Daytime formation of nitrous acid: A major source of OH radicals in a forest

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[1] Daytime concentrations of HONO, NO_x, OH and photolysis frequencies were measured during the ECHO field campaign in a mixed deciduous forest near Jülich, West-Germany, in summer 2003. Midday measurements show clear evidence for a large, yet unexplained daytime source of HONO (~500 pptv/h), which represents an important net source of OH radicals due to ongoing HONO photolysis. The evidence for a large HONO daytime source is for the first time completely constrained by measured parameters, needed to determine the daytime budget of HONO. The large contribution of 33% to the primary OH production during noon at the top of the forest canopy suggests that the unexplained source of HONO could have an important impact on the photochemical transformation of biogenically emitted volatile organic compounds (VOCs) by OH into partly oxidized VOCs and secondary organic aerosols during their release from forest regions into the troposphere. **Citation:** Kleffmann, J., T. Gavriloaiei, A. Hofzumahaus, F. Holland, R. Koppmann, L. Rupp, E. Schlosser, M. Siese, and A. Wahner (2005), Daytime formation of nitrous acid: A major source of OH radicals in a forest, *Geophys. Res. Lett.*, *32*, L05818, doi:10.1029/2005GL022524.

1. Introduction

[2] It is generally accepted that the photolysis of nitrous acid (HONO), which accumulates in the planetary boundary-layer at night, can be an important source of OH radicals in polluted air in the early morning [*Platt et al.*, 1980; *Calvert et al.*, 1994; *Lammel and Cape*, 1996; *Alicke et al.*, 2003]:

$$(R1) \qquad HONO + h\nu \rightarrow NO + OH$$

The nighttime build-up of HONO up to several ppbv is generally ascribed to direct emissions or heterogeneous conversion of NO_x to HONO [*Calvert et al.*, 1994; *Vogel et al.*, 2003], but the possible mechanisms are not completely understood [*Finlayson-Pitts et al.*, 2003, and references therein]. The knowledge of the daytime chemistry of HONO is even more uncertain, because measured daytime concentrations have been generally at the limit of detection (typ. 0.05–0.2 ppbv). The low observed values were explained with an assumed photostationary state (PSS),

which is dominated by an equilibrium between photo-decomposition (R1) and back reaction of OH with NO,

$$(R2) \qquad NO + OH + M \rightarrow HONO + M$$

with little net effect on OH [*Calvert et al.*, 1994]. Heterogeneous production of HONO as observed during night may constitute a net source of OH during daytime [*Harrison et al.*, 1996; *Alicke et al.*, 2002, 2003], but has little impact on the concentrations of HONO and OH at midday [*Alicke et al.*, 2002, 2003].

[3] In some recent field studies, instruments with improved detection limits (0.001–0.050 ppbv) measured HONO concentrations during daytime, which were significantly larger than can be explained by the PSS [*Neftel et al.*, 1996; *Staffelbach et al.*, 1997; *Kleffmann et al.*, 2002, 2003; *Zhou et al.*, 2002a]. A strong daytime source of HONO was postulated to explain the difference [*Staffelbach et al.*, 1997; *Zhou et al.*, 2002a, 2003; *Kleffmann et al.*, 2002, 2003]. The shortcoming of these studies was the lack of directly measured values of the OH concentration and the HONO photolysis frequency, J(HONO). These quantities had to be estimated in order to predict the PSS concentration and thereby the daytime source strength of HONO. In another recent study, HONO and OH were measured in New York city, showing that HONO photolysis contributed about half of the OH production in polluted urban air [*Ren et al.*, 2003]. However, J(HONO) was only modelled in this study and possible reasons for the high HONO concentrations like direct emissions from automobile traffic were not discussed.

[4] The present work is the first one in which all quantities needed to assess the photochemical equilibrium of OH and HONO have been measured. Our results, obtained at a forest site, show strong evidence for an unknown daytime source of HONO, which cannot be explained by emissions or heterogeneous NO_x conversion as observed during night. It is also shown that HONO contributes substantially to the local primary OH production and may therefore have an important influence on the OH oxidation of biogenic VOCs emitted from the forest.

2. Experimental

[5] The measurements were performed during the ECHO (Emission and CHemical transformation of biogenic volatile Organic compounds) campaign in a mixed deciduous forest in Germany at the research centre of Jülich in summer 2003. The measurements were collected simultaneously on a tower at a

height of 38 m, about 8 m above the forest canopy. HONO, OH, and photolysis frequencies were measured *in-situ*, while other gases (e.g., NO_x, O_3, HCHO, and VOCs) were sampled by inlet lines and analyzed at the ground.

