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Effect of near-IR photolysis of HO_2NO_2 on stratospheric chemistry

J. T. Evans and M. P. Chipperfield
School of the Environment, University of Leeds, Leeds, UK

H. Oelhaf, M. Stowasser, and G. Wetzel
Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Universität Karlsruhe, Karlsruhe, Germany

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[1] We use a 3D model to assess the impact of the recently reported near-IR (NIR) photolysis of HO_2NO_2 on global stratospheric chemistry. Including this process in the model leads to a significant reduction in HO_2NO_2 for all latitudes and seasons. The effect is larger at high latitudes with the maximum reduction (>95% near 20 km) in winter. While the basic model strongly overestimates the MIPAS balloon observations of HO_2NO_2 at mid-high latitudes, this discrepancy is largely removed by including the NIR photolysis. In high latitude winter below 25 km the model still overestimates HO_2NO_2 but this may be due to remaining uncertainties in HO_2NO_2 formation/loss rates and modelled NO_2. The NIR photolysis increases model HO_x ($OH + HO_2$). At high latitudes around 18 km HO_x increases by over 30% all-year-round, with much larger enhancements (>70%) near the terminator. However, there is a corresponding NO_x ($NO + NO_2$) decrease of $\sim$10% in high latitude summer. Consequently, at this altitude O_3 decreases by only 1–2%. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties. **Citation:** Evans, J. T., M. P. Chipperfield, H. Oelhaf, M. Stowasser, and G. Wetzel, Effect of near-IR photolysis of HO_2NO_2 on stratospheric chemistry, *Geophys. Res. Lett.*, *30*(5), 1223, doi:10.1029/2002GL016470, 2003.

1. Introduction

[2] Peroxynitric acid (HO_2NO_2) is a relatively minor component of stratospheric NO_y, although it provides a coupling between HO_x and NO_x. It is formed by:

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \quad (1)$$

and removed by photolysis, thermal decomposition and by reaction with OH.

$$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2 \quad (2)$$

$$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M \quad (3)$$

$$HO_2NO_2 + OH \rightarrow H_2O + NO_2 + O_2 \quad (4)$$

While it is well established that HO_2NO_2 photolyses in the UV, recent studies have indicated that photolysis in the near-IR (NIR) is also important. *Donaldson et al.* [1997] first suggested that HO_2NO_2 may photolyse following the excitation of vibrational overtones. Recently, *Roehl et al.* [2002] reported new absorption cross sections in the NIR. *Wennberg et al.* [1999] suggested that NIR photolysis of HO_2NO_2 could be an important source of HO_x at high solar zenith angles.

[3] *Salawitch et al.* [2002] (herafter S2002) used a steady-state photochemical box model to investigate the effect of NIR HO_2NO_2 photolysis on the predicted abundance of this species and HO_x. They used HO_2NO_2 profiles at both mid and high latitudes to separate uncertainties in the photolysis rate from those in other kinetic processes. For HO_2NO_2, S2002 argued that the NIR photolysis will be most important during high latitude spring where large O_3 columns may attenuate the UV flux and the long days favour photolytic sinks. S2002 found that including NIR photolysis resolved a discrepancy between modelled and balloon-observed sunrise HO_2NO_2 during May at 65°–70°N.

[4] In this paper we further investigate the possible importance of NIR HO_2NO_2 photolysis on stratospheric chemistry, and assess its global importance, by including it in a 3D model. We also investigate how its inclusion improves agreement between the model and MIPAS balloon nighttime HO_2NO_2 observations at different latitudes and seasons.

2. MIPAS-B Data

[5] MIPAS-B [*Friedl-Vallon et al.*, 1999] is a balloon-borne Fourier transform spectrometer which measures limb emission spectra at any time of day, though the results used here are from nighttime observations. MIPAS-B measures profiles of a range of species including HNO_3, $ClONO_2$, N_2O_5, HO_2NO_2 and NO_2 which make up most of the components of stratospheric nighttime NO_y. In this paper we have used results from 4 MIPAS flights covering northern mid-high latitudes for: July 2, 1997 (Gap, 42°N, 7°E), January 27, 1999 (Kiruna, 65°N, 19°E), April 30, 1999 (Aire sur l'Adour, 41°N, 2°E) and January 11, 2001 (Kiruna, 65°N, 34°E) [*Wetzel et al.*, 2002; *Stowasser et al.*, 2002].

