HO2 provides insight into their sources [e.g. Salawitch et al., 1994]. In this letter we report twilight observations from a NASA ER-2 aircraft obtained near Fairbanks, Alaska during the 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) campaign. Observations at high latitudes are exceptionally well suited to this analysis: because of the slowly varying source of HOx, [HOx] remains near instantaneous steady state (Pox = d[HOx]/dt) at SZA as large as 93°.

Previously, high-SZA measurements of HOx were made during the 1993 Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE). These observations showed that [HOx] was higher than expected and implied the existence of unknown sources of these radicals present throughout the day. Most pronounced was the rapid onset of [HOx] in the early morning – consistent with nighttime production of a photon-labile hydroxyl-containing species. Some of us speculated that HNO₃ might be hydrolyzed on sulfate aerosols producing HONO [Salawitch et al., 1994]. Subsequent studies showed, however, that such hydrolysis does not occur [Zhang et al., 1997]. After the SPADE observations, Hanson and Ravishankara [1995] discovered that BrONO₂ was hydrolyzed to HOBr in sulfuric acid. This production of HOBr together with the recently discovered transition to a low-lying triplet state of HOBr centered near 500 nm [Barnes et al., 1996] leads to significant production of HOx at sunrise in model calculations [e.g., Lary et al., 1996].

Recent studies have pointed to other processes that produce HOx near twilight. Studies of the photolysis of O₃ have shown that O(¹D) is produced in a spin-forbidden process at wavelengths as long as 411 nm, significantly increasing the production rate of O(¹D) for SZA > 85° [Ravishankara et al., 1998 and references therein]. Recently, Donaldson et al. [1997] have suggested that excitation of vibrational overtones of the OH stretch in HNO₃ and HNO₄ may provide a significant source of HOx at high SZA.

HOx at High SZA During POLARIS

The high-latitude, high-SZA observations obtained during POLARIS are distinct from those of SPADE and provide a different test of HOx photochemistry. Nighttime is shorter; the lower stratosphere is warmer (228 vs. 212 K); total reactive nitrogen (NOy) is a factor of two higher; and [NO₂] is nearly five times larger. In the intervening years, aerosol surface area has declined by more than a factor of five.

In this study we compute the diurnal variation of [OH] and [H₂O₂] using a model constrained with measured values of pressure, temperature, aerosol surface area, and the concentrations of radical precursors (e.g. O₃, H₂O, and CH₄) (Table 1). Inorganic bromine, Br, and chlorine, Cl, are inferred from measurements of their source gases made by the whole air sampler and the airborne gas chromatograph. The O₃ column and its altitude distribution are inferred from Total Ozone Mapping Spectrometer (TOMS) data and from O₃ measurements obtained on the ER-2 and balloon-borne sondes. At SZA < 85°, this technique agrees with overhead O₃ measured by the ER-2 UV/Vis spectrometer. For SZA > 85°, however, the overhead O₃ column inferred from the spectrometer is not considered reliable [C.T. McElroy, personal communication]. TOMS reflectivity measurements are used to constrain the albedo along the flight track.

Interpretation of the HOx observations requires correct representation of NOy in the model because numerous processes couple these radicals. For most of the POLARIS, observations of NO and NO₂ are 20 – 40% larger than calculated using rate coefficients from DeMore et al. [1997] (Gao et al. [1999]; Ostnerman et al. [1999]). To assure calculated NOy at twilight matches observation, we use recently reported rate coefficients for the reactions of OH with HNO₃ and NO₂ [Brown et al., 1999; Dransfield et al., 1999] and account for the remaining model-measurement disagreement (<10%) by relaxing the requirement that the partitioning between NOy and NOx be in steady-state.

Figure 1 shows the measured [HOx] on 30 April and 9 May 1997. For these flights, the pilot flew a 'race-track' pattern...
for nearly seven hours. Minimal variation (±15%) in the mixing ratio of long-lived tracers such as O₃, CH₄, N₂O, and NOₓ was observed at 75° < SZA < 97°. The solid blue line displays a calculation using, with the exception of the reactions noted above, rate coefficients and absorption cross sections from DeMore et al. [1997]. The observed [HO₂] is larger than calculated by essentially a constant 0.75 pptv. Potential systematic errors in the HO₄ observations may be as large as 30% with an additional zero offset of ±0.05 pptv. The precision of the calibration of the instrument, however, is much better: any systematic error will not change significantly from flight to flight or vary with SZA. This precision is critical to this analysis; although differences between the observations and calculated [HO₂] at low SZA are not significant, the fractional variation of the difference with SZA is significant. At 92° SZA, this difference is greater than 60%. The comparison for OH is essentially the same, though the signal-to-noise ratio of the OH observations is lower because its concentration is ten to fifteen times smaller.