[6] HONO was measured with a highly sensitive, home-build long-path absorption photometer (LOPAP®) with a detection limit of $1-2$ pptv at a time resolution of 4 minutes [*Kleffmann et al.*, 2002]. Gaseous HONO is sampled in a stripping coil by a fast chemical reaction in a liquid solution and converted into an azo dye. The product is then detected photometrically by long path absorption in Teflon tubings. A two-channel concept serves to eliminate all known interferences. Artifacts like the heterogeneous HONO formation in sampling lines [e.g., *Zhou et al.*, 2002b] are minimized by an external sampling unit, which contains the stripping coils, without using inlet lines. The concept was recently compared against a DOAS instrument which measured HONO directly in the atmosphere [*Trick*, 2004]. Both techniques observed HONO in the same air mass near the city centre of Milan and showed excellent agreement of the measured concentrations at day and night. Thus, there is no experimental indication for instrumental artifacts in atmospheric measurements by LOPAP.

[7] OH was measured with a newly built laser-induced fluorescence instrument, following the well established concept used previously by the same group [*Holland et al.*, 2003, and references therein]. The radicals are sampled by expansion of ambient air into a low pressure chamber and OH is detected directly by its fluorescence after laser excitation at 308 nm. Calibration is performed by known amounts of OH radicals, which are generated by photolysis of water vapor at 185 nm. The detection limit was $\sim5 \times 10^5$ cm^{-3} in 90 s measurement time.

[8] Photolysis frequencies of O_3, NO_2, HONO, and HCHO were derived from actinic flux spectra measured every 3 minutes by a scanning spectroradiometer [*Hofzumahaus et al.*, 1999]. In addition, $J(O^1D)$ and $J(NO_2)$, were measured with a time resolution of $5-6$ s by calibrated filter radiometers, which showed good agreement with the spectroradiometer results. As in previous campaigns [e.g., *Kraus and Hofzumahaus*, 1998], an essentially linear correlation was observed between $J(NO_2)$ and $J(HONO)$. This relationship was used to interpolate the $J(HONO)$ data by means of the $J(NO_2)$ filter radiometer signals, in order to obtain highly time resolved $J(HONO)$ data.

[9] NO and NO_2 were measured with a chemiluminescence analyzer (ECO PHYSICS TR480) equipped with a photolytic converter for NO_2 to NO conversion. The resulting detection limit was 5 and 10 pptv for NO and NO_2, respectively, with a time resolution of 60 s. Measurements of HCHO were based on the Hantzsch method and fluorometric detection using a commercial instrument (AL 4001, Fa. Aero Laser). The detection limit was 30 pptv and the time resolution 3.5 minutes. Biogenic VOCs were analyzed by an online GC-FID and anthropogenic VOCs were measured from whole air samples, collected in SilcoSteel™ canisters using a standard GC-FID system.

3. Results and Discussion

[10] HONO concentrations were measured from 30 June to 1 August 2003 and showed diurnal cycles similar to those
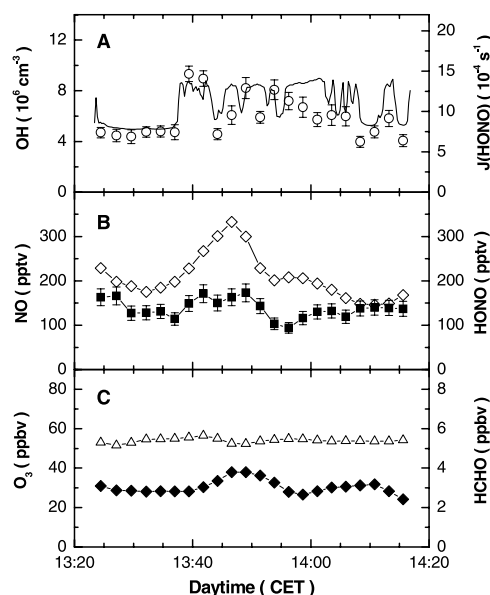

Figure 1. Measurements of trace gases and J(HONO) above a forest canopy at 38 m height, close to the research centre Jülich, Germany, on 29 July 2003. (a) OH radicals (open circles) and J(HONO) (solid line); (b) NO (open diamonds) and HONO (filled squares); (c) O_3 (open triangles) and HCHO (closed diamonds). Error bars indicate the 1σ precision of the measurements.

reported previously [*Harrison et al.*, 1996]. HONO increased slowly every night, reaching $0.5-2$ ppbv, followed by rapid photodecomposition after sunrise until minimum values ($0.04-0.3$ ppbv) were reached at day. In order to investigate the daytime PSS of HONO, a one hour period at noon on the 29 July 2004 was chosen for conditions, such that the expected PSS should be quickly established due to intense insolation, causing a short photolytic HONO lifetime ($10-20$ min.). The mean HONO concentration of about 140 pptv (Figure 1) was similar to the mean concentration during the whole campaign for this time of the day. The concentration of OH showed changes between 4×10^6 cm^{-3} and 9×10^6 cm^{-3}, partly due to variations in the solar ultraviolet radiation, as seen from J(HONO) (Figure 1a).