3. Photochemical Model

[6] We have used the SLIMCAT three-dimensional (3D) chemical transport model (CTM) and a 1D 'stacked box' column version. SLIMCAT is an off-line 3D CTM first described in [*Chipperfield et al.*, 1996]. Horizontal winds

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Table 1. 3D and 1D Model Experiments

Run	Model	Dates	Comments
B3	3D	10/91–8/01	Basic model
N3	3D	9/96–1/01	As B3 + NIR photolysis
B1	1D	MIPAS flights	Basic model
C1	1D	MIPAS flights	Constrained with MIPAS data
N1	1D	MIPAS flights	Constrained + NIR photolysis
HN1	1D	MIPAS flights	As N1 + updated HO_x kinetics
KN1	1D	MIPAS flights	As N1 + min k_1, max k_3, k_4

and temperatures are specified using meteorological analyses and vertical transport is diagnosed from calculated heating rates. The model contains a detailed stratospheric chemistry scheme (see *Chipperfield* [1999]) and uses photochemical data from *Sander et al.* [2000]. The 1D model (with no vertical transport) uses the same chemical module as the 3D CTM and is used for calculating the full diurnal cycle from the standard 3D model 12 UT output.

[7] NIR photolysis of HO_2NO_2 was included in the chemical scheme using the photodissociation cross section and solar flux values of *Roehl et al.* [2002]. For the temperature-dependent bands the 240 K cross section values were used, which was the lowest temperature at which all laboratory data was available. For the ν_2 band *Roehl et al.* [2002] provide data down to 224 K. Use of this data would decrease our calculated photolysis due to NIR absorption in the cold lower stratosphere by about 17%.

[8] The basic 3D model (run B3) was integrated from October 1991 until August 2001 using UKMO analyses. The model run had a horizontal resolution of 5° lat. × 7.5° lon. A second run (N3, including NIR HO_2NO_2 photolysis) was initialised from run B3 and integrated from September 1996 until January 2001. To compare with the correct time of the MIPAS observations, the 1D model was initialised from the 12 UT output of run B3 or N3 at the appropriate location. For the non-January flights the 1D model was also used to investigate the sensitivity of HO_2NO_2 to a range of photochemical parameters. In each case the model was integrated for 5 days (i.e., much longer than the photochemical lifetime of HO_2NO_2 of $\sim$1 day) so that a repeating diurnal cycle was obtained. The flights of January 1999 and 2001 do not have sufficiently long daylight periods for the 1D model to be used in this way. To permit the most critical comparison of the model with the balloon observations, all of the 1D runs except B1 (the basic model) were constrained with MIPAS observations of temperature, CH_4, H_2O and total NO_y. As well as including the effects of NIR photolysis, 1D model runs were performed to minimise HO_2NO_2 by decreasing the rate of reaction (1), and maximising the rates (3) and (4), within the limits given by *Sander et al.* [2000], and by specifying the rates of the reactions $HO_2 + O_3$ and $OH + O_3$ using a previous recommendation [*DeMore et al.*, 1997]. The model runs are summarised in Table 1.

