

Near IR photolysis of HO₂NO₂: Implications for HO_x

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[1] We report observations and calculations of peroxyoxynitric acid, HO₂NO₂, in the stratosphere and upper troposphere. The simulations show that photolysis of HO₂NO₂ via excitation of purely vibrational modes at wavelengths longward of 760 nm (the near IR) can dominate loss of this species. Consideration of this photolytic pathway reduces calculated HO₂NO₂, resolving a large discrepancy between standard model calculations and observations of HO₂NO₂ at high-latitude spring. The lower calculated abundance of HO₂NO₂ reduces the efficiency of the OH + HO₂NO₂ sink of HO_x. Consideration of this process leads to large increases in calculated HO_x (20 to 60%) for high-latitude spring and better agreement with observed stratospheric abundances of HO_x. Near IR photolysis of HO₂NO₂ alters the coupling between NO_x and HO_x in stratospheric and upper tropospheric photochemical models. *INDEX TERM*: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry

1. Introduction

[2] Peroxyoxynitric acid, HO₂NO₂, is important to the photochemistry of the upper troposphere and stratosphere. It is formed by:



and removed by photolysis as well as reaction with OH:



Assuming reaction (2) produces H₂O and O₂, the sequence (1) + (2) catalyzes the loss of HO_x.

[3] The first measurements of HO₂NO₂ were based on spectra obtained by the Atmospheric Trace Molecule Spectroscopy experiment [Rinsland *et al.*, 1986]. Subsequent laboratory measurements of HO₂NO₂ line parameters [May and Friedl, 1993] improved the precision of these and other remote observations of HO₂NO₂ [e.g., Sen *et al.*, 1998]. Previous studies focused on profiles obtained at mid-latitudes, where the discrepancy between modeled and measured HO₂NO₂ is small [Sen *et al.*, 1998], well within the range of model uncertainty.

[4] Recently, new measurements of photodissociation cross sections of HO₂NO₂ have been reported for both the UV [Knight *et al.*, 2002] and the near IR [Roehl *et al.*, 2002]. The near IR study was motivated by the suggestion

that photodissociation by excitation of vibrational overtones would significantly increase the overall photolysis rate of HO₂NO₂ [Donaldson *et al.*, 1997]. In light of these new laboratory data, we examine here remote observations of HO₂NO₂ obtained at mid- and high-latitudes and in situ measurements of HO₂ from high-latitude spring.

2. Observations and Model Description

[5] Measurements of HO₂NO₂ were obtained by the JPL MkIV balloon-borne Fourier Transform Infrared spectrometer using solar occultation at 35°N on Sept. 25, 1993 during sunset and at high-latitude (65 to 70°N) on May 8, 1997 during sunrise. Details of these flights are given by Sen *et al.* [1998] and Osterman *et al.* [1999].

[6] Absorption of sunlight by the unresolved Q branch of HO₂NO₂ is apparent in measured spectra near 802.7 cm⁻¹ (Figure 1). The high spectral resolution of MkIV allows this broad absorption feature to be separated from the stronger, narrower absorption lines of O₃, H₂O, and CO₂. Profiles of the volume mixing ratio (vmr) of HO₂NO₂ (Figures 2 and 3) are based on band intensities reported by May and Friedl [1993], which have an estimated accuracy of 20%. Measured profiles of HO₂NO₂ are provided in tabular form in the auxiliary material.¹ We also examine in situ measurements of HO₂ obtained aboard the ER-2 aircraft near 64°N during spring of 1997 [Wennberg *et al.*, 1999].

[7] The photochemical model has been used in many previous studies [e.g., Sen *et al.*, 1998; Osterman *et al.*, 1999]. The abundance of radicals (e.g., NO₂ and HO₂) and reservoir compounds (e.g., HO₂NO₂) are calculated by balancing the production and loss of each species integrated over 24 hours. For analyses of MkIV data, abundances of long-lived precursors such as O₃, H₂O, NO_y, and Cl_y are specified from MkIV observations. Profiles of Br_y are based on correlations with N₂O; aerosol surface area is based on zonal, monthly mean profiles from the Stratospheric Aerosol and Gas Experiment II. Constraints for the MkIV simulations are provided in tabular form in the auxiliary material.¹ The model is similarly constrained by observations of long-lived precursors, aerosol surface area, etc. for analyses of the ER-2 data. These calculations were carried out as described by Wennberg *et al.* [1999], using the constraints given in Table 1 of that paper.

