

Strong daytime production of OH from HNO₂ at a rural mountain site

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[1] Nitrous acid and OH were measured concurrently with a number of other atmospheric components and relevant photolysis frequencies during two campaigns at the Meteorological Observatory Hohenpeissenberg (980 m a.s.l.) in summer 2002 and 2004. On most of the 26 measurement days the HNO₂ concentration surprisingly showed a broad maximum around noon (on average 100 pptv) and much lower concentrations during the night (~30 pptv). The results indicate a strong unknown daytime source of HNO₂ with a production rate on the order of $2-4 \times 10^6 \text{ cm}^{-3}\text{s}^{-1}$. The data demonstrate an important contribution of HNO₂ to local HO_x levels over the entire day, comparable with the photolysis of O₃ and HCHO. On average during the 2004 campaign, 42% of integrated photolytic HO_x formation is attributable to HNO₂ photolysis. **Citation:** Acker, K., D. Möller, W. Wieprecht, F. X. Meixner, B. Bohn, S. Gilge, C. Plass-Dülmer, and H. Berresheim (2006), Strong daytime production of OH from HNO₂ at a rural mountain site, *Geophys. Res. Lett.*, 33, L02809, doi:10.1029/2005GL024643.

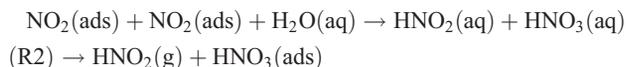
1. Introduction

[2] Nitrous acid (HNO₂) is a key component in tropospheric oxidant chemistry due to its potential contribution to the formation of the hydroxyl radical, OH. Beside nitric acid it has been detected in air (rain water) in the 1850s [Engler, 1879] and attributed to formation while thunderstorms. HNO₂ was measured for the first time in ambient air by Perner and Platt [1979], and numerous subsequent laboratory, field, and modelling studies were conducted to explain the observed atmospheric concentrations. These cannot satisfactorily be explained, neither by homogeneous gas reaction R1,



which is too slow, nor by direct emissions from combustion processes, which are too small.

[3] Presently heterogeneous reaction of NO₂ with water on terrestrial surfaces is suspected to be a main HNO₂ source, especially during the night:



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Recent studies [Svensson *et al.*, 1987; Lammel and Cape, 1996; Kleffmann *et al.*, 2003; Finlayson-Pitts *et al.*, 2003; Stutz *et al.*, 2004] show, that the kinetics of R2 is first order in NO₂. Moreover the NO₂ conversion frequency depends on the surface to volume ratio and the surface properties, respectively, and seems to be similar in urban as in rural areas. The amount of surface adsorbed water appears to play a crucial role.

[4] The major sink for atmospheric HNO₂ is photolysis producing OH radicals:



[5] In addition, HNO₂ can also be removed to a few percent by direct reaction with OH:



Surprisingly, our present study as well as other recent work show that even at noon HNO₂ photolysis R3 may produce OH formation rates comparable to ozone photolysis [Alicke *et al.*, 2002; Aumont *et al.*, 2003]. Despite the rapid photolysis process unexpectedly high values of HNO₂ (100–400 pptv) have been detected during the day in urban but also rural regions [Febo *et al.*, 1996; Zhou *et al.*, 2002; Trick, 2004; Acker *et al.*, 2005].

[6] Assuming photo-stationary state (PSS) between reactions R1, R3 and R4 one may deduce an estimate for the “unexplained” daytime source of HNO₂ missing in the balance. Kleffmann *et al.* [2005] found that the “missing” daytime HNO₂ source was up to a factor of 64 more efficient than heterogeneous HNO₂ production via R2. Already in 1987 Akimoto *et al.* [1987] suggested that a photocatalytic enhancement of HNO₂ formation would explain an excess OH production observed in smog chamber experiments, but without giving a mechanistic explanation. Recently, George *et al.* [2005] studied the effect of light in the range 300–500 nm on the uptake kinetics of NO₂ on various surfaces containing photosensitive organic substrates. They found that under humid conditions the photo-induced conversion of NO₂ to HNO₂ via electron transfer reactions exceeded the rate of the (dark) reaction R2 by more than one order of magnitude depending on the substrate.

[7] In this study we will present the first concurrent measurements of HNO₂ and OH including diurnal variations obtained during two field campaigns at Hohenpeissenberg in rural southern Germany. From the diurnal profiles the contributions of HNO₂ photolysis to OH radical formation are derived and the missing HNO₂ source is estimated.

