



## Occurrence of atmospheric nitrous acid in the urban area of Beijing (China)

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### HIGHLIGHTS

- ▶ The HONO levels have been measured in the winter and summer of 2007 at Beijing.
- ▶ The temporal and diurnal variations and the meteorological effects were examined.
- ▶ HONO (PSS) explained 83% and 48% of HONO levels in winter and summer, respectively.
- ▶ The HNO<sub>3</sub> and fine particulate NO<sub>3</sub><sup>-</sup> photolysis contributed weakly as HONO source
- ▶ Processes J<sub>NO2</sub> dependent on aerosol and ground surfaces were HONO sources in summer.

### ARTICLE INFO

#### Article history:

Received 10 August 2012

Received in revised form 19 December 2012

Accepted 19 December 2012

Available online 4 February 2013

#### Keywords:

Nitrous acid  
Nitrogen oxides  
Annular denuder  
Heterogeneous chemistry  
Hydroxyl radical  
Urban area

### ABSTRACT

The atmospheric concentrations of nitrous acid (HONO) have been measured during two field campaigns in the winter and summer of 2007 at Beijing (China). The results were discussed from the standpoint of temporal and diurnal variations and meteorological effects. The daily average HONO concentrations were in the range of 0.03–2.91 ppb and didn't show temporal variation between the winter and summer periods. The temporal trends seemed to be largely affected by meteorological conditions. HONO concentrations showed very typical diurnal variations during intensive winter and summer periods. Nitrogen oxides were key precursors of HONO formation and the HONO/NO<sub>2</sub> values were higher than those reported for direct emission (<1%), indicating the prevalence of secondary chemical HONO formation on direct emission during both periods.

We used a pseudo steady state approach (PSS), which included homogeneous and heterogeneous reactions and direct emission, explaining on average about 83% and 48% of the observed HONO levels during the intensive winter and summer periods, respectively. The daytime unknown HONO production was on average 2.58 ppb h<sup>-1</sup> during the summer period. The HNO<sub>3</sub> and fine particulate NO<sub>3</sub><sup>-</sup> photolysis contributed weakly as HONO source. Including these sources in the PSS calculation, we explained about 53% of the observed HONO levels. The results showed that heterogeneous J<sub>NO2</sub> dependent processes on aerosol and ground surfaces, involving NO<sub>2</sub> as HONO precursor, were HONO sources during the summer measurements.

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### 1. Introduction

Nitrous acid (HONO) plays an important role in the tropospheric photochemistry. It acts as a relevant source of tropospheric hydroxyl radicals (OH) by its rapid photolysis (300 nm < λ < 405 nm):



in the early morning, especially during sunrise (Harrison et al., 1996), enhancing photooxidation processes, such as the formation of tropospheric ozone (O<sub>3</sub>) and other secondary atmospheric pollutants (PAN,

fine particles). Recent field and modeling studies have shown that HONO photolysis contributes significantly to the OH production, not only in the early morning, but also throughout the day, with a total averaged contribution of up to 60%, i.e. up to two orders of magnitude larger than ozone and formaldehyde photolysis sources. These studies explained that a strong and unknown daytime HONO source should exist (Zhou et al., 2002; Aumont et al., 2003; Kleffmann et al., 2006; Acker et al., 2006a; Elshorbany et al., 2009) and that its source strength was on the order of 500–600 ppt h<sup>-1</sup> and 90 ppt h<sup>-1</sup> for rural and polar environments, respectively (Kleffmann et al., 2005; Acker et al., 2006b; Villena et al., 2011).

HONO has also direct and indirect negative health effects, especially in indoor environments during the use of unvented combustion processes, such as gas space heaters and stoves (Febo and Perrino,

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1991; Vecera and Dasgupta, 1994). It has been shown to irritate the mucous membranes and the respiratory and pulmonary systems of asthmatics (Rasmussen et al., 1995) and to react with secondary and tertiary amines to form carcinogenic nitrosamines, in particular by wall reaction of HONO with nicotine in indoor environments (Pitts et al., 1978; Sleiman et al., 2010).

Despite its importance on atmospheric chemistry, the HONO budget in the troposphere, its source strengths and formation mechanisms, particularly during daytime, remains unclear. Four types of HONO formation pathways were identified: direct emission, homogeneous gas reactions, heterogeneous reactions and surface photolysis reactions (Calvert et al., 1994; Bejan et al., 2006; Kleffmann, 2007).

Direct HONO emissions by traffic related combustion processes, biomass burning, heating, and industrial burn have been identified and quantified (Kirchstetter et al., 1996; Kurtenbach et al., 2001). The emission HONO/NO<sub>x</sub> ratios are found to be 0.3–0.8% (Kurtenbach et al., 2001), but these values are generally lower than that from the field observations and cannot solely explain the observed atmospheric concentrations, indicating that the atmospheric HONO is mostly secondarily formed.

Several HONO producing reactions in the gas phase have been suggested, but they have been found to be of minor importance, being much too slow under atmospheric conditions. Among them, only the homogeneous recombination of the NO and OH radicals:

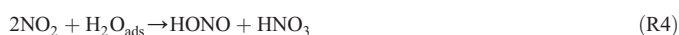


contributes to significant HONO amounts under conditions of elevated NO concentrations, particularly during daytime (Vogel et al., 2003; Volkamer et al., 2010; Wong et al., 2011), but this process competes with photolysis. Most recently Li et al. (2008) showed that HONO can be formed upon the gas-phase reaction of photolytically excited NO<sub>2</sub> with water:



However, this mechanism is still under discussion and does not significantly seem to contribute to the atmospheric HONO formation (Crowley and Carl, 1997; Carr et al., 2009; Amedro et al., 2011; Sörgel et al., 2011; Wong et al., 2011). Recently, Bejan et al. (2006) and Kleffmann (2007) proposed the gas-phase HONO production during the photolysis of aromatic compounds containing ortho-nitrophenols and a noontime HONO production of 100 ppt h<sup>-1</sup> was estimated for urban conditions. However, all these authors pointed out the need of further studies to better understand the role of this process as daytime HONO source.