[8] The simulations shown below for both the MkIV and the ER-2 data use three sets of kinetic parameters. The first, based on the most recent evaluation [Sander *et al.*, 2000], is referred to as the *JPL00* model. The second set, denoted *Model B*, uses several modifications of potential importance for HO₂NO₂: a) the rates for OH + O₃ and HO₂ + O₃ from

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¹Auxiliary material is available via Web browser or anonymous FTP from ftp://kosmos.agu.org, directory "apend"; subdirectories in the ftp site are arranged by paper number. Information on electronic supplements is at http://www.agu.org/pubs/esupp_about.html.

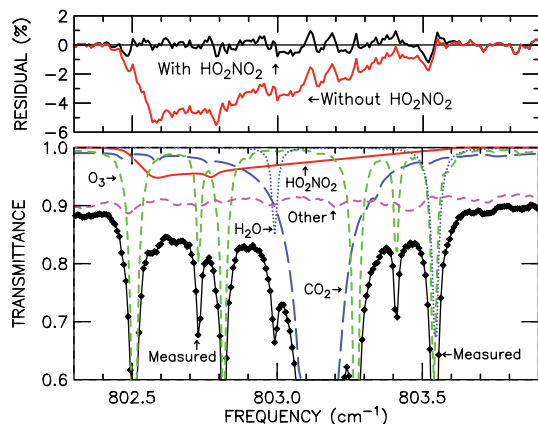


Figure 1. *Bottom Panel:* Measured transmittance (diamonds connected by black lines) for a MkIV spectrum obtained on May 8, 1997 with a tangent altitude of 10.4 km. The estimated contribution of the unresolved Q branch of HO₂NO₂ to the transmittance is shown (red line). Contributions from other species are also shown, as indicated. *Top Panel:* Calculated residuals to the measured transmittance found by the retrieval algorithm, allowing for absorption by HO₂NO₂ (black line) and neglecting absorption by HO₂NO₂ (red line).

JPL97 [DeMore *et al.*, 1997] are used because they better describe the ratio of HO₂ to OH observed in the lower stratosphere and because they are in better agreement with laboratory studies published subsequent to *JPL00* [Lanzendorf *et al.*, 2001]; b) the reaction Cl + HNO₄ is included at a rate of 10⁻¹³ cm³ sec⁻¹ [Simonaitis and Leu, 1985]; c) UV absorption cross sections for HO₂NO₂ recently measured by Knight *et al.* [2002] are adopted. A third set of calculations uses the same set of kinetic parameters as *Model B*, except

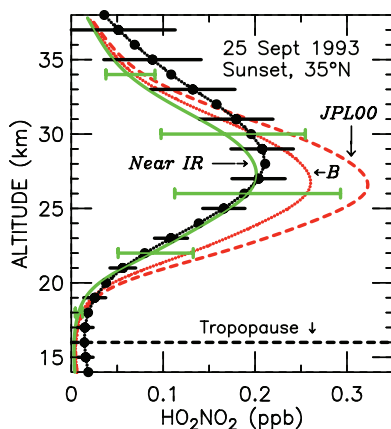


Figure 2. Profile of HO₂NO₂ measured by MkIV on Sept. 25, 1993 at 35°N (points w/ error bars) compared to model simulations for three sets of kinetic parameters: 1) *JPL00*; 2) *Model B* (see text); 3) *Near IR* photolysis of HO₂NO₂ plus *Model B*. Error bars for observed HO₂NO₂ represent 1 σ precision. The 1 σ uncertainty in calculated HO₂NO₂ for the *Near IR* model, based on uncertainties in rate constants of its formation and loss processes, is shown by the error bars bounded by vertical line segments.