2. Experiment

[8] Measurements were performed in the summers of 2002 (3–12 July) and 2004 (29 June–14 July) at the

Meteorological Observatory Hohenpeissenberg (48°N, 11°E) at about 300 m above the surrounding countryside (mainly forest and pastures) and ~18 m above ground level which roughly corresponds to the canopy level of the closest trees on the steep slopes of Hohenpeissenberg. At this observatory the German Weather Service operates its Global Atmosphere Watch program (GAW), featuring the monitoring of a broad range of meteorological and atmospheric chemical parameters including OH (www.dwd.de/gaw), hence providing a platform for detailed research studies [Handisides *et al.*, 2003; Mannschreck *et al.*, 2004]. There are no significant industrial sources in the vicinity, the nearest major city is Munich ~70 km NE, dominating wind direction is SW.

[9] HNO₂ was measured by a coupled wet denuder sampling/ion chromatography analysis technique described by Acker *et al.* [2005]. At a sample air flow of 10 l min⁻¹ and analysing the solutions containing the scavenged acid after 15 min of preconcentration, the detection limit was 3 pptv. OH was measured by chemical ionization mass spectrometry [Berresheim *et al.*, 2000] based on complete titration of OH with ³⁴SO₂ and detection of the corresponding gaseous bisulfate anion (H³⁴SO₄⁻). At 5 min signal integration the detection limit was 1.4 × 10⁵ cm⁻³.

[10] Photolysis-frequencies were obtained from spectral actinic flux measurements, the spectro-radiometer consisted of actinic flux quartz receptor optics, a 10 m quartz fibre, a double-monochromator, and a UV sensitive photomultiplier [Hofzumahaus *et al.*, 1999].

[11] In 2004 additional O₃ measurements were performed at a foothill site 710 m a.s.l., 2 km south of the observatory.

[12] Since the temporal resolution of HNO₂ was poorest (15 min), all measured quantities were averaged over the HNO₂ measurement periods to create a synchronized data set for further analysis.

3. Results

[13] To our surprise the highest HNO₂ mixing ratios were consistently measured during daytime in both campaigns, showing either a broad maximum or several distinct peaks occurring between 0800 and 1600 Central European Time (CET), see Figures 1 and 2. This daily variation differs from that generally observed elsewhere, i.e., accumulation of significant HNO₂ levels at night, followed by a rapid decrease after sunrise due to efficient photolysis via R3. At Hohenpeissenberg, average noontime levels reached 110 pptv in both years whereas nighttime minimum values were significantly lower in 2002 (10–20 pptv) compared to 2004 (~40 pptv). During night the station of the hilltop site is mostly out of the stable nocturnal boundary layer of the foothill area. Night-time measurements at the hilltop site are therefore more characteristic for the so-called residual layer, which resembles the fully mixed convective (daytime) boundary layer of the day before, with low to moderate NO_x levels (Figure 2). The diurnal profiles of O₃ (Figure 1d) measured simultaneously at 980 m and 710 m a.s.l. respectively demonstrate the strength of nighttime decoupling and effective daytime mixing between foothill and hilltop layers. Higher hilltop wind speeds were observed in 2004 compared to 2002 (Figure 1c), and may have weakened the

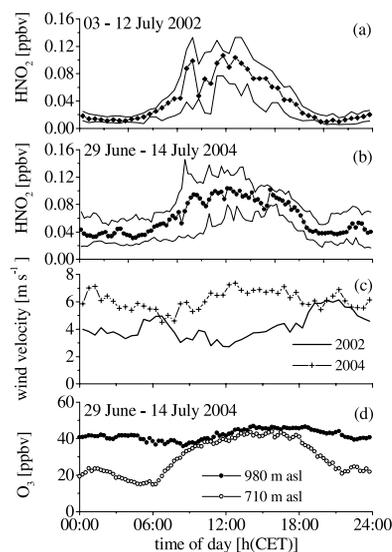


Figure 1. Diurnal variation of HNO₂ at Hohenpeissenberg averaged for the periods 03 July–12 July 2002 (a) and 29 June–14 July 2004 (b), given as median and 0.25 and 0.75 quartiles. In (c) the averaged wind velocity (median) is shown for both periods. Additionally in (d) the diurnal variation (medians) of O₃ at Hohenpeissenberg summit is compared with O₃ at a foothill site, both averaged for the period 29 June–14 July 2004.

nighttime decoupling (by mechanic turbulence). Therefore the higher nighttime HNO₂ concentrations in 2004 (Figure 1b) compared to 2002 (Figure 1a) may be caused by occasional turbulent transport of foothill accumulated HNO₂ to the hilltop.