4. Results

[9] Figure 1 compares profiles of selected NO_y species observed by MIPAS for the 4 balloon flights with model runs B1 and C1. In high latitude winter/spring the peak observed HO_2NO_2 volume mixing ratio (vmr) is $\sim$0.06 parts per billion (ppbv) near 28 km (though the flight of January 11, 2001 measured very low HO_2NO_2). In mid-latitude summer the HO_2NO_2 peak vmr is larger and around 0.1–0.2 ppbv. Results from model run B1 (based on 3D run B3 initialised in 1991) produces a reasonable simulation of total NO_y under all conditions, although differences approach a factor of 2. However, there are differences and a more critical comparison of the modelled NO_y partitioning is obtained by comparison with run C1, which is constrained by MIPAS. This run performs well in reproducing the mid-latitude profiles of NO_2 and N_2O_5. However, for high latitudes the model generally overestimates the nighttime observations of NO_2 and N_2O_5 below 20–25 km except for NO_2 in 2001 when the model underestimates the observations. In high latitude winter the abundance of NO_2 and N_2O_5 is much lower than at mid-latitudes and is sensitive to heterogeneous conversion on aerosols. These differences in wintertime nighttime NO_2 may affect the modelled HO_2NO_2 abundance although this production (which needs HO_2 and therefore sunlight) should mainly be determined by late-fall chemistry.

[10] For HO_2NO_2 model run C1 overestimates the observations on all 4 flights below 30 km but especially in the high latitude winter lower stratosphere.

[11] The comparison of modelled and observed HO_2NO_2 is further investigated in Figure 2 which shows results from 4 1D runs constrained by MIPAS. Including the NIR photolysis causes a large decrease (factor of 2–10) in HO_2NO_2 in high latitude winter/spring. For January 11, 2001 and January 27, 1999 including NIR photolysis brings the model into much better agreement with the observations. Model run N1 lies within the MIPAS error bars for altitudes down to about 27 km. The model does, however, still overestimate HO_2NO_2 at lower altitudes. This may be due to remaining uncertainties in the gas-phase chemistry of HO_2NO_2 and partly related in 1999 to the model's overestimate of NO_2.

[12] Although the effect of the NIR photolysis is smaller at mid-latitudes, its inclusion in the model also improves the

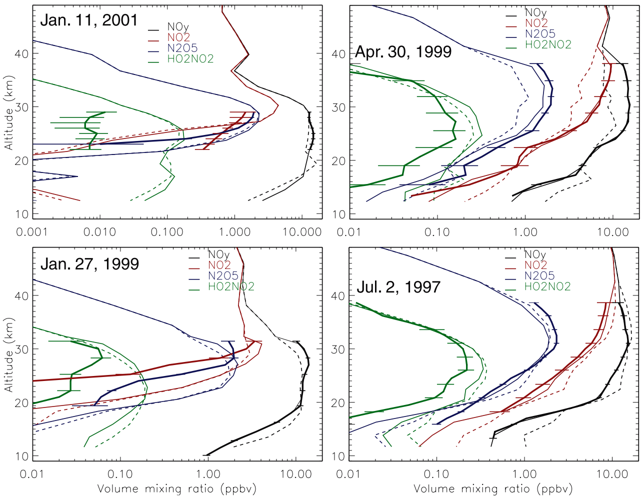

Figure 1. Comparison of NO_y, NO_2, N_2O_5 and HO_2NO_2 observed by MIPAS-B (solid line with error bars) with model calculations from runs B1 (dotted line) and C1 (solid line) for (a) January 11, 2001, (b) January 27, 1999, (c) April 30, 1999, and (d) July 2, 1997. The MIPAS error bars indicate the 1σ total error. Note different x-axis range in (a).

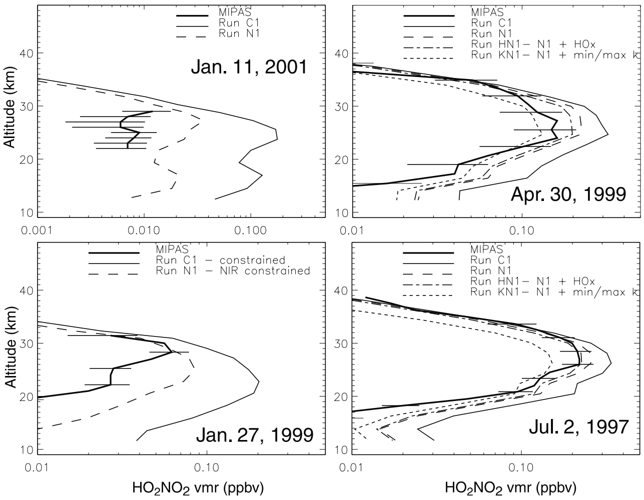

Figure 2. Comparison of MIPAS-B HO_2NO_2 profiles with model calculations from runs C1, N1, HN1 and KN1 for (a) January 11, 2001, (b) January 27, 1999, (c) April 30, 1999, and (d) July 2, 1997. The MIPAS error bars indicate the 1σ total error.