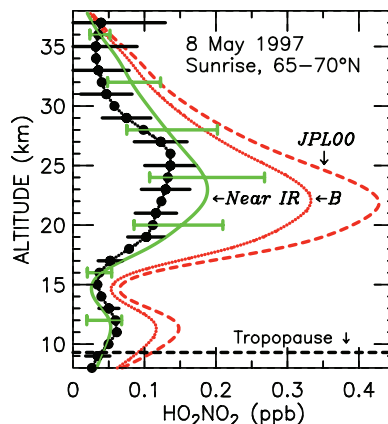


Figure 3. Same as Figure 2, for May 8, 1997 at 65 to 70°N.

photodissociation of HO₂NO₂ in the near IR is added. This calculation, referred to as *Near IR*, uses values for cross sections, quantum yields, and solar flux given in Table 3 of Roehl *et al.* [2002].

3. HO₂NO₂ Comparisons

[9] Figures 2 and 3 show comparisons of calculated and observed HO₂NO₂. Calculated profiles found using *JPL00* kinetics exceed observed levels of HO₂NO₂ at mid-latitudes for altitudes between ~20 to 30 km. However, this discrepancy is well within the calculation uncertainty, based on considerations such as a factor of 2 uncertainty in the photolysis rate of HO₂NO₂ [DeMore *et al.*, 1997]. For high-latitude springtime, *JPL00* kinetics over estimates observed HO₂NO₂ by as much as a factor of 4. The discrepancy at high-latitude is significant considering uncertainties in both measured and modeled HO₂NO₂.

[10] Uncertainties in NO_x chemistry can not explain the discrepancy between measured HO₂NO₂ at high latitude spring and the *JPL00* simulation. The model simulates observed profiles of NO₂ and NO quite well (differences typically less than 10% for all three sets of kinetic parameters) for both mid-latitudes and high-latitudes, as shown in the supporting material.¹ Revisions to the rates of OH + NO₂ + M and OH + HNO₃ in *JPL00* account for earlier discrepancies between modeled and measured NO₂ at both mid- and high-latitudes [e.g., Osterman *et al.*, 1999].

[11] The kinetic parameters adopted for the *Model B* simulation result in lower values of calculated HO₂NO₂ and better agreement with observation. The difference in calculated HO₂NO₂ compared to the *JPL00* simulation is almost entirely due to the change in the rate constants of OH + O₃ and HO₂ + O₃. This change lowers modeled HO₂ and increases OH; both of these effects lead to reductions in calculated HO₂NO₂. The rate of the Cl + HO₂NO₂ reaction, included here for completeness, is about a factor of 100 too slow to affect either HO₂NO₂ or HCl. The Knight *et al.* [2002] UV cross sections result in nearly identical photolysis rates of HO₂NO₂ as *JPL00* kinetics for both mid- and high-latitudes: weaker absorption between ~280 to 325 nm using the Knight *et al.* data is compensated by contributions to photolysis longward of 325 nm. The Knight *et al.* measurements do, however, increase our confidence that

uncertainties in UV photolysis of HO₂NO₂ can not account for measured HO₂NO₂ at high latitudes.

[12] Inclusion of near IR photolysis of HO₂NO₂ leads to good agreement between measured and modeled HO₂NO₂ at both mid- and high-latitudes. Contributions from the near IR dominate photolytic loss of HO₂NO₂ below ~24 km at mid-latitudes and below about ~28 km at high-latitudes. The calculated photolysis rate due to excitation of purely vibrational modes is nearly an order of magnitude larger than estimated by Wennberg *et al.* [1999] because, as discussed by Roehl *et al.* [2002], excitation of the first overtone of OH stretching frequency (near 1.4 μm) was found to have a significant quantum yield for dissociation.

[13] Near IR photolysis has a larger effect at high-latitude spring because of: *a*) strong attenuation of UV light by the high ozone slant column (this lowers the UV contribution to HO₂NO₂ photolysis compared to mid-latitudes); *b*) long days (the IR contribution to HO₂NO₂ photolysis depends essentially on length of sunlight). Calculated contributions to loss of HO₂NO₂ by UV photolysis, near IR photolysis, and reaction with OH are shown in the supplemental material.¹ The fact that near IR photolysis makes the largest contribution to calculated HO₂NO₂ for the region of the atmosphere where standard models (e.g., *JPL00* or *Model B*) most strongly overestimate measured HO₂NO₂ provides compelling evidence for the importance of this mechanism.

4. Implications for HO_x

[14] Figure 4 illustrates the effect of near IR photolysis of HO₂NO₂ on HO_x. The increase in calculated HO_x is modest (2 to 6%) below ~28 km at mid-latitudes. The increase is dramatic (20 to 60%), however, for high-latitude spring at altitudes below ~28 km. The perturbation extends into the upper troposphere (UT) for both regions and is large (50 to 60%) in the UT at high-latitudes.