Errors in the representation of bromine chemistry cannot account for all the differences shown in Figure 1. The heterogeneous reaction of BrONO₂ with H₂O is calculated to convert more than 60% of the Br₂ to HOBr over night, leading to a rapid increase in calculated [HO₂] in the early morning. The blue dashed line (Figure 1) shows a calculation without this hydrolysis reaction. We use a reaction probability (γ) of 0.8. By assuming γ = 1 and increasing our estimate for Br₂ by −30%, the agreement with measured [HO₂] at sunrise is significantly improved. These changes however, do not improve agreement at sunset. Furthermore, recent laboratory data suggest that γ is likely 2–4 times smaller at T = 230 K [D. Hanson, personal communication].

Including the spin-forbidden production of O(¹D) in the photolysis of O₃ (Figure 1) has a negligible effect on [HO₂] at high SZA because production of HO₂ is dominated by processes involving reservoir species such as HNO₃, HNO₄, and HOB₃. The HO₄ sink exceeds the calculated source by nearly a constant amount for SZA ≤ 93°.

The local actinic flux at 20 km divided by the flux at the top of the atmosphere (F/F₀) depends strongly on SZA for wavelengths < 650 nm in the POLARIS atmosphere (solid lines). With heavy aerosol loading during the 1993 SPADE campaign (defined in Salawitch et al. [1994]), F/F₀ (dashed lines) was much lower at high SZA. Aerosol optical depth is determined from remote observations by the SAGE II instrument.
HOBr rather than by O(3P) chemistry (Figure 2). For example, the minor HOx source from thermal decomposition of HNO2 is calculated to exceed production from O(3P) chemistry by a factor of five at SZA = 90ø, even when the spin forbidden process is included. We have assumed an O(3P) quantum yield of 0.06 for 329 < ) < 411 nm.

The red dotted line in Figure 1 displays a calculation that includes the dissociation of HNO2 and HNO4 by photoexcitation of overtones of the OH vibrational stretch. The HNO4 overtone intensities used here are from Donaldson et al. [1998]. Excitation of the OH stretch (ν1) in HNO2 to 5ν1 (5 quanta) is partially dissociative and we use the quantum yield from Donaldson et al. [1997]. Only 3 quanta of excitation of the OH stretch are required to exceed the N-OOH bond strength in HNO2 (D=-22.8 kcal mole-1 [Zabel, 1995]). The gas-phase cross sections for this transition are unknown. We assume measurements of the HNO4 cross sections obtained in the full model and the strength of the HOx sink determined in the gas-phase cross sections scale similarly. Note that the HOx observed during the POLARIS measurements at 12.9/1780 pptv cannot be used to distinguish between sources of HOx between 12.9/1780 pptv.

The requirement that the missing HOx sources be produced by solar radiation at ℜ > 650 nm places a significant constraint on the stratospheric aerosol loading. Although included, the increase in calculated [HOx] between the red dashed and dotted lines is entirely due to the different photolysis rate of HNO4. Although included, the increase in the photolysis rate of HNO2 is calculated to exceed production from O(3P) chemistry by a factor of five at SZA = 90ø, even when the spin forbidden process is included. We have assumed an O(3P) quantum yield of 0.06 for 329 < ℜ < 411 nm.

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This result is largely insensitive to assumptions about the UV cross sections of HNO₃. The two studies used in the JPL evaluation differ significantly at λ > 310 nm [Molina and Molina, 1981; Singer et al., 1989] and the DeMore et al. [1997] recommendation does not extend beyond 325 nm. We have assumed that the UV cross section for HNO₃ is 0 for λ > 325 nm. We have performed sensitivity studies to this assumption and find that our conclusion about the need for an additional HO₃ source is not sensitive to these cross sections because the actinic flux at λ < 400 nm is negligible at these SZA. The same is true for uncertainty in the ozone profile; a smaller ozone column above the ER-2 improves agreement at low SZA but does not change the model result at high SZA.

What spectroscopic transition could produce this photolysis? The 3ν₁ overtone of HNO₃ is five times too weak. It is possible that combination bands of 2ν₁ may be involved. These transitions have not been observed, however, and the thermochemistry of HNO₃ is sufficiently uncertain that it is unclear whether excitation of these modes would be dissociative. Perhaps a singlet-triplet transition exists in HNO₃ as has been shown to occur in HOB₃ [Barnes et al., 1996]. Photolysis of HNO₃ in a transparent region of the red / near-IR with an integrated band cross section of only 2.5 x 10⁻²⁰ cm² molecule⁻¹ nm matches the required source of HO₃ (Figure 1). This increased photolysis rate would reduce the calculated importance of HNO₃ both as a NO₃ reservoir and a HO₃ sink. Work is underway at Caltech to study the photodissociation of HNO₃ in the red / near-IR.

Conclusion

High-SZA observations of HO₃ have demonstrated that a source of HO₃ = 3 x 10⁹ molecules cm⁻³ s⁻¹ persisting to very high SZA is missing from the photochemical description of the stratosphere. The source likely involves photolysis in the red or near IR because the optical depth of the atmosphere at shorter wavelengths is large at high SZA. Until the source molecules are identified, however, we cannot determine the extent to which these processes are important globally.

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