agreement with the MIPAS observations. While run C1 clearly overestimates the observations, run N1 has around 22% less HO_2NO_2 and is much nearer the MIPAS error bars. Changing the production/loss rate of HO_2NO_2 within the limits given by *Sander et al.* [2000] could account for any remaining discrepancies. However, S2002 noted that use of the *DeMore et al.* [1997] rates for OH + O_3 and HO_2 + O_3, which are in better agreement with recent laboratory studies than those in *Sander et al.* [2000] for these reactions and which also lead to better agreement with the measured [HO_2]:[OH] in the lower stratosphere, reduces calculated HO_2NO_2 by ~25% in high latitude summer. In model run HN1 we have applied similar changes and they tend to improve the agreement for the 4 flights considered.

[13] We now investigate the global effects of including the NIR photolysis. Figure 3 illustrates the effect on model O_3, HO_2NO_2, HO_2 and OH in the NH spring at 460 K (~18 km). This is the level of the largest changes in the model. The maximum reduction in HO_2NO_2 is over 75% at high latitudes. As discussed by S2002 the NIR photolysis of HO_2NO_2 is a source of HO_x under twilight conditions. Figure 3 shows the large enhancements of OH and HO_2 near the terminator which exceed 70%. This change in HO_x leads to a modest decrease in O_3 of 1–2% near 50–60°N, with a slight increase at the pole.

[14] The effect of including NIR photolysis at all latitudes over the whole annual cycle at 460 K in the lower stratosphere is shown in Figure 4. The basic model run B3 shows largest HO_2NO_2 at high latitudes and this peaks during summer when the precursors HO_2 and NO_2 are a maximum. Inclusion of NIR photolysis leads to 40% less HO_2NO_2 in the tropics, with larger reductions towards high latitudes. The maximum reduction (up to 95%) occurs during polar winter. The high latitude summer decrease is ~50%. The largest percentage changes in HO_x follow a similar pattern to HO_2NO_2. There is only a small change in the tropics, ~30% enhancement in high latitude summer and up to 70% enhancement near the polar night terminator. In high latitude summer inclusion of the NIR photolysis decreases NO_x by ~10%. This 'buffering' between HO_x and NO_x [e.g., *Wennberg et al.*, 1994; *Nevison et al.*, 1999] results in only a small net change in O_3 which shows a reduction of 1% at northern high latitudes. A similar reduction is also seen at southern mid-high latitudes, although during the Antarctic O_3 hole periods run N3 has up to 5% more O_3 than run B3. In this case model ClO_x is decreased by more rapid deactivation.

5. Summary

[15] Inclusion of NIR photolysis in a stratospheric model significantly reduces the calculated abundance of HO_2NO_2; the largest decrease in high latitude winter near 18 km is over 95%. This improves the agreement between the modelled HO_2NO_2 and MIPAS-B observations at both high and mid-latitudes. These large changes in HO_2NO_2 also lead to large % changes in HO_x near the high latitude terminator. Summertime HO_x increases of 30% are accompanied by NO_x decreases (due to formation of HNO_3) of ~10%. The subsequent change in modelled O_3 near 20 km for current conditions is only 1–2%. Although this change