[15] Changes in calculated HO_x are largest for high latitude spring below ~28 km for reasons described above (weaker UV and longer days result in a stronger perturbation to HO₂NO₂) plus the presence of characteristically high levels of NO_x. The loss of HO_x by (1)–(2) is catalyzed by NO_x; for the *JPL00* simulation, this cycle plays a stronger role in HO_x photochemistry at high-latitude spring com-

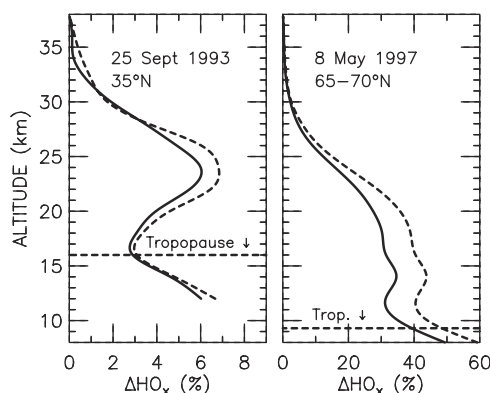


Figure 4. Calculated change in 24 hour average HO_x (OH + HO₂) when near IR photolysis is added to a simulation based on *Model B* kinetics (solid line) and to a simulation based on *JPL00* kinetics (dashed line).

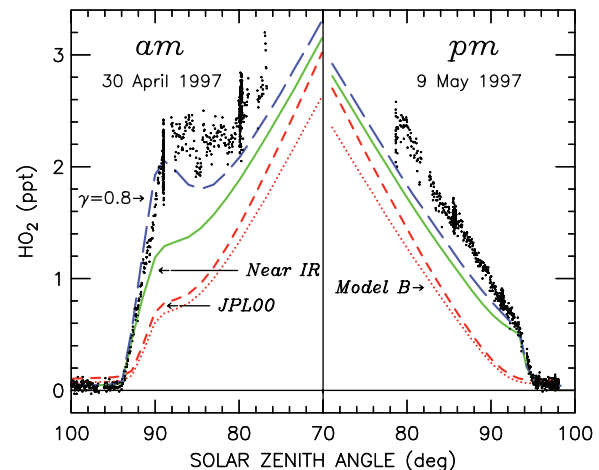


Figure 5. Observations of HO₂ obtained on the morning of April 30, 1997 and the afternoon of May 9, 1997 from the ER-2 aircraft near 64°N in the lower stratosphere compared to model simulations using the three sets of kinetic parameters described in Figure 2. A fourth simulation, allowing for a reaction probability of 0.8 for BrONO₂ hydrolysis within the *Near IR* model, is also shown.

pared to mid-latitudes. The effect of near IR HO₂NO₂ photolysis on calculated HO_x depends, therefore, on ambient NO_x. This dependence is important for assessing the tropospheric implications of this process.

[16] The influence of near IR photolysis of HO₂NO₂ on HO_x is further illustrated in Figure 5, which compares modeled and measured HO₂ in the lower stratosphere near 64°N during spring. The *JPL00* simulation significantly underestimates measured HO₂ throughout the day. An important change in the *JPL00* kinetic parameters, relative to *JPL97*, is a reduction in the reaction probability (γ) for BrONO₂ hydrolysis from 0.8 to ~0.2 for the temperature and humidity of these observations. This change reduces the morning rise of HO₂ due to photolysis of HOBr apparent in the *JPL97* simulation of Wennberg *et al.* [1999]. *Model B* kinetic parameters result in a slight increase in calculated HO₂. Allowing for near IR photolysis leads to a ~20% increase in 24 hr average HO₂ and better agreement with the observed rise of HO₂ in early morning due to rapid photolysis of HO₂NO₂ at high solar zenith angles. Nonetheless, measured HO₂ and OH (figure shown in supplemental material¹) are still underestimated by this model.