[14] On a daily basis HNO₂ and OH levels closely followed temporal variations in solar insolation as reported for example by J(HNO₂) in Figure 2. Linear correlation coefficients $r^2 = 0.48$ (HNO₂) and $r^2 = 0.86$ (OH) were obtained with regard to J(HNO₂) in 2004. On the other hand, the correlation of HNO₂ with NO₂ is much poorer; considering all data, $r^2 = 0.016$ is obtained. On average, a HNO₂ to NO₂ ratio of 0.063 ± 0.06 (1 σ) is obtained, similar to values found at other rural and urban sites [Stutz *et al.*, 2004; Kleffmann *et al.*, 2003; Acker *et al.*, 2005] and the ratio is higher during daytime (0.089) compared to nighttime (0.034). The correlation between HNO₂ and the relative humidity (all data) is also poor and even negative ($r^2 = 0.129$).

4. Discussion

[15] Our results indicate that some other factors than gas phase NO₂ concentration and relative humidity were controlling the temporal HNO₂ distribution. The strong correlation with solar radiation suggests a substantial light-induced production of HNO₂. HNO₂ maxima at noon and comparably lower concentrations at night have also been observed at other mountain stations. Kleffmann *et al.* [2002] reported measurements at 2650 m a.s.l. near Mt. Zugspitze, Germany, with HNO₂ levels increasing from 10 to 30 pptv and a simultaneous increase in J(HNO₂) during the onset of sunny conditions. A correlation of HNO₂ and

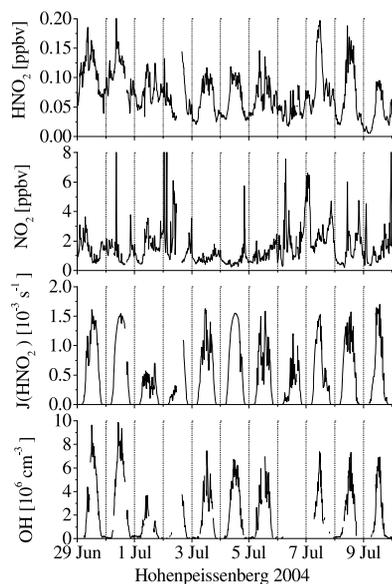


Figure 2. Time series of HNO₂, NO₂, photolysis frequency J(HNO₂), and OH measured between 29 July and 09 July 2004 at Hohenpeissenberg.

solar radiation was also observed at Whiteface Mountain (1483 m a.s.l., USA) by *Huang et al.* [2002]. They suggested that elevated HNO₂ were produced by heterogeneous surface sources in conjunction with upslope winds. HNO₂ peaks observed during mid-morning hours at a rural site in Pinnacle State Park (515 m a.s.l., USA) were attributed to the evaporative release of HNO₂/nitrite from dew originally trapping these compounds near the ground [*Zhou et al.*, 2002]. The authors also proposed nitrate/HNO₃ photolysis on wet surfaces as a major candidate for the missing HNO₂ source. However, in atmospheric simulation chamber experiments [*Rohrer et al.*, 2005] the latter process was found to be negligible.

[16] In the following we estimate the strength of the “unknown” daytime HNO₂ source and the production rate of OH from HNO₂ photolysis. First we assume that during midday the HNO₂ PSS conditions quickly establish, since the HNO₂ life-time with respect to photolysis is about 10–15 min. It is further assumed that the only important homogeneous gas phase reaction forming nitrous acid was R1. Based on the measured values of OH, NO and J(HNO₂) and using R1, R3 and R4 (with corresponding rate constants k_1 and k_4 taken from Atkinson et al. [2004] photostationary HNO₂ mixing ratios were calculated for bright sunny days in 2004 ($J(\text{NO}_2) \geq 6 \times 10^{-3} \text{ s}^{-1}$). Daytime maximum PSS levels of 4 pptv on 30 June, 5 pptv on 04 July, and 45 pptv on 08 July were obtained, significantly lower than corresponding observed HNO₂ levels (Figure 2). The ratio of the gas phase HNO₂ source to the sinks, R1/(R3 + R4), varied between 0.03 (on 30 June, 04 July) and 0.24 (on 08 July) around noon, indicating, that a major additional HNO₂ source is required to make up the balance. A contribution is expected from the heterogeneous conversion of NO₂ to HNO₂, according to R2. Most likely the ground and forest canopy on the mountain slope around the station contribute as reactive surfaces to this pathway, whereas aerosols could be neglected (with 50–250 $\mu\text{m}^2 \text{ cm}^{-3}$ aerosol

surface and at 1 ppbv NO₂ the max. HNO₂ production is only $10^3 \text{ molecule cm}^{-3} \text{ s}^{-1}$). Since the exact mechanism of R2 is unknown, the source strength may be estimated from the measured increase of the HNO₂/NO_x ratio in the late evening hours and the assumption that the rate is independent of the time of day [*Alicke et al.*, 2002; *Kleffmann et al.*, 2003]. An upper limit of thus determined k_2 values of $2 \times 10^{-6} \text{ s}^{-1}$ is estimated for the Hohenpeissenberg data. With this value and reactions R1–R4, the total HNO₂ source/sink ratio increases only slightly (0.05–0.34). Apparently the heterogeneous HNO₂ production according to R2 is of minor importance as a daytime source.