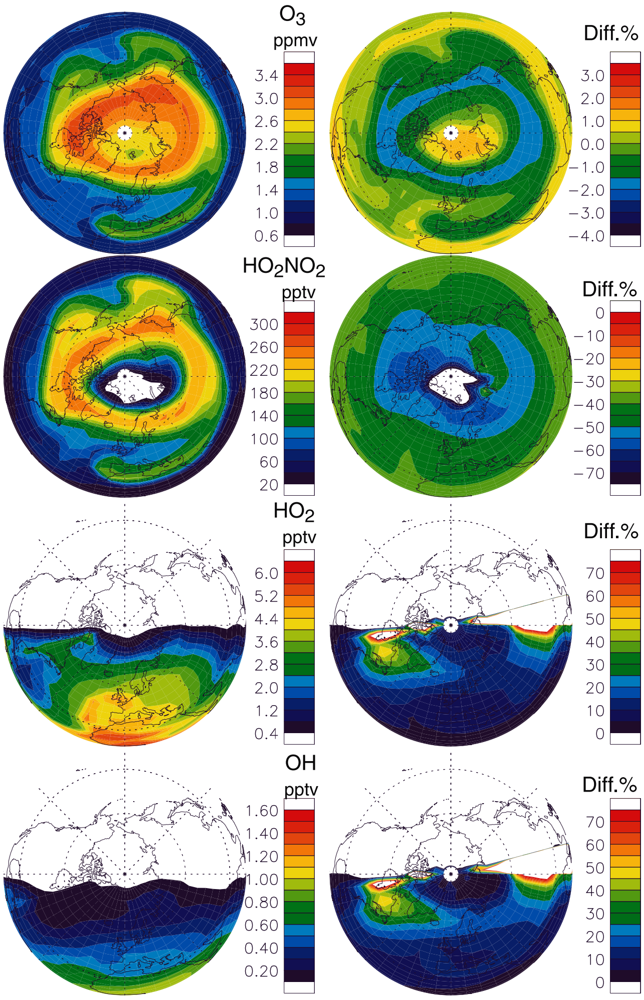

Figure 3. Maps of chemical species from run B3 (left), and difference between run N3 and B3 (right), at 460 K for O_3, HO_2NO_2, HO_2, and OH at 12 UT on March 13, 1997.