Currently, heterogeneous NO<sub>2</sub> reactions on different surfaces are considered as major HONO sources, along with the homogeneous formation and direct emissions. A proposed pathway for HONO formation in the atmosphere is the NO<sub>2</sub> hydrolysis on wet surfaces:



Laboratory studies indicate that the kinetics of reaction (R4) is likely to be first order in NO<sub>2</sub> (Kleffmann et al., 1998a; Finlayson-Pitts et al., 2003 and references therein) and depends on various parameters including the gas phase NO<sub>2</sub> concentration, the surface water content, relative humidity and the surface area density (Finlayson-Pitts et al., 2003 and references therein; Stutz et al., 2004). Kleffmann et al. (1998a,b) derived uptake coefficients (γ) of about 10<sup>-6</sup> and of about 10<sup>-7</sup> for NO<sub>2</sub> on a surface with adsorbed pure water and with acidic solutions, respectively, while γ values of 10<sup>-8</sup>–10<sup>-7</sup> can be referred by Finlayson-Pitts et al. (2003). Other studies proposed the heterogeneous

HONO production from the NO<sub>2</sub> reduction by organics adsorbed on surfaces with a reaction of the type:



where red<sub>ads</sub> and ox<sub>ads</sub> means a reduced and an oxidized site on the surface (Ammann et al., 1998, 2005). Kleffmann et al. (1999) investigated heterogeneous NO<sub>2</sub> conversion on different carbonaceous surfaces determining that the initial γ value of 10<sup>-6</sup> decreased with NO<sub>2</sub> consumption increasing (to <10<sup>-8</sup>) and that without any recycling mechanism, atmospheric HONO formation on soot surfaces is not of major importance. Aubin and Abbatt (2007) summarized the literature initial γ values for NO<sub>2</sub> on various black carbon substrates showing that they ranged from 0.1 to 10<sup>-8</sup>, but that 10<sup>-5</sup> was the most frequently reported value.

Photosensitized NO<sub>2</sub> conversion on humic acid surfaces could explain the recently observed high daytime HONO concentrations in the atmosphere (George et al., 2005; Stemmler et al., 2006, 2007). Stemmler et al. (2007) suggested, that the photochemical HONO production on organic aerosol may be comparable to that observed in the near ground atmosphere only at places with exceptional high pollution by organic aerosol and nitrogen oxides, such as in biomass burning plumes or in mega-cities.

The light-induced NO<sub>2</sub> conversion on soot aerosol surface has been also recognized as a surface reaction producing HONO with γ values of about 10<sup>-7</sup> and 10<sup>-8</sup> for initial NO<sub>2</sub> concentrations of 16 ppb and 120 ppb, respectively (Monge et al., 2010), thus it is not an important HONO source.

The photolysis of adsorbed nitric acid (HNO<sub>3</sub>) or nitrate (NO<sub>3</sub><sup>-</sup>) at wavelengths around 300 nm (R6) was identified as a daytime HONO source in rural environments and could serve as an important pathway for the remobilization of deposited HNO<sub>3</sub> (Clemittshaw, 2006; Zhou et al., 2002, 2003, 2011).



Another HONO formation mechanism involves the reversible acid-base reaction of nitrite ion (NO<sub>2</sub><sup>-</sup>) in the soil producing HONO and its following partitioning between gaseous and aqueous phases (Su et al., 2011).



The HONO production rate by reaction (R7) is function of land use, pH value, NO<sub>2</sub><sup>-</sup> concentration, temperature and water amount within the soil (Li et al., 2012). However, Su et al. (2011) recommended other studies to understand the real impact of reaction (R7) on agricultural and natural environments. The lacking understanding of the HONO formation processes leads to accurately measure HONO when the budget of OH or NO<sub>x</sub> is considered.

Only few studies have been devoted to HONO field measurements in China and they reported high HONO levels in urban areas, such as Beijing, Shanghai and Guangzhou (Hu et al., 2002; Hao et al., 2006; Qin et al., 2006, 2009), as well as in rural regions, such as Xinken in the South of the PRD (Su et al., 2008a,b). For example, a maximum of 12 ppb was observed in Guangzhou (Hu et al., 2002; Qin et al., 2009) and 7 ppb was measured in Shanghai (Hao et al., 2006). Unexpected high daytime HONO levels (4–6 ppb) were also reported at Guangzhou (Zhang et al., 2008; Qin et al., 2009) and at Beijing (Wu et al., 2009) as well as at the rural site of Xinken (Su et al., 2008a,b).

Actually, HONO can be measured by various techniques such as spectroscopic techniques, wet chemical techniques and off-line samplers. Among the spectroscopic techniques, which allow detecting directly gas phase HONO, the most established and reliable is differential optical absorption spectroscopy (DOAS). DOAS detects HONO by its specific UV absorption ranges with detection limits in the order of 100 pptv (Platt et al., 1980). Other absorption techniques

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