[17] The discrepancy between measured HO₂ and OH and the *Near IR* model calculation is not significant given the estimated possible 30% systematic error in the HO_x measurements [Wennberg *et al.*, 1999] (see auxiliary material¹). However, the precision of the HO_x data is much better; e.g., any systematic error will not vary with solar zenith angle (SZA). The shapes of HO₂ vs. SZA and OH vs. SZA from the *Near IR* simulation agree well with observed SZA dependencies. The discrepancy between measured and modeled HO_x for the *JPL00* and *Model B* simulations is significant because the measured shape of HO_x vs. SZA differs considerably from the model calculations.

[18] Nonetheless, it is interesting to speculate on possible reasons for the shortfall between calculated HO_x from the

Near IR simulation and the HO_x observations (assuming the HO_x calibration is correct). It is unlikely that this shortfall can be entirely due to errors in the photolysis rate of HO₂NO₂. Sensitivity studies indicate the integrated morning burst of HO_x supplied by photolysis of HO₂NO₂ is limited once photolysis becomes the dominant sink of HO₂NO₂ (e.g., the concentration of HO₂NO₂ becomes inversely proportional to its photolysis rate). If the rate of OH + HO₂NO₂ is reduced to its lower limit, then calculated HO_x within the Near IR simulation lies close to the observations. Similarly, if this reaction does not yield H₂O with 100% efficiency, model and measured HO_x are in better agreement.

[19] Another possible explanation of the measured HO_x is that γ of BrONO₂ hydrolysis, for conditions of these observations, is considerably faster than 0.2. The JPL00 recommendation for BrONO₂ hydrolysis is based on laboratory results extrapolated to water activity levels of the lower stratosphere. The model simulation labeled " $\gamma = 0.8$ " in Figure 5 shows that the observed morning burst of HO₂ might be supplied by photolysis of both HO₂NO₂ and HOBr. The slight timing difference between the measured morning rise of HO₂ and the $\gamma = 0.8$ simulation could be indicative of errors in the calculated actinic flux, errors in the photolysis rate of HOBr and/or HO₂NO₂, or supply of HO_x from some other precursor. The good agreement between the modeled and measured early morning rise of NO suggests the actinic flux calculation is carried out correctly [Gao et al., 2001]. Calculations shown in the supplemental material¹ indicate that BrONO₂ hydrolysis, in the absence of near IR photolysis of HO₂NO₂, is unable to account for the observed fall off of HO₂ with increasing SZA in the evening regardless of assumptions regarding γ or Br _{γ} .

5. Concluding Remarks

[20] Near IR photolysis of HO₂NO₂, first suggested by Donaldson et al. [1997], alters the coupling between NO_x and HO_x. In the lower stratosphere (LS), HO_x radicals are the dominant sink for photochemical loss of O₃. The increased levels of HO_x suggested by this analysis will likely result in greater sensitivity of calculated O₃ to perturbations such as increases in stratospheric H₂O. In the upper troposphere (UT), production of ozone via oxidation of carbon monoxide and other hydrocarbons proceeds via coupled HO_x-NO_x photochemistry. The efficiency of this chemistry is thought to become limited at moderate concentrations of NO_x due to loss of HO_x by reactions (1) and (2) [e.g., Jaeglé et al., 2001]. The reduced efficiency of this sink implies that production of UT ozone will be positively correlated with the abundance of NO to higher levels of NO_x than is found in many models.

[21] We conclude by noting that space-borne observations of HO₂NO₂ can provide significant advances in

constraints on the photochemistry of the UT and LS. Measurements of HO₂NO₂ co-located with observations of NO₂ provide a means to determine concentrations of HO₂. Near IR photolysis reduces the lifetime of HO₂NO₂, simplifying the interpretation of observations. There is hope that observations of HO₂NO₂ will become available in the near future, since it is measured by the Michelson Interferometer for Passive Atmospheric Sounding instrument aboard the ESA ENVISAT spacecraft and is a "special product" of the Tropospheric Emission Spectrometer to be launched on the NASA Aura spacecraft.

[22] **Acknowledgments.** We thank Gary Knight and Coleen Roehl for making available measurements of HO₂NO₂ cross sections prior to publication and the anonymous reviewers for helpful comments. This work was funded by the NASA Upper Atmosphere Research, Atmospheric Chemistry Modeling and Analysis, and Atmospheric Effects of Aviation Programs. Research at the Jet Propulsion Laboratory, California Institute of Technology, is performed under contract with the National Aeronautics and Space Administration.

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