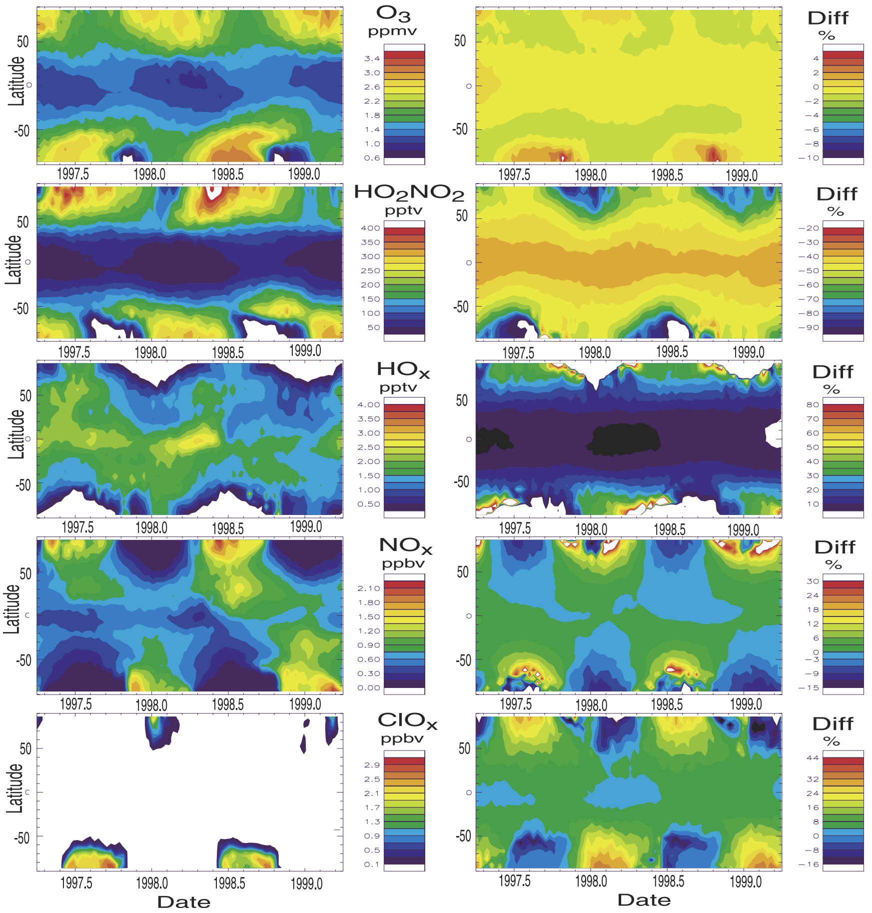

Figure 4. Zonal mean of chemical species from run B3 (left), and difference between run N3 and B3 (right), at 460 K for O_3, HO_2NO_2, HO_x, NO_x (= NO + NO_2), and ClO_x (= Cl + ClO + $2Cl_2O_2$) for 1997–1999.

is relatively small the modified sensitivity of O_3 to HO_x and NO_x may mean that this process will alter the modelled response of O_3 to perturbations in stratospheric NO_y and H_2O. An investigation of this will require long-term model simulations.

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References

Chipperfield, M. P., Multiannual simulations with a three-dimensional chemical transport model, *J. Geophys. Res.*, *104*, 1781–1805, 1999.

Chipperfield, M. P., et al., Analysis of UARS data in the southern polar vortex in September 1992 using a chemical transport model, *J. Geophys. Res.*, *101*, 18,861–18,881, 1996.

DeMore, W. B., et al., Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 12, *JPL Publ.*, *97-4*, 1997.

Donaldson, D. J., et al., Atmospheric radical production by excitation of vibrational overtones via absorption of visible light, *Geophys. Res. Lett.*, *24*, 2651–2654, 1997.

Friedl-Vallon, F., et al., The balloon-borne Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B2)—Instrument and Results, in *Optical Spectroscopic Techniques and Instrumentation for Atmospheric and Space Research III*, *Proc. SPIE*, *3756*, 9–16, 1999.

Nevison, C. D., S. Solomon, and R. S. Gao, Buffering interactions in the modeled response of stratospheric O_3 to increased NO_x and HO_x, *J. Geophys. Res.*, *104*, 3741–3754, 1999.

Roehl, C. A., et al., Photodissociation of HNO_4 in the near IR, *J. Phys. Chem. A*, *106*, 3766–3772, 2002.

Salawitch, R. J., et al., Near IR photolysis of HO_2NO_2: Implications for HO_x, *Geophys. Res. Lett.*, *29*(16), 1762, doi:10.1029/2002GL015006, 2002.

Sander, S. P., et al., Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation no 13, *JPL Publ.*, *00-3*, 2000.

Stowasser, M., et al., A characterization of the warm 1999 Arctic winter by observations and modeling: NO_y partitioning and dynamics, *J. Geophys. Res.*, *107*(D19), 4376, doi:10.1029/2001JD001217, 2002.

Wennberg, P. O., et al., Removal of stratospheric O_3 by radicals—In-situ measurements of OH, HO_2, NO, NO_2, ClO, and BrO, *Science*, *266*, 398–404, 1994.

Wennberg, P. O., et al., Twilight observations suggest unknown sources of HO_x, *Geophys. Res. Lett.*, *26*, 1373–1376, 1999.

Wetzel, G., et al., NO_y partitioning and budget and its correlation with N_2O in the Arctic vortex and in summer mid-latitudes in 1997, *J. Geophys. Res.*, *107*(D16), 4280, doi:10.1029/2001JD000916, 2002.

M. P. Chipperfield and J. T. Evans, School of the Environment, University of Leeds, Leeds LS2 9JT, UK. (martyn@env.leeds.ac.uk)

H. Oelhaf, M. Stowasser, and G. Wetzel, IMK, Forschungszentrum Karlsruhe, Universität Karlsruhe, Karlsruhe, Germany.