[11] The measured HONO values may be compared to model results based on the gas phase reactions that are known to play a significant role in the atmosphere [*Calvert et al.*, 1994] (Figure 2, reactions (R1)–(R3)). Two approaches were used to simulate the HONO concentration, using the measured values of OH, NO and J(HONO) as model input. The first approach (PSS) assumes an instantaneous photoequilibrium, which is described by the following expression:

$$[HONO]_{PSS} = \frac{k_2[NO][OH]}{J(HONO) + k_3[OH]} \tag{1}$$

Here, $k_2 = 9.8 \times 10^{-12}$ cm^3 s^{-1} and $k_3 = 6.0 \times 10^{-12}$ cm^3 s^{-1} are the rate constants for the respective reactions at T = 298 K, p = 1010 hPa [*Atkinson et al.*, 2004]. From equation (1) a mean concentration of about 11 pptv HONO is calculated, more than one order of magnitude smaller than
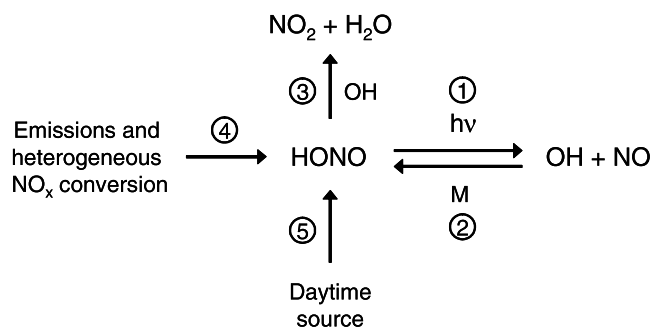
Figure 2. Schematic of the chemistry of HONO in quasi-equilibrium with OH radicals in the atmosphere. The circled numbers denote different processes that influence the concentration of HONO in the gas phase.
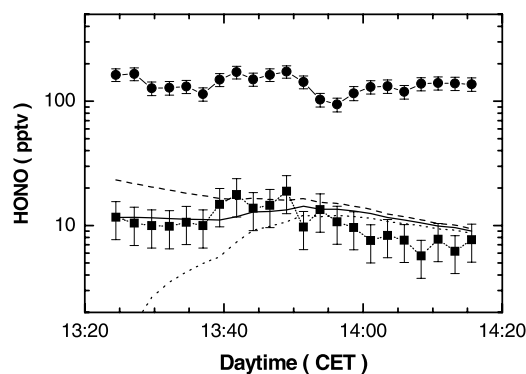

Figure 3. Comparison of measured HONO concentrations with model predictions for a pure gas phase mechanism (reactions (1)–(3) in Figure 2): Solid line with dots denotes the measured HONO data; solid line with squares denotes the PSS calculation; the different lines represent time dependent model runs (see text) with different starting values: $[HONO]_{initial} = 0$ (dotted line), $[HONO]_{initial} = [HONO]_{PSS}$ (solid line), and $[HONO]_{initial} = 2 \times [HONO]_{PSS}$ (dashed line). Error bars on the PSS values denote the accuracy due to experimental uncertainties of the input parameters.

the measurements. The discrepancy clearly cannot be explained by the measurement and model errors (Figure 3).

[12] Since the model input parameters varied significantly on short time scale (Figure 1), the assumption of an instantaneously established PSS might not be justified. Therefore, in a second approach, the HONO concentration was simulated by a time dependent model. The differential rate equations for reactions (R1)–(R3) were mathematically integrated using the FACSIMILE code (AEA Technology) and the measured time series of OH, NO and J(HONO) were used as input parameters. As a sensitivity test, three different initial HONO concentrations were used in the model (Figure 3). While the three model runs differ significantly in the initial phase, the results to the end of the runs converge and are only slightly affected by the starting conditions. The time dependent model predictions differ somewhat from the PSS model result, but neither model approach can explain the much higher measurements.