[17] Overall, a missing daytime HNO₂ source of $(3 \pm 1) \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ (1σ) is calculated from a simple R1–R4 balance equation under conditions with $J(\text{HNO}_2) > 1 \times 10^{-3} \text{ s}^{-1}$ during the 2004 campaign. This required source is larger than the NO_x sink due to reaction of NO₂ with OH, which implies a (typically two-fold) cycling of NO_x through HNO₂ (with subsequent photolysis) before NO₂ is converted into HNO₃. Thus, we have a substantial daytime source leading to a HNO₂ increase until noon despite its fast photolysis. However, the nature of this source remains unknown. One possible source mechanism may involve heterogeneous formation on organic films on ground and vegetation surfaces with directly photo-catalyzed electron transfer to NO₂, as recently suggested by *George et al.* [2005]. However, also yet unconsidered photochemical processes in the gas phase leading to HNO₂ formation cannot be excluded.

[18] The production rate of HO_x(= OH + HO₂) radicals was calculated from the measured photolysis frequencies and mixing ratios of O₃, HNO₂, and HCHO as

$$P(\text{HO}_x) = J(\text{O}^1\text{D})[\text{O}_3]\Phi_{\text{OH}} + J(\text{HNO}_2)[\text{HNO}_2] + 2J(\text{HCHO})_r[\text{HCHO}] \quad (1)$$

(with Φ_{OH} = OH yield of the O(¹D) + H₂O reaction under the measurement conditions, $J(\text{O}^1\text{D})$ = photolysis frequency O₃ → O(¹D), and $J(\text{HCHO})_r$ = photolysis frequency HCHO → H + HCO).

[19] In Figure 3 results are shown for 04 July 2004. Clearly, the important role of HNO₂ (corrected for (R4) which removes HO_x) is evident. Photolysis of HNO₂ starts at larger solar zenith angles compared to photolysis of HCHO and O₃, and particular in the morning contributions from HNO₂ photolysis are even higher than from O₃ photolysis. If the HNO₂ concentration is calculated from PSS, its HO_x production rate would be substantially underestimated. Based on equation (1), a 42% contribution of HNO₂ photolysis to the integrated HO_x formation at the top of Hohenpeissenberg was calculated for the 2004 campaign.

5. Conclusion

[20] HNO₂ and OH concentrations were measured together with other trace gases at Hohenpeissenberg on 16 days in summer 2004 and on 10 days in summer 2002. The results demonstrate the important role of HNO₂ as radical source both in the morning, when photolysis starts, but also throughout the entire day. Between 0900 and 1500 CET the contribution of HNO₂ photolysis to HO_x production is comparable to that of ozone and formaldehyde. Diurnal cycles of HNO₂ with maximum concentrations

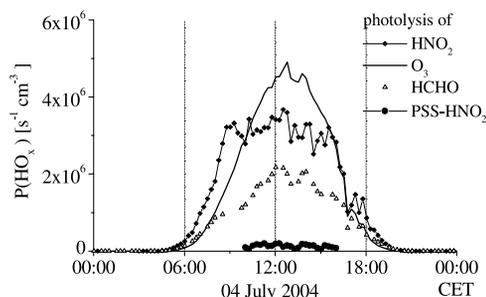


Figure 3. HO_x radical production rates P(HO_x) at Hohenpeissenberg for 04 July 2004 from the photolysis of HNO₂ (closed diamonds), HCHO (open triangles), O₃ (solid line), and HNO₂ (closed circles) calculated from PSS neglecting the unknown daytime source.

around noon were observed despite its effective photolytic decay. The ratio of known HNO₂ sources to sinks varied around noon between 0.05 and 0.34 indicating a major daytime source still missing in this balance. Better characterization of the unknown source mechanism is the subject of further studies currently in progress. This includes measurements of HNO₂ at the Hohenpeissenberg observatory and in the valley below to study in more detail the relative contributions to local HNO₂ levels from direct emission, transport, and heterogeneous production.

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