[13] To obtain agreement, an additional HONO source is required. A potential candidate is the process R4 (Figure 2) responsible for the observed build-up of HONO at night. Assuming that the HONO formation is first order in the NO_x concentration [*Vogel et al.*, 2003], an apparent conversion rate coefficient of $1.2 \times 10^{-6} \text{ s}^{-1}$ can be determined from the measured increase of the $HONO/NO_x$ ratio at night for the ECHO campaign. This value is in good agreement with other studies [*Alicke et al.*, 2002, 2003; *Vogel et al.*, 2003; *Kleffmann et al.*, 2002, 2003] and was used to estimate a mean HONO source strength of 8 pptv/h for midday of July 29. Its inclusion into the model increases the calculated HONO concentrations only marginally by ~18%, but not by an order of magnitude. Therefore, we propose an additional, yet unknown daytime source of HONO for our measurement site. To match the PSS model value with the measurements, a source strength of ~500 pptv/h is required, which is a factor 64 more efficient than the night-time source.

[14] Our evidence for the daytime source is based completely on measured quantities, confirming previous conjectures of a daytime source in urban and rural air, inferred from measurements of HONO and NO alone [*Zhou et al.*, 2002a; *Kleffmann et al.*, 2002, 2003; *Vogel et al.*, 2003]. It has been supposed that such daytime formation of HONO originates on ground surfaces and depends on solar radiation [*Zhou et al.*, 2002a, 2003; *Kleffmann et al.*, 2002, 2003; *Vogel et al.*, 2003]. Based on laboratory results, photolysis

of nitrate and nitric acid on humid surfaces has been proposed as a possible mechanism [*Zhou et al.*, 2002a, 2003; *Ramazan et al.*, 2004]. In another recent investigation, light-driven HONO formation was observed on wall surfaces in an atmospheric simulation chamber [*Rohrer et al.*, 2004], but photolysis of nitrate could be definitely excluded as an explanation. Thus, there appear to exist different light-dependent processes that could possibly explain our field results.

4. Atmospheric Implications

[15] The existence of the daytime HONO source has a number of important implications. To quantify the relevance at our measurement site, the primary production of OH was compared for different radical sources, i.e. the photolysis of O_3, HONO, HCHO, and ozonolysis of unsaturated VOCs (alkenes, terpenes) (Table 1). Using the procedure outlined in a previous study [*Alicke et al.*, 2003] and subtracting the loss rate of OH due to reaction with NO (R2), a total net OH production rate of $(8-11) \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ is derived with contributions of 33% by HONO, 31% by HCHO, 28% by

Table 1. Major Chemical Processes Forming OH in the Troposphere [*Finlayson-Pitts and Pitts*, 1997]

Chemical Processes
$O_3 + h\nu \ (\lambda < 340 \text{ nm}) \rightarrow O(^1D) + O_2$
$O(^1D) + H_2O \rightarrow OH + OH$
$HONO + h\nu \ (\lambda < 400 \text{ nm}) \rightarrow OH + NO$
$HCHO + h\nu \ (\lambda < 370 \text{ nm}) \rightarrow H + HCO$
$\rightarrow H_2 + CO$
$H + O_2 + M \rightarrow HO_2 + M$
$HCO + O_2 \rightarrow HO_2 + CO$
$HO_2 + NO \rightarrow OH + NO_2$
$Alkene + O_3 \rightarrow \ldots \rightarrow OH + \text{other products}$

O$_3$, and 8% by ozonolysis of VOCs. Here the photolysis of HONO represents the dominant OH source, followed closely by the photolysis of HCHO and O$_3$ with about equal contributions. These processes initiate the formation of high OH concentrations up to almost 10^7 radicals per cm^3 (cf. Figure 1), which rapidly oxidize biogenic VOCs (e.g., isoprene, terpenes), emitted from the forest canopy, in about 10–30 minutes.

[16] If our results are applicable to other forest areas, daytime formation and photolysis of HONO could have a general major impact on the net emission of biogenic VOCs and their oxidation products from the source region. This and indications for daytime formation of HONO in other environments [*Kleffmann et al.*, 2002, 2003; *Vogel et al.*, 2003; *Zhou et al.*, 2001, 2002a; *Ren et al.*, 2003] suggest that the general role of HONO for the photochemistry in the lower troposphere has been significantly underestimated in the past. Firstly, tropospheric chemistry models do not currently contain HONO formation processes as reported in this study and may therefore underpredict the concentration of OH. Secondly, in ground-based field experiments, where OH and many other atmospheric parameters were measured for critical tests of tropospheric photochemistry models [see, e.g., *Heard and Pilling*, 2003], measurements of HONO as a possible precursor of OH were mostly missing. New field experiments will therefore be needed that include sensitive HONO measurements to re-evaluate our understanding of the relative importance of key processes in tropospheric trace gas degradation.

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